


SYNTHESIS OF 2-ARYL THIO ARYL CYANAMIDES FROM 2-IODO ARYL ISOTHIOCYANATES IN ONE POT THREE COMPONENT REACTION BY USING IRON AS A CATALYST
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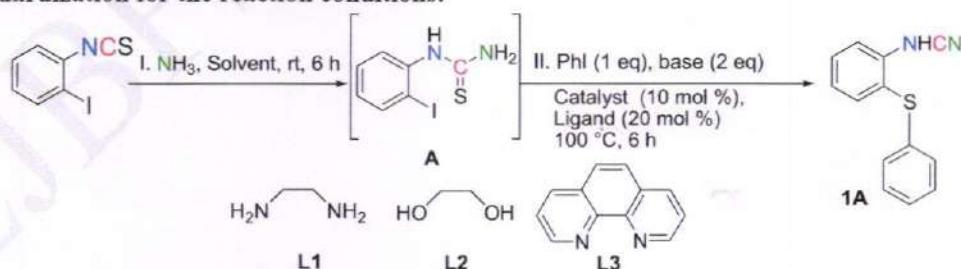
INTRODUCTION

Due to its unique reactivity, cyano group is recognized as important building block and is found in various bioactive molecules and functionalized materials.^[1] Cyanamides are useful precursors and important synthetic intermediates for the synthesis of biological, medicinal and pharmaceutically important hetero-cycles.^[2] Since the cyano group is easy removal from cyanamide and N-alkyl or N-aryl imides,^[3] they often represent as a useful protecting groups in the synthesis of secondary and tertiary amines containing heterocycles.^[4] Aromatic cyanamides have also been prepared by both classical and ancient methods.^[5]

In recent years, the formation of carbon-heteroatom bonds^[6] towards the synthesis of heterocyclic compounds has been developed through cross-coupling reactions using transition-metal-catalysis. Among these, carbon-sulfur bond formation has received much attention due to the presence of this moiety in many molecules that are of biological, pharmaceutical and material interest.^[7] Recently the above said moieties containing compounds like 2-(arylthio) aryl cyan-amides from 2-halophenyl

thiourea via domino C-S cross-coupling reaction using copper as catalyst.^[8] But to the best of our knowledge no one has reported in the presence of iron.

Therefore, herein, we wish to demonstrate the one-pot synthesis of 2-(arylthio) aryl cyanamides from 2-iodoaryl isothiocyanate and aryl iodides using cheap, readily available and air stable iron source as catalyst under milder conditions.

Table 1: Standardization for the reaction conditions.


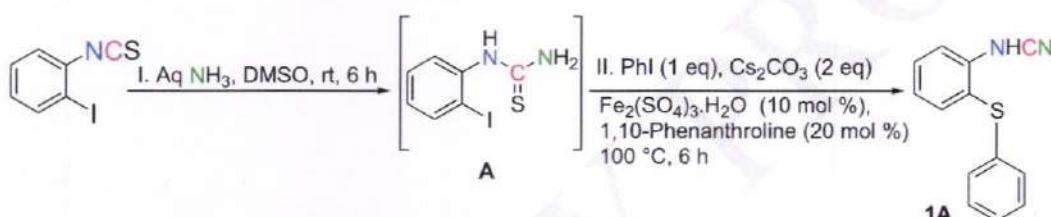
Entry	Solvent	Catalyst	Base	Ligand	Conversion ^[b]	
					A	1A
1	EtOH	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	L3	100	n.d.
2	EtOAc	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	L3	100	n.d.
3	n-Hexane	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	L3	n.d.	n.d.
4	n-Heptane	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	L3	n.d.	n.d.
5	H_2O	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	L3	70	n.d.
6	DMF	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	L3	45	55
7	DMSO	$\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$	$\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	L3	45	55

8	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	KOH	L3	25	75
9	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	K ₂ CO ₃	L3	40	60
10	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	Cs ₂ CO ₃	L3	n.d.	100
11	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	Cs ₂ CO ₃	L1	75	25
12	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	Cs ₂ CO ₃	L2	55	45
13	DMSO	Fe(NO ₃) ₃ .9H ₂ O	Cs ₂ CO ₃	L3	n.d.	100
14	DMSO	FeCl ₂	Cs ₂ CO ₃	L3	n.d.	100
15 ^c	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	Cs ₂ CO ₃	L3	50	50
16 ^d	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	Cs ₂ CO ₃	L3	35	65
17	DMSO	Fe ₂ (SO ₄) ₃ , H ₂ O	Cs ₂ CO ₃	-	79	21
18	DMSO	-	Cs ₂ CO ₃	-	100	n.d.

[a] Reaction conditions: 2-Iodophenyl isothiocyanate (1 mmol), solvent (2 mL), Aq NH₃ (2 mL), 6 h, room temperature, then, iodo benzene (1 mmol), catalyst (10 mol %), ligand (20 mol %), base (2 mmol), 6 h, 100 °C. [b] Isolated yield. [c] Catalyst (5 mol %) was used. [d] Cs₂CO₃ (1.5 equiv) was used. n.d. = not detected.

2-Iodo phenyl isothiocyanate reacts with aq ammonia in the presence of DMSO to afford 2-iodo phenyl thiourea as an intermediate, which reacts with iodo benzene using iron source as catalyst under below shown reaction

conditions to obtain the target product as 2-phenylthio phenyl cyanamide via domino intra and inter molecular C-S cross-coupling reaction (Scheme 1).



Scheme 1

Initially, the optimization of the reaction conditions was performed using 2-iodophenyl isothiocyanate as model substrates with different solvents at room temperature (Step 1). We could observe that the substrate proceeded reactions with aq NH₃ and in the presence of EtOH, EtOAc, DMF and DMSO at room temperature to get the corresponding thiourea A in complete conversion, that, gratifyingly, proceeded an domino intra and inter molecular C-S cross-coupling reaction with iodobenzene using 10 mol % Fe₂(SO₄)₃, H₂O, 20 mol % Ligand (1,10-Phenanthroline) and 2 equiv Cs₂CO₃ at 100 °C temperature to give target product 1A in complete conversion. In case of solvent optimization, non-polar solvents like n-hexane and n-heptane couldn't proceed the reaction. Green solvent H₂O could give thiourea (1st step) in 70% conversion, that couldn't proceed the domino C-S cross-coupling reaction (2nd step). Various bases were examined and among them Cs₂CO₃ could give target product in complete conversion (Table 1, entry 10). Other bases (K₃PO₄·3H₂O, K₂CO₃ and KOH) could give less effect for the formation of target product. In a set of ligands L1-L3 screened, L3 was found to be the most effective in comparison to L1-L2 (Table 1, entries 11-12). Both iron (II) and iron (III) sources (Fe₂(SO₄)₃, H₂O, Fe(NO₃)₃.9H₂O and FeCl₂) exhibited a similar catalytic activity (entries 10 and 13-14). Lowering the amount of base (1.5 equivalent) or the iron source (5 mol %) led to the domino C-S cross-coupling reaction to afford target product in less conversion (Table 1, entries 15-16). The reaction was also checked in the

absence of ligand, unfortunately, the reaction could give target product in 21% conversion only (Table 1, entry 17). Control experiments confirmed that the reaction didn't proceed (step 2) in the absence of the catalyst and ligand and the thiourea was recovered intact (Table 1, entry 18).

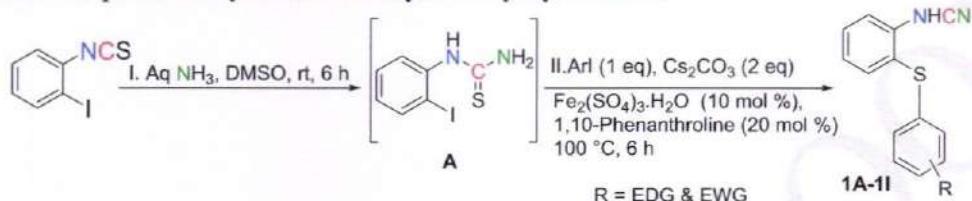
Having optimization reaction conditions in our hand, we further pursued the scope of the process with respect to the other substrates. Aryl iodides having electron donating groups 4-Me and 4-OMe proceeded reactions to afford their domino coupled products 1B and 1C in 95% and 97% yields, respectively. Aryl iodides bearing weak electron withdrawing substituent's 4-Cl and 4-F could give their respective target products 1D and 1E in 91% and 88%. Aryl iodides possess strong electron withdrawing groups 2-NO₂ and 4-CN gave their final products in less yield. It might be occurred as these have strong electron withdrawing capacity. Finally, we have also checked reaction with 2,4-diMe iodobenzene and it could give target product in decent yield. Aryl iodide contain bulkier group 2'-Bu carried out the reaction under optimized reaction conditions to give respective 2-(arylthio) aryl cyanamide 1I in 82% yield. Similarly, phenyl isothiocyanate bearing 4-Me, 4-OMe, 4-Cl, 4-F, 4-CN, 2-NO₂, 2,4-di-Me, 3,4-di-Me and 2'-Bu substituents readily carried out reaction with iodobenzene to give their final products 1J-R in 70-95% yields. The above-mentioned results clearly confirm that the substrates having electron donating

and *-*withdrawing groups are compatible with this process to afford the substituted 2-(arylthio) aryl cyanamides in good to high yield.

According to literature reports and experimental evidence the mechanism is proposed (Scheme 2). 2-Iodophenyl isothiocyanate reacts with aqueous NH₃ to provide *N*-2-iodophenyl thiourea A, which can undergo oxidative addition with Iron(I) species (thiourea may reduce Iron (III) to Iron(I) active

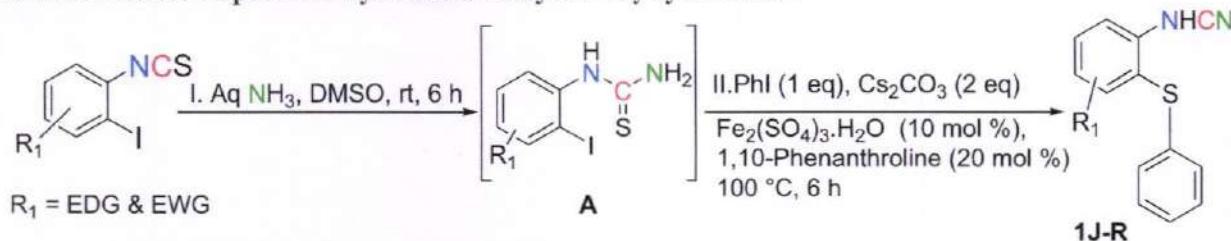
species) to yield Iron(III) intermediate P. It may give 2-aminobenzothiozole X through intramolecular *C*-*S* cyclization using base via intermediate Q. On the other hand, iodobenzene can undergo oxidative addition with Iron(I) species to give intermediate R, which can carry out inter molecular *C*-*S* cross-coupling reaction with 2-aminobenzothiozole X to afford intermediate S that can complete catalytic cycle via reductive elimination to obtain 2-arylthio aryl cyanamide 1A.

Table 2: Substrate scope for the synthesis of 2-arylthio aryl cyanamides.

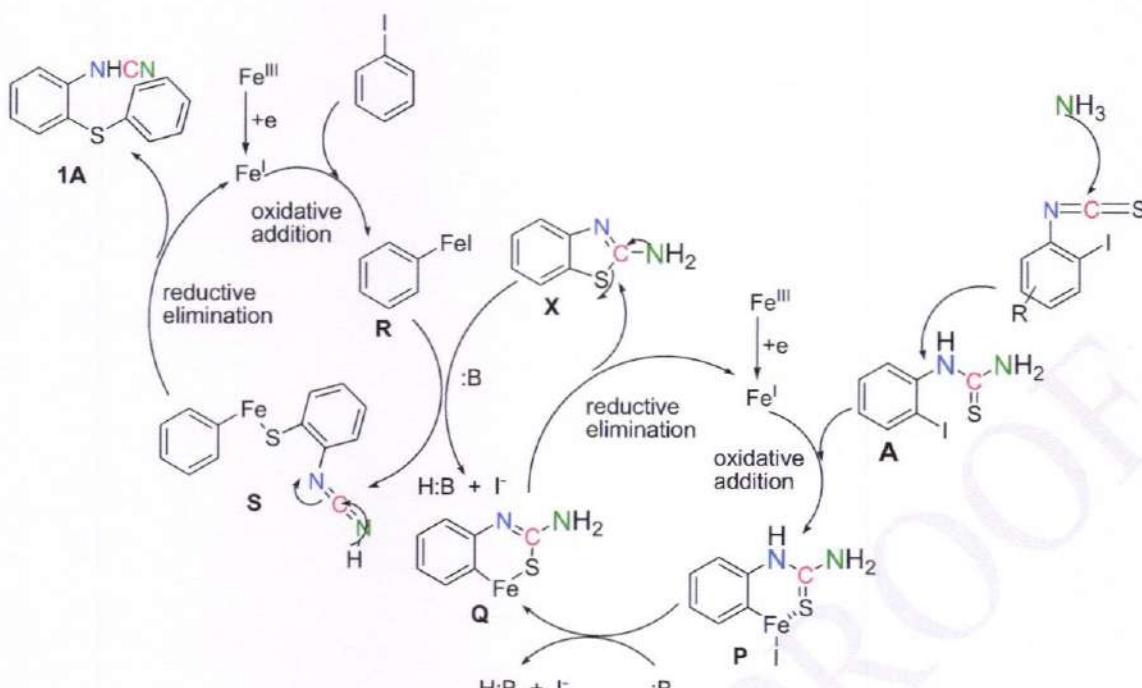


Entry	Substrate	Product	Isolated yield (%) ^b
1			1A 95
2			95
3			97
4			91
5			88
6			77
7			76
8			90
9			82

Table 3: Substrate scope for the synthesis of 2-arylthio arylcyanamides.



Entry	Substrate	Product	Isolated yield (%) ^b
1			1J 95
2			1K 95
3			1L 90
4			1M 83
5			1N 75
6			1O 70
7			1P 82
8			1Q 85
9			1R 77



Scheme 2: Proposed mechanism.

We have developed neat, clean and efficient methodology for the synthesis of 2-halo aromatic cyanamides. During the reaction process we couldn't observe any other byproducts (no other products could observe except cyanamide only). The reactions are rapid and facile and accomplished under mild reaction conditions. All the substrates could obtain their target products in good to excellent yields.

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DEVELOPMENT AND VALIDATION OF A SENSITIVE AND STABLE HSGC-MS/MS METHOD FOR SIMULTANEOUS DETERMINATION OF TWO N-NITROSAMINE IMPURITIES IN OMEPRAZOLE SODIUM DRUG SUBSTANCES AND DRUG PRODUCTS BY USING QUALITY BY DESIGN APPROACH

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Abstract:

Nitrosamine impurities in angiotensin II receptor antagonists containing a tetrazole group represent an urgent concern for active pharmaceutical ingredient (API) manufacturers and global regulators. Regarding safety, API manufacturers must develop methods to monitor the levels of each nitrosamine impurity before individual batch release. In this study, we developed and validated a sensitive, selective, and high throughput method based on headspace gas chromatography-mass spectrometry with Multiple reactions monitoring mode (MRM) (HSGC-MSMS) for the simultaneous determination of two nitrosamines, namely, N-Nitrosodimethylamine (NDMA) and N-nitrosodiethylamine (NDEA) in Omeprazole sodium drug substances and products by using quality by design approach.

The quantification of two nitrosamines in Omeprazole sodium drug substances and products ranged from 0.07 ppm with respect to the sample concentration of 1000 mg/mL with good sensitivity in LOQ level. The limit of quantification is 0.021 ppm and limit of detection is 0.007 ppm for NDMA and NDEA with respect to the sample concentration of 1000 mg/mL with good sensitivity in the proposed method. The calibration curves of the assay ranged from 0.035 to 0.105 ppm with limits of quantitation of 0.021 ppm for NDMA and NDEA. The recoveries of two N-nitrosamines in selected Omeprazole sodium drug ranged from 85% to 115%. The precision was in the acceptance criteria of below 10% for NDMA and NDEA. Other validation parameters, including specificity, robustness, ruggedness, solution stability met the validation criteria.

Therefore, this proposed HSGC-MSMS method exhibited good sensitivity and precision, high accuracy, and fast analysis speed, which provide a reliable method for quality control of two N-nitrosamines in Omeprazole sodium drug substances and products. This method is applied for pharmaceutical dosage forms, results met the with the specifications. In conclusion, it will be useful to quantify the low-level nitrosamines in Omeprazole sodium drug substances and products.

Index Terms: Omeprazole sodium, N-Nitroso dimethyl amine, N-nitroso diethyl amine, HSGC-MS/MS, method development and validation.

I. INTRODUCTION

Nitrosamines are organic chemical compounds that may be present in low levels in a variety of products that people are exposed to every day. Air, water, and consumer products such as processed meats, alcoholic beverages, cosmetics, and cigarette smoke all contain nitrosamines [1]. N-nitrosamines have been classified as 'probable human carcinogens' by the International Agency for Research on Cancer [2] and were listed as a representative "cohort of concern" of mutagenic carcinogens in the International Council for Harmonization of Technical Requirements for Pharmaceuticals for Human Use (ICH) guidance for industry M7 (R1) [3]. In 2018, the nitrosamines N-nitrosodiethylamine (NDEA) and N-nitrosodimethylamine (NDMA) were detected in several API used in the treatment of hypertension and related medicines. After thorough investigations, regulatory agencies have outlined that the formation of nitrosamines is possible in the presence of secondary, tertiary, or quaternary amines and nitrite salts under acidic reaction conditions. The starting materials, intermediates, reagents, solvents, catalysts, active pharmaceutical ingredient (API), or API degradants may participate in reactions and form nitrosamines in certain processing conditions. Contaminated reaction materials in the manufacturing process such as recycled solvents are a potential root cause of nitrosamines in drug products. Excipients and packing materials may contain nitrosamine precursors to generate nitrosamines in drug products. Regulatory agencies have guided manufacturers to follow risk assessment, acceptable intake (AI) limits, and multiple analytical test procedures to control nitrosamines [4, 5].

The U.S. FDA has reported that low concentrations of NDMA have been detected in some metformin products, and no sample of metformin exceeds the acceptable daily intake for NDMA [6]. When nitrosamine impurities have been detected in several pharmaceutical products, many countries announced interim limits for NDMA and NDEA recall based on the acceptable daily intake of the sartan drug substances (valsartan, irbesartan, fimasartan, rosartan potassium, olmesartan, candesartan), metformin and ranitidine [7,8,9].

Since the Omeprazole sodium products produced by several pharmaceutical companies were proven to contain potential contamination with carcinogenic nitrosamine impurities, namely, N-nitrosodimethylamine (NDMA) and N-nitroso diethylamine(NDEA) (Fig. 1). 5-methoxy-2-(((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)sulfinyl)-1H-benzo[d]imidazole is a substituted benzimidazole compound and a prototype anti-secretory agent, being the first "proton pump inhibitor" widely used for the prophylaxis and treatment of gastro-duodenal ulcers and for the treatment of symptomatic gastro-oesophageal reflux [10]. There is a potential for the presence or formation of NDMA and NDEA in the Omeprazole drug substance and drug product.

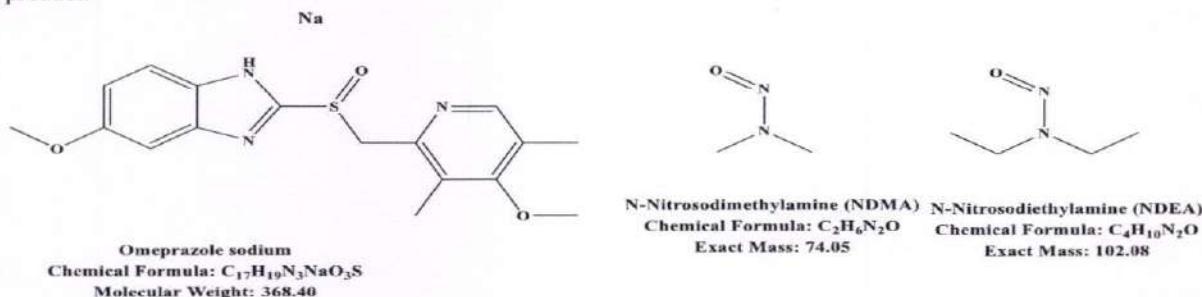


Figure 1: Molecular structures of Omeprazole sodium and two N-nitrosamines

Literature review has been proved that the multiple analytical methods are also published by regulatory agencies for the determination of Genotoxic impurities, nitrosamines in various drug substances and drug products by using [11-17]. And determination Omeprazole assay in its bulk and pharmaceutical dosage forms [13],[18-21]. However, no approach is reported for the trace-level quantification of NDMA and NDEA in the Omeprazole sodium drug substance and drug products by using HSGC-MS/MS so far. So, our proposed work is very necessary for the quantification of two N-nitrosamine impurities at low level in Omeprazole sodium drug substances and products. However, these were not suitable for rapid and high-throughput analysis in the pharmaceutical industry. Here in, we have developed a simple, sensitive, accurate, and reproducible HSGC-MS/MS method for the detection of two N-nitrosamines in Omeprazole sodium drug substances and products. The obtained LODs and LOQs met the sensitivity requirements set by FDA. Then, this developed method was validated according to the International Council for Harmonization (ICH) guidelines [22,23] in terms of sensitivity, linearity, accuracy, precision, specificity, and stability.

Based on Control of Nitrosamine Impurities in Human Drugs requirements, FDA has established the interim acceptable daily intake limits for N-nitrosamines. For two N-nitrosamine impurities specifications are calculated by the maximum daily dosage (360mg/day) of Omeprazole sodium. The specifications of NDMA and NDEA impurities were calculated by using 'Accepted Intake limit' is divided by 'maximum daily dosage' of Omeprazole sodium (360mg/day). European Medicines agency has published the maximum daily intake as 96 ng for NDMA and 26.5 ng for NDEA and no guidance on suitable acceptable daily intake for rest of the possible nitrosamines. By considering the worst case, 26.5 ng will be considered for the NDMA & NDEA nitrosamine which was considered in the evaluation study. The calculated Interim limits for NDMA and NDEA are shown in Table-1.

Table 1: Interim limits for NDMA and NDEA in Omeprazole set by FDA

Name of Nitrosamine Impurity	Accepted Intake limit (ng/day)	maximum daily dosage (mg/day)	Accepted Intake limit (ppm=AI/MDD)	Taken limits (ppm)
NDMA	96	360	0.27	0.07
NDEA	26.5	360	0.07	0.07

METHODS**Chemicals and reagents**

The N-Nitrosodimethylamine (NDMA), N-Nitrosodiethylamine (NDEA) standards and Omeprazole sodium drug substance were purchased from local well known Laboratories, Hyderabad, India. Millipore Milli Q purification system was used from Bangalore, India. HPLC grade DMSO was purchased from Rankem (Mumbai, India). Millipore Milli Q purification system purchased from Bangalore, India.

Instrumentation and optimized HSGC-MS/MS conditions

Analyses of two N-nitrosamines were performed on a SHIMADZU GC-MS-TQ8040NX system. VF-Wax ms capillary column (30m × 0.25mm i.d., 1.0 μ m) was used as the analytical column in this work. MS/MS detection was carried out on a SHIMADZU TQ-GC triple quadrupole mass spectrometer with electron ionization (EI) ion source. The GC oven program utilized an initial oven temperature of 40 °C, held for 5 min, raised firstly at 20 °C·min⁻¹ to 240 °C finally held for 5 min. The total run time was 20 min. Helium as the carrier gas was set at a flow of 1.0 mL/min. The injection volume was 1 μ L in the split ratio is 10:1. HS Oven temperature, Sample line temperature, Transfer line temperature were set to be 150°C, 160°C & 170°C. HS vial Equilibrating time, GC cycle time and Injection time were set to be 15 min, 30 min & 1.0 min.

Both the interface temperature and ion source temperature were set to be 250°C & 230°C. The MS was operated in EI mode at 70 eV with a quadrupole temperature of 150 °C. The solvent cut time was 5 min and end time was 15 min and multiple reactions monitoring (MRM) mode was selected as the data acquisition for the quantitative determination of two kinds of Nitrosamine GTIs. The precursor ions and product ions of two N-nitrosamine GTIs, as well as the optimized collision energy (CE) were summarized in Table 2.

Table 2: Optimized MRM fragments and CE

Impurity Name	CH1 m/z	CH1 CE(V)	Q3 Resolution
NDMA	74.00 > 42.00	20	High
NDEA	102.00 > 85.10	5	High

Preparation of Sample and Impurity Standard solutions**Preparation of Diluent**

Prepared the homogeneous mixture of DMSO and water in the ratio of 80:20 (v/v) respectively and mix well.

Preparation of Nitrosamine Impurities standard solution (0.07 ppm)

Accurately weight and transfer about 70 mg of each nitrosamine impurity in 100 mL of volumetric flask and diluted to the volume with diluent and sonicated about 1 min (stock solution-1). Pipette 0.5 mL of the stock solution-1 into a 50 mL volumetric flask and dilute to the desired concentration with diluent (stock solution-2). Further pipette 0.5 mL of the above stock solution-2 into a 50 mL volumetric flask and dilute up to the mark with diluent (stock solution-3). Further pipette 0.5 mL of the above stock solution-3 into a 50 mL volumetric flask and dilute up to the mark with diluent (Standard solution was prepared with respect to 1000 mg/mL of Omeprazole sodium sample). The standard Headspace vials were prepared with 1 mL of the Standard solution and sealed the vial with aluminum closure.

Preparation of Omeprazole sodium Drug substance (1000 mg/mL)

Weigh and transfer 1000 mg of Omeprazole sodium sample into a 20 mL Headspace vial and add 1.0 mL of diluent and immediately sealed with aluminum closure.

Preparation of Omeprazole Drug product (1000 mg/mL)

Crush the appropriate number of Omeprazole tablets equivalent to 1000 mg of Omeprazole sodium sample and accurately weigh and transfer into 20 mL of headspace vial, adds 1 mL of diluent and immediately sealed with aluminum closure.

RESULTS**Method Optimization**

The stationary phase, column length, film thickness, and column diameter have a large impact on the retention and peak shape of the analytes. Based on the trial-and-error methodology with the literature review, the optimal separation of nitrosamines was achieved when the capillary surface was modified by polyethylene glycol residues at the length of 30 m. The

optimal chromatographic separation and retention were achieved using a column dimension of 30×0.25 mm i.d. and a film thickness of $1 \mu\text{m}$ coated with polyethylene glycol stationary phase. The temperature programming is also a very important parameter to influence peak separation. An initial constant temperature at 40°C for 5 min followed by an increase at a rate of 20°C can provide the best separation with a resolution greater than 1.5 between NDMA and NDEA at the retention times of 11.85 and 12.47 min, respectively. We optimized, HS oven temperature (140-160°C), Sample line temperature (150-170°C), and Transfer line temperature (160-180°C). After optimized, choose the HS oven temperature 150°C, Sample line temperature 160°C, and Transfer line temperature 170°C. Different diluents were checked, NMP, DMSO and DMF etc. for sample and impurities solubility. For this study, DMSO: Water (80:20v/v) was used, and advantages in terms of volatility and polarity were achieved. More importantly, Omeprazole sodium and impurities are soluble and can be extracted entirely and dissolved in pre mixed solution of DMSO: water (80:20v/v).

The GC-MS/MS conditions for the simultaneous determination of two nitrosamines in Omeprazole sodium was optimized to ensure reliability, selectivity, and sensitivity. Initially, the mass parameters were optimized to achieve the highest sensitivity with a consistent response. NDMA (m/z 74) and NDEA (m/z 102 were tuned on a single quadrupole mass spectrometer in the electron ionization (EI) mode under the selected ion monitoring (SIM) acquisition method. These particular ions were used for quantification. In addition to the parent ions, the major daughter ions of NDMA (m/z 42) and NDEA (m/z 85.10) were qualitatively monitored for confirmation. Alternatively, the ion ratio calculation between the parent and daughter ions was also quantitatively used in the confirmatory objective.

METHOD VALIDATION

The proposed determination method for two N-nitrosamine GTIs has been validated according to the (ICH) guidelines [19] through the following parameters, such as specificity, system precision, method precision, linearity, LOD, LOQ, accuracy, Robustness, Ruggedness and solution stability.

Specificity:

To demonstrate the specificity of the proposed method, Omeprazole sodium and the mixture solution of two N-nitrosamine standards were subjected to the HSGC-MS/MS analysis. In Fig. 2, no interference peaks in the N-nitrosamine standard and the Omeprazole sodium were observed at the retention times of two N-nitrosamines and resolution was greater than 1.5 between NDMA and NDEA at the retention times of 11.85 and 12.47 min, respectively. This indicates that HSGC-MSMS method for the determination of two N-nitrosamines in Omeprazole sodium showed good specificity.

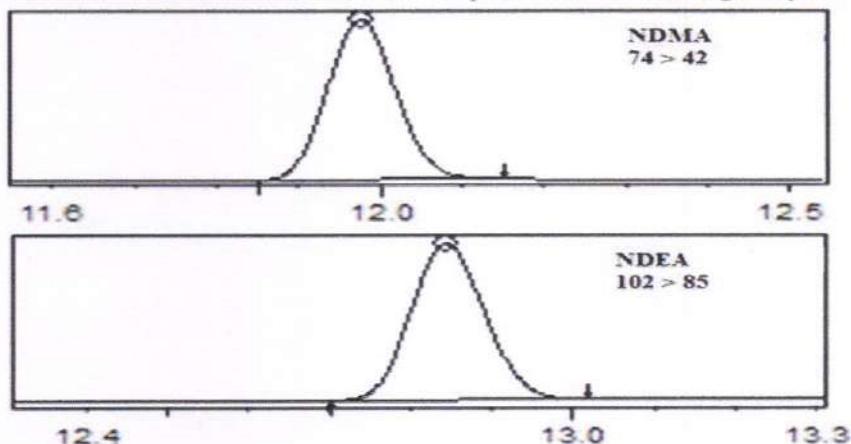


Figure 2: Standard two N-nitrosamine impurities (NDMA & NDEA)

System precision

System precision was established by six measurements of the standard solution at the 100% concentration levels on the same day. Six injections of standard two N-nitrosamines solution were injected into the HSGC-MS/MS system to evaluate the system precision of developed method. The obtained %RSD two N-nitrosamines impurities were not more than 10%. The corresponding data is shown in Table 3.

Method precision

The gas chromatographic method precision was verified by analyzing the Omeprazole sodium drug sample spiked with two N-nitrosamines impurities at specification limits. The method precision was vented as mean concentration quantified and relative standard deviation of six quantified values of two N-nitrosamines impurities. The relative standard deviation was noticed as $\leq 10\%$, which proved that HSGC-MSMS method was precise for quantification of two N-nitrosamines impurities in Omeprazole sodium drug. The corresponding data was shown in Table 4.

Table 3: System precision data for two N-nitrosamines impurities

No. of Injections	NDMA area	NDEA area
1	53425	9355
2	55632	9456
3	58025	8465
4	52506	8726
5	57456	8399
6	55693	8589
ACVG	55456	8832
STDV	2169	459
% RSD	3.91	5.20

Table 4: Method precision data for two N-nitrosamines impurities

No. of Preparations	NDMA area	NDEA area
1	59862	9632
2	58269	9745
3	59023	9526
4	55789	9756
5	56128	9285
6	58692	9968
ACVG	57961	9652
STDV	1640	233
% RSD	2.83	2.41

Limit of Detection (LOD) and Quantization (LOQ)

The LODs were defined as 3 times the signal-to-noise (S/N) ratio, and the corresponding LOQs were S/N = 10. The matrix effect (ME) value was calculated according to the following equation. LODs and LOQs results were summarized in Table 5.

$$ME(\%) = \frac{Slope \text{ of } matrix \text{ matched } curve - Slope \text{ of } solvent \text{ curve}}{Slope \text{ of } solvent \text{ curve}} \times 100$$

Table 5: LOD and LOQ data for two N-nitrosamines impurities

Nitrosamine Impurity	LOQ Concentration (in ppm) w.r.t sample	LOQ Avg. Area(n=6)	LOD Concentration (in ppm) w.r.t sample	LOQ Avg. Area (n=3)
NDMA	0.021	16833	0.007	5481
NDEA	0.021	2714	0.007	887

Linearity

The approach was verified for linearity in accordance with ICH recommendations. Prepare five different concentrations and LOQ concentration from stock solution. The peak area of each level is assessed after injection into the chromatographic apparatus. A graph with concentration on the x-axis and peak area on the y-axis issued to compute the correlation coefficient. The linear regression coefficients of determination (*r*) for two N-nitrosamines were over 0.995 in the corresponding concentration range, which meant a good linearity and suitable for quantitative analysis. The results and correlation graphs were summarized in Table 6 & Fig.3.

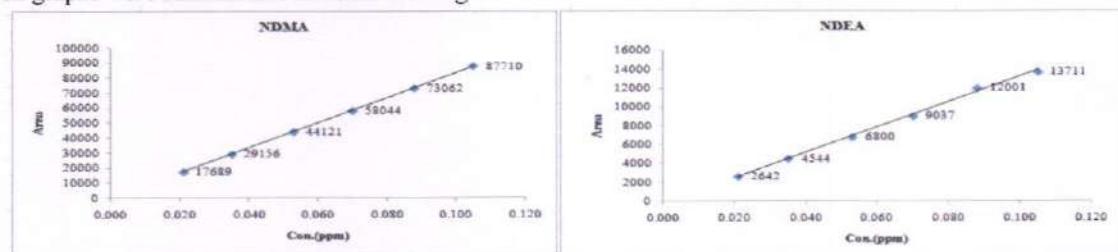
**Fig.3: Correlation coefficient graph for two N-nitrosamines impurities**

Table 6: Linearity data for two N-nitrosamines impurities

Con.(ppm)	NDMA Avg. area (n=2)	NDEA Avg. area (n=2)
0.021	17689	2642
0.035	29156	4544
0.053	44121	6800
0.07	58044	9037
0.088	73062	12001
0.105	87710	13711
Correlation coefficient (r)	1.000	0.999
SLOPE	831873	134187
Intercept	54	-197

Precision at LOQ

The quantification limit values for two N-nitrosamines impurities were confirmed by precision examination *i.e.*, the determined percent relative standard deviation of the responses of six injections. The relative standard deviation was noticed as $\leq 10\%$. This confirmed that, HSGC-MS/MS quantification method is very sensitively precise at LOQ level. The corresponding data is summarized in Table 7.

Table 7: LOQ precision data for two N-nitrosamines impurities

No. of Injections	NDMA area	NDEA area
1	16856	2933
2	16236	2599
3	17865	2611
4	15999	2778
5	16456	2498
6	17586	2866
ACVG	16833	2714
STDV	752	171
% RSD	4.47	6.29

Accuracy

The accuracy of the procedure was evaluated by spiking two N-nitrosamines with Omeprazole sodium samples individually at 0.021 ppm (LOQ), 0.035 ppm, 0.07 ppm and 0.105 ppm with respect to sample concentration of 1000 mg/mL. At each level three preparations were done. The results exhibited that the recoveries for NDMA and NDEA in Omeprazole sodium drug substances ranged from 91.69 to 111.31%. The accuracy of the method was demonstrated by the fact that the recovery for each impurity at each level was within $100 \pm 15\%$. The obtained results indicated that the proposed method is accurate for nitrosamine analysis in the proposed Omeprazole sodium drug substances and drug products.

Robustness

It assists to find out the effect of slight variations in the different chromatographic conditions. Robustness of the method was checked by varying the HS oven Temperature 145°C & 155°C and Ion source Temperature 225°C & 235°C. The standard two N-nitrosamine impurities were injected for six times under each changed method parameter. The relative standard deviation was calculated at each varying condition and obtained results (% RSD) were not more than 10%.

Ruggedness

Ruggedness of the method was evaluated by performing the sample analysis in six replicates using different analysts on different days. The % RSD was calculated for day wise and analysts wise as well as individual and cumulative for two N-nitrosamine impurities and the results were obtained within the acceptance criteria (RSD is not more than 10.0%) indicating the method is rugged within the specified range.

Solution stability

Solution stabilities of two N-nitrosamines impurities in diluent solutions were evaluated by preparing specification level (0.07 ppm) standard solutions and analyzing them every 6 h, 12 h, 24 h & 48 h against a freshly prepared standard. All the solutions were kept in the dark place at 25°C. Clearly, the percentage variation of these stock solutions was in the range of $100 \pm 10\%$ which indicated that these stock solutions were stable for at least 48 h.

Applications in Omeprazole dosage forms

This HSGC-MS/MS analytical method was used to determine two N-nitrosamine GTIs in commercial Omeprazole products, and no N-nitrosamines were found in commercial Omeprazole products. Therefore, the proposed method can be confidently employed for the Omeprazole products containing the pharmaceutical two N-nitrosamines impurities. So, it can be used in the routine quality control of dosage form in Pharma industries.

DISCUSSION

Analytical quality by design (QbD) [23] with HSGC-MS/MS method was developed for quantification of two N-nitrosamine GTIs in Omeprazole sodium drug substances and combined dosage forms. Target profile was retention time, plate count and resolution. The developed method was validated according to ICH guidelines [19]. Different method validation parameters like linearity Co-relations should not less than 0.995. The percentage recoveries at each level are between 85.0% and 115.0%. LOD for NDMA and NDEA is 0.007ppm and LOQ for NDMA and NDEA is 0.0021ppm with respect to Omeprazole sodium sample concentration. The %RSD is obtained less than 10% for system precision, method precision and ruggedness and robustness. As per our proposed HSGC-MSMS method, sample and standard solutions were stable up to 48 hours. And this is method is applied for pharmaceutical dosage forms. So our proposed work is when compared with other literature works, method was found to be novel, simple, sensitive, accurate, precise, economical, and rapid for the estimation of two N-nitrosamine impurities in Omeprazole sodium drug substances and combined dosage forms.

CONCLUSION:

In this work, the HS-GC-MS method was developed and validated for the quantitation of NDMA and NDEA in Omeprazole sodium drug substances and drug products. The headspace injection technique was applied to serve as an online sample preparation in residual impurity analysis, thereby offering benefits concerning the efficient removal of potential interference and High-throughput routine analysis. The complete method validation was performed using the Q2(R1) ICH guidelines [19]. The method should be further fully investigated for its accuracy, precision, and other validation parameters using the acceptable limits of nitrosamines in each substance. The LOQ and LOD of the developed method were far below the US FDA and EMA interim limits of the corresponding nitrosamines in Omeprazole sodium drug substances. The overall results indicated that the developed method is reliable and useful for determining the levels of two nitrosamines in Omeprazole sodium drug substances and drug products.

LIST OF ABBREVIATIONS:

APCI: Atmospheric pressure chemical ionization; HSGC-MS: Head space gas chromatography mass spectroscopy; MRM: Multi reaction monitoring; APIs: Active pharmaceutical ingredients; FDA: Food and Drug Administration; GTI: Genotoxic impurity; EI: Electron ionization; SIM: Selected ion monitoring; ICH: International Council for Harmonization; LOD: Limit of detection; LOQ: Limit of quantification; MRM: Multiple reactions monitoring; NDMA: N-nitrosodimethylamine; NDEA: N-nitrosodiethylamine; DMSO: Dimethyl sulfoxide; RSD: Relative standard deviation; S/N: Signal to noise.

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Study the Impact of Endosulfan Pesticide on behavioral responses in the Fresh Water Fish Labeo Rohita

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ABSTRACT Static renewal test was conducted to determine the toxicity of technical grade (91.06% purity) insecticide Endosulfan on the freshwater fish Labeo Rohita. Fishes were exposed to various concentrations of insecticide Endosulfan for 96 hours and the percent mortality was recorded. Behavioral responses and morphological deformities were studies in the experimental periods. Fish in toxic media exhibited irregular erratic and darting swimming movements. The behavioral and morphological changes may be due to the formation of amino acids by degradation of proteins with concentration of pesticide.

Keywords: Endosulfan, Labeo Rohita, Behavioral changes, Amino acids and Proteins.

INTRODUCTION

Endosulfan is an off patent organo chlorine insecticide and acaricide that is being phased out globally. Endosulfan becomes a highly controversial agrichemical due to its acute toxicity. Potential for bioaccumulation, and role as an endocrine disruptor, because of its threats to human health and the environment, a global ban on the manufacture and use of Endosulfan was negotiated under the Stockholm convention in April 2011. More than 80 countries including the European Union, Australia, New Zealand several west African nations, the United States, Brazil, and Canada had already banned it or announced phase outs by the item the Stockholm convention ban was agreed upon². It is still used extensively in India, China, and few other countries. It is produced by Makhteshim Agan and several manufacturers in India and China despite laws against its use. It is also used in few countries.

Endosulfan is a derivative of hexachlorocyclopentadiene, and is chemically like aldrin, chlordane and heptachlor and it is obtained by Diels – Alder reaction³. Endosulfan is one of the most toxic pesticides in the market today. It is used in agriculture sector to control insect pests including white fly, aphids, leafhoppers, Colorado potato beetles and cabbage worms. Due to its unique mode of action, it is useful in resistance management; however, as it is not specific, it can negatively impact populations of beneficial insects. It is, however, considered to be moderately toxic to honey bees, and it is less toxic to bees than organophosphate insecticides. Endosulfan is acutely neurotoxic to both insects and mammals, including humans. The US EPA classifies it as Category I: "Highly Acutely Toxic" based on a LD50 value of 30 mg/kg for female rats, while the World Health Organization classifies it as Class II "Moderately Hazardous" based on a rat LD50 of 80 mg/kg. It is a channel antagonist, and a Ca²⁺, Mg²⁺ATPase inhibitor¹³

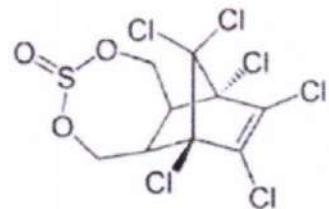


Figure 1. Structure of Endosulfan

A major part of the world's commercial food is being supplied from fish source and it is essential to secure the health of fishes. In India, as much as 70% of the chemical formulations employed in agricultural practices are believed to affect non-

target organisms and to find their way to freshwater bodies ultimately polluting them. Labeo Rohita (rohu) is an herbivorous cyprinid fish that inhabits the tropical lowland river systems of Pakistan, northern India, Nepal, Bangladesh, and Myanmar. Rohu is the most important of the Indian 'major carps' and is the world's 10th highest cultured finfish by production volume. The major producing countries are India, Bangladesh, and Myanmar. Rohu is also a substantial component of stock enhancement programs in floodplains and open waters in these countries, and it has been widely translocated both within and external to its natural range. Its high growth potential, coupled with high consumer preference, have established rohu as the most important freshwater species cultured in India, Bangladesh, and other adjacent countries in the region.



Figure-1a: Fresh water fish Labeo Rohita

MATERIALS AND METHODS

Labeo Rohita fingerlings weighing 5+0.5 grams and average length of 7 cm were collected from the Government fish seed farm at Ponnuru, Guntur District, Andhra Pradesh, India and acclimatized to laboratory conditions for 7 days in large plastic tubs previously washed with potassium permanganate to free walls from any microbial growth physicochemical characters of water was followed APHA Method4. Acclimatized conditions are temperature 27+ 10c, pH: 6.8+0.05 at 270c and dissolved Oxygen (D.O) 6.9 to 7.4 mg L-1. In actualization time, we have supplied food regularly by commercially available fish feed. For this investigation technical grade Endosulfan (91.06%) was used and brought from Agrochemical Industries Limited Guntur, A.P. India. Pesticide column 250 mm length and 4.8 mm diameter samples filtered through PALL life sciences filter paper 0.45 mic. Membrane 13 mm diameter size. Preparation of sample solution: We have taken the effected organs form pesticide

induced fish into boiling test tube and added the pure Hexane (AR) then boiled. After heated fish absorbed pesticide settled at inside of the test tube walls, and then removed the fish organ from the test tube bottom and again added hexane for dissolving the pesticide in the test tube walls. This sample solution is used for the behavioral study of pesticide induced fish by using HPLC analysis. Analysis of Endosulfan by HPLC: Concentrations of Endosulfan in the test medium was confirmed by High-performance liquid chromatography (HPLC) and this method described by Mr. Johnson5. The HPLC analysis was operated by using a UV detector with a mobile phase. Mobile phase consisting of acetonitrile (20%), water (20%), and methanol (60%) then run through a C18 column with a flow rate of 1.0 ml/ minute and then analyzed the peaks of Endosulfan in sample solutions.

Table 1. Concentration of Endosulfan pesticide observed in fish organs.

Conc. of Pesticide(ml)	Gill(m g/ml)	Head(m g/ml)	Digestive system(mg/mg ml)	Liver(mg ml)	Muscle(m g/ml)	Total observed pesticide(mg/ml)
1.0 ml	0.0410	0.0460	0.0320	0.0300	0.0100	0.1590
2.0 ml	0.0501	0.0470	0.0370	0.0310	0.0154	0.1805
3.0 ml	0.0517	0.0548	0.0398	0.0326	0.0271	0.2068
4.0 ml	0.0580	0.0601	0.0416	0.0329	0.0281	0.2159
5.0 ml	0.0621	0.0642	0.0450	0.0390	0.0302	0.2998
6.0 ml	0.0662	0.0690	0.0480	0.0410	0.0306	0.2544
7.0 ml	0.0710	0.0782	0.0485	0.0462	0.0317	0.2756

The protein changes are observed in various tissues after the pesticide induced along with control was graphically represented in Figure 2.

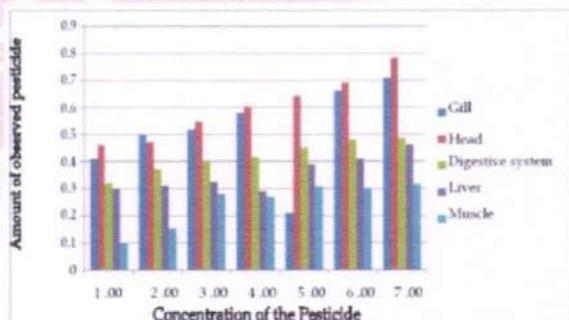


Figure 2. Pesticide absorbance by fish organs in different volumes.

RESULTS AND DISCUSSION

Proteins are primary importance of the living world and only because of their peculiar biological specificity among various types and these are responsible for many metabolic changes in total fish organs. These proteins are main energy sources to

play an important role in the maintenance of blood glucose⁶ (Fig 2). It is the most fundamental biochemical constituent present abundantly in the body of fish and this result presented in Table 1. The insignificant alteration of proteins at the end of 45 hours and it was observed in the tissues suggesting that the fish tend to resist the sudden stress for shorter duration⁷. Later with increases of time the decreases of protein content. The significant and maximum depletion was observed in the head and minimum in muscle. However, increases of consumer concentration of the pesticide decreases the protein in tissues of the fish Labeo Rohita the present analysis coincides with the reported data that the protein content in muscle and liver⁸⁻¹².

Formation of Amino Acids: After consuming of the pesticide, proteins were degraded and to form amino acids, then change the sequence of amino acids from original sequence in the isopropyl alcohol medium. In this chapter, we can report the measuring of amino acid quantity after degradation of proteins in fish body by applying the chlorpyrifos pesticide. In this research work, after the consumed the pesticides, proteins are degraded and to form amino acids, then change the sequence of amino acids from original sequence in the isopropyl alcohol medium. In this paper we have report the measuring of amino acids quantity after degradation of proteins in fish body by applying the Endosulfan pesticide in fish. These results are shown in Table 2.

Table 2. Endosulfan pesticide effect on fish body

Cone. of pesticide(mg/lit)	Leucine (mg/lit)	Tyrosine (mg/lit)	Tryptophan (mg/lit)	Valine (mg/lit)	Phenylalanine(mg/lit)
1.00	24	73	16	41	35
2.00	37	11	17	56	41
3.00	49	96	19	68	47
4.00	62	144	23	85	61
5.00	74	16	29	98	73
6.00	88	178	32	115	94
7.00	115	202	38	153	122

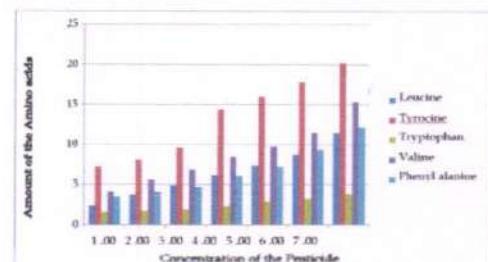


Figure 3. Change in Amino Acids by absorbing concentration of Pesticide

Tryptophan amino acid is not affected in protein degradation at low concentrations. But Tyrosine valine, Leucine is degraded at all concentration of Endosulfan pesticide. These results are shown in figure 4.

APPLICATIONS

Due to the formation of amino acids by degradation of proteins with concentration of pesticide the behavioral and morphological changes occur in the freshwater fish Labeo Rohita.

CONCLUSIONS

The present study proved that the Endosulfan is highly toxic and detrimental impact on the behavioral responses of Labeo Rohita at sub level concentration and any alterations caused by the pesticide may lead to variations of total proteins in fish body. Therefore, the amount of Endosulfan pesticide in the aquatic systems should be monitored then control the usage pesticide because the decreasing nutria valent value and mortality of fish. The histopathological changes in certain vital tissues like head, gill, liver, muscle and digestive system in the fish Labeo Rohita exposed to sub lethal and lethal concentrations of Chlorpyrifos, Cypermethrin and Endosulfan were studied. Endosulfan caused highly marked pathological changes in the gill than liver and digestive system. Endosulfan also caused profound pathological changes under chronic exposures in liver tissues of the fish Labeo Rohita. All these changes indicate the hepatoma toxic nature of Endosulfan. Since Endosulfan is an Chlorinated Hydrocarbon compound, it is neuro poisons.

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FORM 2

THE PATENT ACT, 1970

(39 OF 1970)

&

THE PATENT RULES, 2003

COMPLETE SPECIFICATION

[SEE SECTION 10 AND RULE 13]

TITLE: COMPOSITION AND METHOD FOR THE PREPARATION OF NANOPARTICLES WITH CONTROLLED RELEASE PROPERTIES FOR DRUG DELIVERY APPLICATIONS

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COMPOSITION AND METHOD FOR THE PREPARATION OF NANOPARTICLES WITH CONTROLLED RELEASE PROPERTIES FOR DRUG DELIVERY

APPLICATIONS

FIELD OF THE INVENTION

The present invention generally relates to drug delivery applications. More specifically, the invention relates to composition and method for the preparation of nanoparticles with controlled release properties for drug delivery applications.

BACKGROUND OF THE INVENTION

The field of drug delivery has witnessed significant advancements aimed at enhancing therapeutic efficacy and patient compliance. One promising approach involves the use of nanoparticles as carriers for controlled release of therapeutic agents. These nanoparticles provide numerous benefits, such as improved drug stability, targeted delivery, and prolonged release kinetics.

Traditional drug delivery systems often suffer from limitations such as rapid drug degradation, non-specific distribution, and insufficient drug concentrations at the desired site of action. To overcome these challenges, researchers have explored the use of biocompatible polymers to encapsulate therapeutic agents within nanoparticles. This approach offers several advantages, including protection of the drug from enzymatic degradation, controlled release kinetics, and enhanced bioavailability.

Poly(lactic-co-glycolic acid) (PLGA) is a commonly employed biocompatible polymer in nanoparticle-based drug delivery systems. PLGA possesses desirable properties, such as biodegradability, biocompatibility, and tunable release kinetics. By adjusting the ratio of lactic acid and glycolic acid units in the polymer, the degradation rate and release profile of encapsulated drugs can be precisely controlled.

would offer precise control over the release kinetics, enable targeted delivery to specific cells or tissues, and improve therapeutic outcomes.

In light of these considerations, the present invention provides a novel composition and method for the preparation of nanoparticles with controlled release properties. The invention addresses the limitations of existing drug delivery systems, offering an innovative approach to optimize drug delivery for various applications, including oral, intravenous, transdermal, and inhalation routes.

BRIEF DESCRIPTION OF THE FIGURES

FIG. 1: Schematic diagram of the pulse-heat aerosol reactor (PHAR) system used for synthesis of nanoparticle matrices with controlled properties comprised a pulse-heating zone followed by a perforated diluter and an isoaxial sampler. The key variables in aerosol reactor design were maintaining laminar flow of the aerosol and minimizing particle losses by diffusion and sedimentation and provision for imposing pulse-heat with alternate heating and quenching by dilution air.

FIG. 2: Number particle size distributions of nanoparticle aerosol lipid matrices synthesized using stearic acid in cyclohexane solutions at gas temperature of 298 K and 383 K (pulse), of varying concentrations, (a) 0.01 mg·cm⁻³, (b) 0.1 mg·cm⁻³, (c) 1 mg·cm⁻³ and (d) 10 mg·cm⁻³, measured using scanning mobility particle sizer. The mobility diameters ranged from 47-183 nm with a unimodal distribution and geometric standard deviation of 1.5-1.8.

DETAILED DESCRIPTION OF THE INVENTION

The present invention discloses a composition and method for the preparation of nanoparticles with controlled release properties for drug delivery applications. The composition comprises biocompatible polymer matrix nanoparticles encapsulating therapeutic agents, while the method involves a series of steps to achieve efficient and targeted drug delivery.

centrifugation, filtration, or dialysis, ensuring the production of high-quality nanoparticles suitable for drug delivery applications.

In addition to the core steps, the method can also involve optional modifications to the surface of the nanoparticles. This can be achieved by attaching targeting ligands to enhance the specificity of drug delivery. Targeting ligands can include antibodies, peptides, aptamers, or other molecules that recognize specific receptors or markers expressed on target cells or tissues.

The resulting nanoparticles exhibit controlled release properties, allowing for sustained drug delivery over a predetermined period of time. The release kinetics can be precisely controlled by adjusting the properties of the polymer matrix, including its molecular weight, composition, and degradation rate. The composition and method provide versatility in tailoring the release profile to match the therapeutic needs of different drugs and diseases.

The nanoparticles prepared using this composition and method can be formulated into a drug delivery system by incorporating them into a pharmaceutically acceptable carrier. Such carriers can include gels, creams, or injectable formulations, depending on the intended route of administration and desired application.

The following specific example is not intended to be limitive but only illustrative.

FIG. 1, a prototype pulse-heat aerosol reactor (PHAR) was designed and fabricated for control of particle properties through aerosol dynamics. The pulse-heating zone has an internal diameter and heated length of 38 mm and 80 mm, respectively. The aerosol flow rate was fixed at $3 \text{ L} \cdot \text{min}^{-1}$, with a flow Reynolds number of ~ 109 and a pulse time of one second. Stokes number for atomized droplets (mean diameter 300 nm) flowing in the reactor is in the order of 10^{-5} , implying that droplets follow gas streamlines and do not undergo impaction. Evaporating droplets flowing along with the gas streamlines are expected to undergo negligible drop breakup, internal solute circulation/motion and asymmetric solute concentration distribution. Thus the droplet evaporation process is expected to be uniform leading to isotropic particle properties. In the prototype PHAR, heating was provided to the pulse-heat zone to attain a gas temperature of (low and high $383 \pm 1 \text{ K}$) using heating tape of 250 W. Gas temperature in the pulse-heat zone was measured using a platinum resistance temperature detector (RTD, PT100) interfaced with a digital controller. The magnitude of temperature was fixed based on the required evaporation rate to produce particles of

proteins, peptides, nucleic acids, vaccines, antibiotics) for treatment of various diseases and disorders.

Example Illustrating the Disclosure

Experiments were done to produce stearic acid nanoparticles, in PHAR, with controlled size and morphology at varying evaporation rates. The pulse-heat aerosol reactor (PHAR) system used to study effect of pulse-heat on synthesis of nanoparticle matrices (FIG. 4) comprises of a collision-type air jet atomizer. The atomization device could also comprise of any device based on ultrasonic, electro spray, evaporation-condensation or FEAG principle of aerosol generation. The PHAR is designed with a pulse-heat zone, wherein a heat pulse of controlled temperature (heating element) and duration (flowrate of gas) is applied to the droplet aerosol to control the rate of evaporation. A perforated-wall aerosol diluter is provided to quench the temperature and aerosol dynamics mechanisms immediately after the pulse-heating. A scanning mobility particle sizer was placed downstream for measurement of mobility diameter. Any other nanoparticle size distribution measurement device including, ELPI, hypersonic impactor can be used in-lieu of or in addition to the SMPS. The standard upstream pressure of the atomizer was 35 psig. The solution, of lipid in a selected organic solvent (stearic acid in cyclohexane of varying concentrations, $0.01 \text{ mg}\cdot\text{cm}^{-3}$, $0.1 \text{ mg}\cdot\text{cm}^{-3}$, $1 \text{ mg}\cdot\text{cm}^{-3}$ and $10 \text{ mg}\cdot\text{cm}^{-3}$), was fed with a syringe pump at a flow rate of 0.6 mL/min . The resulting atomized droplets were suspended in a nitrogen flow through the PHAR, where droplet evaporation at a controlled rate, followed by quenching of aerosol dynamics was used to produce nanoparticles with controlled size, morphology and crystallinity.

Stearic acid nanoparticle matrices of mobility diameters of $47\text{-}183 \text{ nm}$, with a unimodal size distribution of geometric standard deviations (GSD) (1.5-1.8), were obtained in PHAR by fixing the gas temperatures, at 298 K and 383 K (pulse), to obtain the varying evaporation rates. For a given concentration, stearic acid nanoparticles of smaller mobility diameters were synthesized at lower evaporation rates, while nanoparticles with larger mobility diameters were synthesized at higher evaporation rates. The differences in the mean mobility diameters of stearic acid nanoparticles synthesized at higher evaporation rates, using larger concentrations ($1 \text{ mg}\cdot\text{cm}^{-3}$ and $10 \text{ mg}\cdot\text{cm}^{-3}$), were statistically significant (at the 95% confidence level; $P=0.002$, by t-test) than those synthesized at lower evaporation rates (Table 1). TEM images of nanoparticle matrices (FIG. 3 a), synthesized at 298 K using stearic acid in cyclohexane solution of $10 \text{ mg}\cdot\text{cm}^{-3}$, showed

I/WE CLAIM:

1. A composition for drug delivery comprising:
 - Nanoparticles comprising a biocompatible polymer matrix; and
 - A therapeutic agent encapsulated within said nanoparticles.
2. The composition of claim 1, wherein said biocompatible polymer matrix comprises poly (lactic-co-glycolic acid) (PLGA).
3. The composition of claim 1, wherein said therapeutic agent is selected from the group consisting of small molecules, proteins, peptides, nucleic acids, and combinations thereof.
4. A method for preparing nanoparticles with controlled release properties, comprising the steps of: a. Dissolving a biocompatible polymer in an organic solvent to form a polymer solution; b. Adding a therapeutic agent to said polymer solution to form a drug-polymer solution; c. Emulsifying said drug-polymer solution in an aqueous phase to form an emulsion; d. Removing the organic solvent from said emulsion to obtain nanoparticles with controlled release properties; and e. Collecting and purifying said nanoparticles.
5. The method of claim 4, wherein said organic solvent is selected from the group consisting of dichloromethane, chloroform, ethyl acetate, and combinations thereof.
6. The method of claim 4, wherein said aqueous phase comprises a surfactant to stabilize the emulsion.
7. The method of claim 4, further comprising the step of modifying the surface of said nanoparticles with a targeting ligand.

**COMPOSITION AND METHOD FOR THE PREPARATION OF NANOPARTICLES
WITH CONTROLLED RELEASE PROPERTIES FOR DRUG DELIVERY
APPLICATIONS**

ABSTRACT

The present invention relates to a composition and method for the preparation of nanoparticles with controlled release properties for drug delivery applications. The composition comprises biocompatible polymer matrix nanoparticles encapsulating therapeutic agents, providing a platform for efficient and targeted drug delivery. The biocompatible polymer matrix, such as poly (lactic-co-glycolic acid) (PLGA), ensures biocompatibility and controlled release of the therapeutic agents. The therapeutic agents can include small molecules, proteins, peptides, nucleic acids, or combinations thereof. The method involves dissolving the biocompatible polymer in an organic solvent to form a polymer solution, followed by adding the therapeutic agent to obtain a drug-polymer solution. This solution is then emulsified in an aqueous phase, forming an emulsion. Subsequently, the organic solvent is removed from the emulsion, resulting in the formation of nanoparticles with controlled release properties. The nanoparticles are collected, purified, and optionally modified with targeting ligands for enhanced specificity.

COMPLETE SPECIFICATION - DRAWINGS

Sheet No. 2

Total No. of Sheets. 2

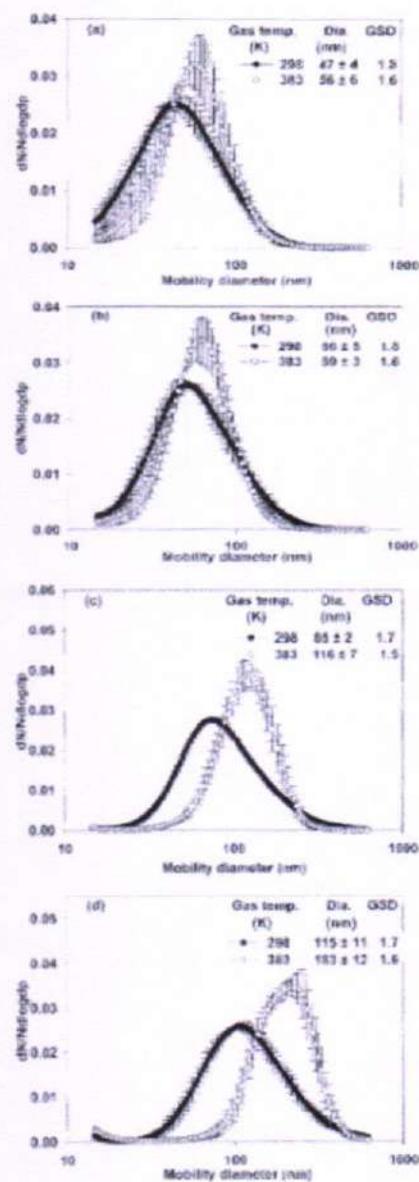


FIG. 2

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(54) Title of the invention : METHOD FOR THE SYNTHESIS OF QUANTUM DOTS WITH TUNABLE OPTICAL PROPERTIES FOR USE IN PHOTOVOLTAIC DEVICES

(51) International classification :B82Y 100000, B82Y 200000, H01G 092000, H01L 310320, H01L 310352

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(57) Abstract :

METHOD FOR THE SYNTHESIS OF QUANTUM DOTS WITH TUNABLE OPTICAL PROPERTIES FOR USE IN PHOTOVOLTAIC DEVICES ABSTRACT The present invention discloses a method for the synthesis of quantum dots with tunable optical properties for use in photovoltaic devices. The method involves the controlled growth of quantum dots by manipulating reaction conditions and adjusting parameters to achieve desired sizes, compositions, and optical characteristics. The synthesized quantum dots offer tunability in terms of bandgap, absorption, and emission wavelengths, making them suitable for efficient light absorption and power conversion in photovoltaic devices. The method begins by providing a precursor solution containing semiconductor materials and capping ligands. The reaction conditions, including temperature, pressure, and reaction time, are carefully controlled to promote the growth of quantum dots with specific properties. The size of the quantum dots is controlled by adjusting the concentration of the precursor solution and the reaction time, while the composition is manipulated by varying the stoichiometry of the semiconductor materials.

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(54) Title of the invention : Synthesis and Application of Copper Manganese Doped Nickel Oxide Nanoparticle as a Versatile Agent for Antimicrobial and Anticancer Treatment

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(57) Abstract :

The present invention relates to the synthesis and application of copper manganese doped nickel oxide nanoparticles as a versatile agent for antimicrobial and anticancer treatment. The nanoparticles are carefully synthesized with controlled sizes and compositions. They exhibit broad-spectrum antimicrobial activity against bacteria, fungi, and viruses, while selectively inducing cytotoxicity in cancer cells. The nanoparticles can be functionalized with targeting ligands for specific delivery to tumor sites, enhancing their efficacy in inhibiting tumor growth. Coating medical devices with these nanoparticles reduces the risk of device-associated infections. Additionally, the nanoparticles can be used in pharmaceutical compositions for combined antimicrobial and anticancer therapy.

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(54) Title of the invention : STABILITY STUDIES AND OPTIMIZATION CHARACTERISTICS OF FE3O4 - MAGNETIC NANOCOMPOSITE FOR HEAVY METAL REMOVAL APPLICATION

(51) International classification :C02F0001280000, C02F0101200000, B01J0020280000, C02F0001620000, B01J0020220000

(86) International Application No :NA

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(57) Abstract :

7. ABSTRACT This research delves into the evaluation and enhancement of a Fe₃O₄ magnetic nanocomposite tailored for the effective removal of heavy metals from diverse aqueous solutions. The significance of this work lies in its direct application to environmental and industrial contexts, where heavy metal contamination poses a severe threat. The study scrutinizes the nanocomposite's resilience under various environmental conditions, encompassing shifts in pH levels, ionic strengths, and temperature ranges, all of which are pivotal in real-world applications. Moreover, it delves into the fine-tuning of its characteristics, focusing on optimizing its heavy metal adsorption capacity and magnetic behavior for efficient post-capture separation. The culmination of this research holds great promise for addressing critical challenges in heavy metal remediation, offering a sustainable, efficient, and customizable solution with substantial benefits for environmental and human well-being.

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(54) Title of the invention : CHITOSAN STABILIZED FE₃O₄ - MAGNETIC NANOCOMPOSITE SYNTHESIS, CHARACTERIZATION, AND VERSATILE APPLICATIONS

(51) International classification :A61K0049180000, B01J0020280000, C02F0001280000, A61K0049080000, B82Y0025000000

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(57) Abstract :

7. ABSTRACT The invention pertains to the synthesis and characterization of a chitosan stabilized Fe₃O₄ magnetic nanocomposite. This nanocomposite combines the magnetic properties of Fe₃O₄ nanoparticles with the biocompatibility and stability of chitosan. The synthesis involves coating Fe₃O₄ nanoparticles with chitosan, crosslinking with glutaraldehyde, and thorough characterization using techniques such as TEM, XRD, FTIR, and TGA. The resulting nanocomposite exhibits a core-shell structure with a chitosan shell, making it suitable for a broad spectrum of applications. It finds utility in drug delivery, serving as a magnetic resonance imaging (MRI) contrast agent, and as an efficient tool for environmental remediation by separating pollutants from fluid media. The nanocomposite's advantages include biocompatibility, stability, and versatility. Experimental results confirm its potential for diverse applications, such as controlled drug delivery and environmental cleanup.

No. of Pages : 11 No. of Claims : 9



SECURITY THREATS AND MEASURES AND HOW TO OVERCOME FROM IN SUPERIOR CLOUD

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confidentiality for personal information, and measures to prevent data loss.

Abstract—Cloud computing is a highly popular technology known for its cost-effectiveness, reliability, rapid access, flexibility, and scalability for computer operations. The IT industry has witnessed significant growth in cloud computing adoption. However, IT organizations have raised concerns regarding security in cloud computing due to the outsourcing of essential services to third parties, making it challenging to maintain data security and confidentiality. This paper offers insights into security threats associated with cloud computing and suggests potential countermeasures.

Keywords—Cloud Computing, Security, Threats, Confidentiality.

Introduction

Cloud computing offers a range of computing services, including servers, storage, databases, networking, software, and analytics, delivered over the internet. It functions as a network for storing and sharing resources. In the cloud, you pay only for the services you use, such as storage on a pay-as-you-go basis, reducing operating costs and improving organizational efficiency. In cloud environments, multiple virtual machines can coexist on the same physical server infrastructure.

The main concerns of many IT organizations revolve around areas like external data storage, reliance on the public internet, limited control, multi-tenancy, and integration with internal security systems. Cloud computing differs from outdated technologies due to its vast scale and complete distribution and visualization of resources. To ensure security in the cloud, it is crucial to implement mechanisms like robust authentication,

1 Virtualization:

Cloud computing relies on virtualization, where various virtual machines can operate with different operating systems and run multiple applications while sharing a single underlying physical computer. This approach prevents cloud vendors from the burden of providing individual physical resources to each customer. Instead, it enables efficient resource utilization in the cloud, making virtualization a smart choice.

Fig. 1. Hyper Cycle for Cloud Security, 2020.



1.2 Types of Cloud Environments:

1.2 Types of Cloud Environments

Public Cloud: A public cloud is standard model which providers make several resources, such as applications and storage, available to the public. Public cloud services may be free or not.



Cover Page



Private Cloud: A private cloud refers to cloud computing resources used exclusively by a single business or organization. A private cloud can be physically located on the company's on-site data center. Some companies pay to third-party service providers to host their private cloud. A private cloud is one in which the services and infrastructure are maintained on a private network [5].

Hybrid Cloud: Hybrid cloud is a combination of both public and private cloud that provides and controls some resources internally and has some others for public use.

Community Cloud: The cloud infrastructure is shared among organizations that share the same concerns such as the mission, security requirement and policy. It may own by more organization and it exists on premises or even off-premises.

II.related work

2.1 Types of Cloud Services:

Most cloud computing services fall into three broad categories: Infrastructure as a service (IaaS), Platform as a service (PaaS), and Software as a service (SaaS).

1. Infrastructure as a Service (IaaS): This is the fundamental category of cloud computing services. IaaS allows you to lease IT infrastructure, including servers, virtual machines (VMs), storage, networks, and operating systems, from a cloud provider. You pay for these resources on a usage basis.

2. Platform as a Service (PaaS): PaaS is a cloud computing service that offers an on-demand environment for developing, testing, deploying, and managing software applications. It simplifies the development process by handling the underlying infrastructure, including servers, storage, networks, and databases, allowing developers to focus on creating websites and mobile apps.

3. Software as a Service (SaaS): SaaS is a method of delivering software applications via the internet, where users access and pay for the software, they use on-demand. In the SaaS model, the cloud provider hosts and manages both the software application and its underlying infrastructure. This includes tasks like software updates and security patches. Users can connect to the application through a web browser on various devices [5].

In the SaaS model, the responsibility for security primarily falls on the cloud provider because of the high level of integration and limited customer control. In contrast, the PaaS model offers more extensibility and greater control to the customer [1].

2.2 Issues in Service Models:

Software as a Service Security Issues (SaaS):

Clients relying on service providers must trust them to implement adequate security measures. The provider's responsibility includes ensuring that multiple users cannot access each other's data, which is crucial for user data privacy. Therefore, it's essential for users to verify that appropriate security measures are in place. However, guaranteeing the availability of the application when needed can be challenging.

SaaS software vendors have two common deployment options. They may host the application on their private servers or utilize a third-party cloud computing infrastructure service (e.g., Amazon, Google, etc.) for deployment [3].

Platform-as-a-Service Security Issues (PaaS): In the PaaS environment, data must be accessed, modified and stored. This means data will require decryption and re-encryption, thus introducing key management issues. Encryption challenges are far from the only security issue with PaaS.

Infrastructure-as-a-Service (IaaS) Security Issues: IaaS provides a pool of resources such as servers, storage, networks, and other computing resources in the form of virtualized systems, which are accessed through the Internet [4]. Users are entitled to run any software with full control and management on the resources allocated to them. With IaaS, cloud users have better control over the security

compared to the other models as long there is no security hole in the virtual machine monitor. They control the software running in their virtual machines, and they are responsible to configure security policies correctly.

Global Cloud Computing Market

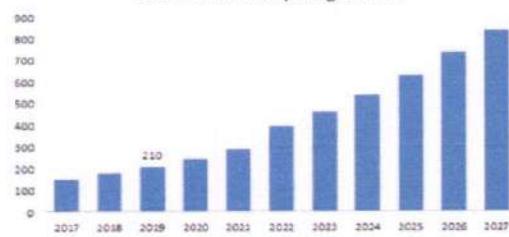


Fig. 2. Global Cloud Computing Market.

2.3 Common Security Threats in Cloud Computing:

Here are descriptions of various cybersecurity threats in cloud computing:



Threats	Description
Third-party Relationships	If a third party fails to maintain the proper coverage and an uncovered event or situation occurs, your organization may face additional risk
Malicious Code Injection	Any code in any part of a software system or script that is intended to cause undesired effects, security breaches or damage to a system. Malicious code is an application security threat that cannot be efficiently controlled by conventional antivirus software alone.
Insecure permissions on Cloud Data	Giving permissions to the unauthenticated & unauthorized users may compromise the data security

Table 2. Types of possible attacks in PaaS

Threats	Description
Data Leaks	Data in the cloud is exposed to the same threats while it is being transferred, stored, audited or processed.
Account Hijacking	Account of User or an Organization is hijacked by Hacker/Attacker gains access to a user's credential. Then the hacker has full authority to perform Unauthorized Activities.
Vulnerabilities in Virtual Machine	Possible covert channels in the colocation of VMs, Unrestricted allocation and deallocation of resources with VMs
Denial of Service Attack	It is a type of attack that tries to make a website or network resource unavailable.

Table 3. Types of possible IaaS

1. Account Hijacking: Account or service hijacking is a type of identity theft that's on the rise. Attackers aim to deceive end users by taking control of their accounts or services.

Threats	Description
Data Access Risk	Data access issue is mainly related to security policies provided to the users while accessing the data. Some of the employees are not given access to certain amount of data.
Identity Theft	Identity theft is the act of a person obtaining information illegally about someone else. They try to find such information as full name, maiden name, address, date of birth, social security number, passwords, phone number, e-mail, and credit card numbers.
Network Security	All data flow over the network needs to be secured in order to prevent leakage of sensitive information. This involves the use of strong network traffic encryption techniques such as SSL and TLS for security
SQL Injection	An unauthorized user tries to access the confidential data in the database by injecting malicious code in to a standard SQL code. This can be reduced by using automatic generated SQL code. And does not allow unauthorized users to enter the database to access the private data.
Phishing Attacks	Phishing" refers to an attempt to steal sensitive information, typically in the form of usernames, passwords, credit card numbers, bank account information or other important data in order to utilize or sell the stolen information.

Table 1. Types of possible attacks in SaaS

2. Malware Injection: In this attack, malicious actors attempt to inject malware or malicious services into the cloud. They create their own malicious service modules or virtual machine instances, trying to make them appear as valid services. If successful, legitimate users are redirected to the malicious service, allowing the attacker's code to execute.



3. Denial of Service (DoS) Attacks: DoS attacks are aimed at making a website or network resource unavailable. Attackers flood the target with a large number of packets in a short time, overwhelming the host and causing it to ignore legitimate requests.

4. Data Breach: Data breaches involve unauthorized access, theft, or use of data. Such breaches have become increasingly common and can have severe consequences.

5. Man-in-the-Middle (MITM) Attack: In MITM attacks, intruders intercept or modify messages between two entities that believe they are communicating directly. This exploit often relies on network packet sniffing and can compromise the security of transactions and data transfers.

6. Side Channel Attacks: Attackers try to place a malicious virtual machine on the same host as the target, using side channel attacks to decode ciphertext and calculate encryption keys. Strong firewall systems can help prevent this.

7. Malicious Insider: Malicious insiders are individuals within an organization who intentionally misuse confidential data for personal gain, potentially compromising the organization's integrity. Privilege planning and security auditing can mitigate this risk.

8. Insecure API: Poorly designed user interfaces (UIs) and APIs can provide hackers with easy access to sensitive data, leading to significant financial, reputational, and business losses.

These threats underscore the importance of robust security measures and practices to protect cloud computing environments and the data they contain.

Proposed work

3.1 Measures for Major Threats in Cloud Computing

Here are some key security practices for maintaining security in a cloud environment:

1. Up-to-Date Intrusion Detection System: Employ an intrusion detection system that can identify unusual network traffic and provide early warnings based on credentials and behavioral patterns. This system acts as an alarm for potential security breaches. Blocking IP addresses that are the source of an attack can help mitigate threats.

2. Select a Reliable Cloud Provider: Choose a reputable and trustworthy cloud service provider that prioritizes security and compliance.

3. Patching and Updating: Keep software and systems up to date by promptly applying security patches and updates as they become available. This helps protect against known vulnerabilities.

4. Data Encryption: Implement robust encryption mechanisms to safeguard data both at rest and during transit. Cloud encryption involves transforming data using mathematical algorithms to conceal it from unauthorized access.

5. User Behavior Monitoring: Continuously monitor the behavior of users with access to the cloud environment. Maintain control over encryption processes and keys, segregate duties, and restrict access to minimize potential risks.

6. Proper Password Management: Enforce strong password management practices, including regular password changes and the use of complex, unique passwords.

7. Access Restrictions: Restrict access to cloud services to authorized users only. Implement multi-factor authentication (MFA) systems, such as smart cards, one-time passwords (OTP), and phone authentication, to enhance security.

8. Use of First-Class APIs: Pay attention to abnormal activities and conduct regular audits. Implement strong protection measures to secure API endpoints, as these are often targeted by attackers.

By following these security best practices, organizations can enhance the security of their cloud environments and reduce the risk of data breaches and unauthorized access.

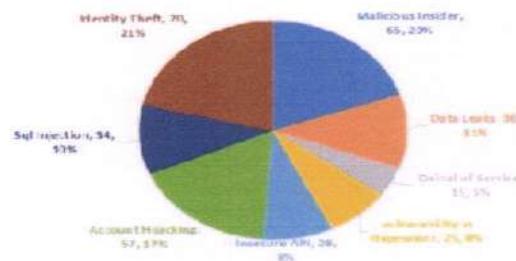


Fig. 3. Possibility of Threat after implementing Security Measures.

IV. Conclusion & future work

The use of cloud computing has become the norm for businesses as well as people in society. Its growth has been seen mainly in the past decade and will continue



to evolve. As rapid growth in cloud computing era the security for private data is also essential, should be given proper authentication.

This paper surveyed the key security issues of Cloud Computing being faced today and the challenges and opportunities that it brings for business community. This research paper analyzed what exactly cloud computing security-related issues are, and discussed data security and privacy protection issues associated with cloud computing across all stages of data life cycle.

By this paper we know various threats in the cloud computing and some measures are proposed to reduce the risks and threats in cloud computing. The cloud still has much to improve on with security and ease of integration, but cloud computing will continue to grow and advance the ability to share and store data in the technological world.

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Threats	Impact (High -2, Low -1)	Risk Percentage before Measures	Risk Percentage after Measures
Malicious Insider	2	65	20
Data Leaks	2	36	11
Denial of Service	1	15	5
vulnerability in Hypervisor	2	25	8
Insecure	2	28	8
Account Hijacking	2	57	17
SQL Injection	2	34	10
Identity	2	70	21

Table 4. Reduction in vulnerability after implementing Securing Methods.



IMPACT OF COVID 19 ON TEACHING, LEARNING AND RESEARCH IN HIGHER EDUCATION

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ABSTRACT

Learners and teachers at all levels of education have been affected by COVID-19 restrictions with rapid adaptations to virtual learning platforms. The impact of COVID-19 on learners is not evenly distributed and children of under-privileged groups, those who live in poverty, those requiring special education, and children who cannot afford digital equipment are more negatively affected by the need for remote learning. Psycho disorders like anxiety and depression have increased as a result of COVID-19 itself and as a consequence of change in mode of learning. Restrictions on traveling, social distance, and funding restrictions affected research work in higher education. Non-medical researchers were slowed down but research in medical field is induced.

KEY WORDS

COVID-19, online teaching, e-learning, research

INTRODUCTION

Corona viruses are a group of viruses which influence people through zoonotic transmission. Covid-19 is a disease that has serious health implications and one of the most significant issues related to this disease is its capability to spread in a rapid manner. The worldwide spread of coronavirus has brought a dramatic change in all fields of human life including teaching, learning and research in higher education.

OBJECTIVES

- To find out the impact of covid on teaching, learning and research in Higher Education
- To estimate the overall impact of Covid-19 on education

METHODOLOGY

The investigation is performed by reviewing various secondary sources like published literary works, case studies and data from government and non-government bodies and from authentic websites. Utmost care is taken to identify only the reliable data in order to provide the true situation as it is the field of education.

EFFECT OF COVID ON TEACHING

The pandemic and lockdown have changed the dynamics of the education sector and thus the field of teaching is obliged to open new grounds for teachers to adopt the virtual environment. Teachers around the world started using technology to get connected with the students which is quite unprecedented to the world of teaching.

Though the situation is tough, teachers came up with a solution through the computers by creating online learning opportunities, virtual classes by which teachers can be connected to their students. It is somewhat different from the normal classroom teaching where direct eye to eye contact between the learner and the instructor is not possible but this is the only best choice left in this situation.

Being a teacher is not just reciting any lesson from the textbook, but it is a continuous lifelong process of learning. In the pandemic situation teachers, along with technicians, learnt and invented many tools for making their lesson interesting for the students of different backgrounds and areas. Online meeting platforms like google meet, zoom, Cisco WebEx have become day to day needs of teachers. Teachers attended several training programmes to learn LMS, Google classroom, A-Z Screen recorder, OBS and so on. It is something wonderful to get connected with someone live through the internet via video. Teachers started making recording videos for repeated use. These recorded videos can be used for unlimited times. There are several options while going to online education and the method and tools will be chosen depending on the context and goal.

Taking class online through live video is one of the best techniques by which a teacher can show slides while giving a lecture simultaneously. Tools like Microsoft PowerPoint, Apple's Keynote, Google slides are useful in creating slides. Software like Camtasia, Bandcamp and Apowersoft etc are useful for the purpose of recording but most of the teachers from Collegiate education in Andhra Pradesh are using the OBS and LOOM platforms. Taking the pandemic situation into consideration, the Commissionerate of collegiate education,

- Trained teachers in Learning Management System (LMS) and nearly 700 videos uploaded in various subjects
- Introduced Virtual Classroom Teaching and now 144 Colleges have virtual Classroom equipment
- All the online classes delivered by the teachers of higher education were recorded and the links were saved.
- Bharat Padhe Online portal is established to share ppts and the information of the video classes nationwide and the same is done by the teachers of higher education in Andhra Pradesh.

There are many options for placing videos and integrating them into learning management systems like Zoom, Ustream, Livestream, Crowdcast, WebinarJam, Skype, Adobe Connect etc. The pre-recorded video hosting options include YouTube, Vimeo and Amazon S3 and among them YouTube is the most popular platform.

At present the governments of different states allowed offline teaching. In higher education blended teaching is going on. The threat of another wave is hanging on the world and any time the necessity of closing educational institutions may appear again. But, the teachers are ready and well trained to face any tough situation in future.

EFFECT OF COVID ON LEARNING

According to the 75th National sample survey, conducted between 2017 June to 2018 June, less than 15% have household internet access. This is more than 42% in urban areas. So, Rural students are lagging behind in non pandemic situations. Later in 2018, as Bharat Net project was launched, more than 2.5 lakhs of village panchayats were provided with internet connection. It prepared some useful grounds for later use.

Research is conducted in the Faculty of Information Technology, Benghazi University, Benghazi, Libya, gave positive output with regard to online education. In the study,

- The students believe that e-learning is useful and it is the scientific method learned on electronic/multimedia forms.
- The learners agree that e-learning is useful and that it helps them to be safe and improve their academic standards.
- The students claim that the low-quality of internet services is the biggest obstacle to its application.
- The students demonstrate that there are limitations to e-learning and that the biggest drawback is, it decreases the workload for teachers and raises the pressure on students.

The same inferences are applicable even to the Indian context. But, since the start of the pandemic the student performance has plummeted across the world. Students are still adjusting to the new change. They are switching from traditional lectures to digital learning but one must admit that it is still proving a challenge for most of the educational institutions. Disenfranchised students whose family income is low, are experiencing a learning loss compared to their peers from high income households. According to some study by Brookings, scholars made learning gains within the first months of online teaching but these figures have continued to drop later.

Adequate access to learning equipment is not available to many students and it is one of the biggest barriers for online teaching and learning. Most institutions were not ready for full-scale digital learning, they couldn't prepare teachers and college students for it. Several students have no proper access to learning material. To disenfranchise communities, getting stable internet connection and digital amenities is a big task. In many situations, students don't have a laptop for class work. Besides, the pandemic's economic burden distracts scholars from routine work. They cannot concentrate and participate equally in their class. It nearly takes five hundred per month to get the minimum required internet connection through mobile phone. It was a big amount for nearly sixty percent of students who are getting education in the government sector and when the students' performance level decreases, the gap between their achievement widens.

Students with special needs must be addressed in this context. At present students with disabilities have limited access to learning materials. Improved learning apps are in scarce supply. So, even though the learning conditions are the same, the gap between student achievement among different classes is widening.

As per the Washington post report, the enrolment rates have decreased by 2.5% universally. These low enrolment figures are the result of pandemic scares and financial instability. But the fact remains that students now seek admission at a lower rate than before. Although no definite information exists about the reasons for these increased drop-out rates, experts point to social factors, including:

1. Bereavement
2. Financial instability
3. Socio-cultural isolation
4. Poor mental and physical health

Many studies are being conducted focussing on mental health of the students in higher education. One research conducted by Amar Prasad Choudhry, published in National Library of Mental Health in which a total of 324 college students participated, of whom 180 (55.6%) were male and 144 (44.4%) were female. After assessment of the psychometric scales, it was found that of the 324 students, 223 (68.8%) had high fear of COVID-19, 93 (28.7%) had moderate to severe depression, and 167 (51.5%) had mild to severe anxiety. As per a study by the U.S. Census Bureau, over 40% of survey respondents showed signs of depression or anxiety and as the lockdown drags on, these figures may continue to rise. Fall in social events on college campuses decreased or even non-existent due to COVID-19 regulation. As human beings are social beings, isolation becomes one major problem to them. The problems of the various categories of the students must be addressed separately and the whole world should give support to them.

EFFECT OF COVID ON RESEARCH IN HIGHER EDUCATION

Before the COVID pandemic, virology research (including influenza) represented less than 2% of all biomedical research. However, the number of laboratories and investigators that have pivoted to address COVID related research questions is astonishing, likely comprising 10–20% of current biomedical investigation, showing the incredible adaptability of the research community. The multinational support rapidly infused for COVID-19 research is in the billions of euros. The sharing of research findings and research data has never been as rapid and efficient.

Travel, social, and funding will also take a serious toll on scientific research worldwide. Research staff and resources have been purposely and purposefully prioritized to COVID-19 activities above all else. Distancing and transmission issues have caused most non-COVID clinical research to be suspended. It resulted in reduction in recruitment of research subjects and a delay in data entry into clinical trial databases. Research-related hiring has been suspended because of restrictions imposed on traveling and young researchers might soon find themselves out of a job if their subject is not the pandemic. Indeed, though government-funded medical research bodies worldwide say they are committed to maintaining the continuity and breadth of research, how the economic downfall will influence government spending remains to be seen. Furthermore, research funding that relies on public fund raising may substantially and many researchers will see a significant decrease in funding opportunities. The global impact the crisis will have on the economy makes it hard to imagine that future research funding will not be substantially affected.

CONCLUSION

The real goal of education is to make the citizen properly accustomed to the world around him/her and try to make it more perfect. Teachers are updating themselves from time to time to get the rapidly changing technology and trying their level best to use the technology to reach their students who are obliged to stay at their homes. Students are facing many problems like poverty, psychological stress and mechanical interaction with their teachers. Though we are going for offline class mode at present, the threat of third wave may lead the world again towards virtual classes. So, it has become impossible to imagine college and university education without digital resources. But as digital learning is many times more costly than normal classroom learning, it is the responsibility of the governments to extend its helping hand to students who are under privileged and it will be the responsibility of the society not to create a digital divide between the rich and the poor. Online education must be more inclusive, and should have connectivity and equitability.

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Dalit Women and Colonial Christianity

First Telugu Bible Women as Teachers of Wisdom

CHAKALI CHANDRA SEKHAR

The paper focuses on the history of the first three Bible women, Mary Wesley, Martha Reuben, and Bathsheba, who came from marginalised communities in Rayalaseema, and emerged as new leaders of social change in the context of colonial modernity and Christianity in the region. The emergence of a modern profession of Bible woman for Dalit women in the 1870s was transformative, opening doors of education, learning, and transforming them into local leaders. Bible women played a pivotal role in the history of Dalits, gender, and missions by shaping the life and community of Dalits and spreading Christianity in Rayalaseema.

While historical studies have examined Bible women and their contribution to the missionary movement in South Asia (Sebastian 2003; Haggis 1998; Kent 1999; Taneti 2013; Mohan 2017), relatively little attention has been focused on studying how the profession of Bible women started in India, particularly in the Telugu-speaking regions, especially the endeavours of the first Telugu Bible women. Based on insights from some of the studies mentioned above, this is an effort to listen to the voice of the first three Bible women of Rayalaseema¹ that have remained silenced by the missionaries and unnoticed by historians. Moreover, in doing so, it analyses their emergence as new leaders of social change and their contribution to the transformation of gender roles and patriarchal structures among the people in Rayalaseema society. The paper draws on archival material, such as colonial administrative reports, as well as a wide range of missionary sources, and additionally uses oral interviews from the field.

In Rayalaseema, Dalit communities (Malas and the Madigas) were the lowest in the social order. For centuries, they were despised and degraded, kept in a state of servitude by the dominant castes.² Further, they were subjected to untouchability and unseeability. Their presence and approach, considered impure, was despised by other castes and even their shadow was believed to be polluting. The caste system, with its hierarchical social structure, did not recognise their social value and did not treat them as human beings. In addition, Dalits were not allowed to access public places, such as temples, schools and drinking water wells (Cornish 1874: 118). However, their encounter with Christianity brought visible changes in their life.

In 1822, protestant mission groups such as London Missionary Society (LMS) established their mission station at Cuddapah in Rayalaseema region. Even though individual conversions of Dalits began in the 1820s, mass conversions among the Dalits in Cuddapah and Kurnool districts took place in 1851 (Porter 1885: 46). Initially, the missionaries focused on the conversion of men, as the wives of missionaries were unable to devote their time and strength entirely for women's work, because of family and household responsibilities. However, in the 1870s, the office of Bible women emerged in Rayalaseema with the expectation that they would find access to families and women, otherwise inaccessible to Christian influence. This office was a direct result of a movement that began in England in the 1850s. Mary, Martha and Bathsheba were

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the first three Bible women in Rayalaseema who emerged as new leaders, availing opportunities that colonial modernity and missionary Christianity provided. Their work as Bible women contributed towards social change for the women in the region.

Evolution of Bible Women

The origin of Bible women in Rayalaseema can be traced back to the office of British Bible women in England, with Ellen Ranyard being a leading name in the movement of Bible women (Kent 2004: 150–51). Ranyard was appalled at the condition of people in the slums of London (Alldridge 1887: 114). This led to the first Bible woman being appointed in 1857 to carry the message of god by selling Bibles to the poor. In addition, Ranyard founded the Bible and Domestic Female Mission (BDFM) to cater to the spiritual needs of women in the slums of urban England. The mothers' meeting was an essential part of this mission (Taneti 2013: 40–42). Ranyard communicated her missionary work to the donours through the magazine *Missing Link* which was widely read by those whom the Bible women worked with. Ranyard's concern for the salvation of women in slums in London later grew into a concern for the salvation of women in India and other countries. This concern found expression in the origin of Bible women in Rayalaseema.

Martha Kilpin, a missionary who lived in Cuddapah, was a regular reader of the *Missing Link* magazine.³ After her retirement, she settled in England, where she conveyed to Ranyard that there were prospects for Bible women in Indian villages, and that she was willing to undertake the correspondence and secure reports, if funding was guaranteed (*Missing Link*, March 1871: 91). Kilpin contributed a series of articles to this magazine and argued for the necessity of Bible women for the conversion of local women, appealing to the readers in England to contribute funds towards the Bible women in Cuddapah mission station (*Missing Link*, April 1871: 124). As a result, in 1871, Mary Wesley and Martha Reuben were appointed as the first and second Bible women in Cuddapah district (*Missing Link*, April 1871: 125). Bathsheba was appointed as the third Bible woman in Nandyal mission station in 1872 (*Missing Link*, July 1873: 208; Lewis 1879: 12). They were the first Bible women in the entire Telugu speaking area. They were accountable to Kilpin and were expected to send monthly reports which were published in *Missing Link*. Kilpin worked as the liaison between BDFM and the local Bible women in Cuddapah in securing salaries and supplies. Each Bible woman's salary was £12 per year. The financial support from BDFM and Kilpin's correspondence together shaped how the office of Bible women evolved in the Telugu speaking areas, particularly Rayalaseema.⁴

Biographical Sketches

Gathering information about Bible women and their work in the missionary reports has its own challenges. As missionaries did not record details of native workers, complete details about the Bible women discussed in the paper was not available.

Information about how they became Christians, their family background, details about their husbands and children is not available. This was because the readers of *Missing Link* wanted to read about the conversions that were results of their funds and prayers, rather than the personal details of the native Bible women. Therefore, their biographical sketches are reconstructed from scattered clues available in missionary literature.

Mary Wesley: Mary Wesley was appointed as the first Bible woman in Cuddapah station along with her son Samuel Wesley who had been trained as a native medical missionary. There is no direct information about her social identity. One can assume that she was from the Dalit community based on the following clues. In one instance, it is seen that working along with her son enabled her to gain access into caste houses where no other Christian (Dalit) woman was allowed (*Missing Link*, April 1871: 125). Another instance refers to a woman named Achamma from a dominant caste who visited a relative undergoing treatment at the missionary dispensary. While staying the night with Mary Wesley, Achamma felt that having a meal cooked by Mary Wesley would break her (Achamma's) caste, so she was given grain and oil to prepare her own food (*Missing Link*, February, 1872: 53).

Mary began her work in Proddatur when a dispensary was established and her son was appointed as a native medical missionary (*Missing Link*, September 1871: 276). As Kilpin recounts, in 1871, Mary visited many houses and read the Bible and conversed with 700 women in the entire year (*Missing Link*, February 1872: 53). She interacted with many female patients who came to the dispensary for medical treatment. She worked in Cuddapah district for three years, and in 1874, when her son was appointed at the Black Town Dispensary in Madras, she moved there and continued her work (*Missing Link*, May 1874: 155; PDGA 1874: 33).

Martha Reuben: In 1871, Martha Reuben was appointed as a second Bible woman in Cuddapah. There was no clear mention of Martha's caste identity in the mission records, but the following quote hints at her background: "She was going into the houses of women of different castes, reading to them the word of God" (*Missing Link*, January 1875: 26). Missionaries wrote this kind of sentences in the context of native workers who were Dalits to point out that even though they were treated as untouchables, they were received by every caste (including Brahmins and Reddys). Another reference was of Martha visiting a village, where she found several women spinning under a tree. Ankamma, who she knew among these women, invited her to sit with them, when "all those women were Sudra caste (a higher caste than her own)" (*Missing Link*, March 1877: 86). These details suggest that she was from the Dalit community. Kilpin reports that Martha had formerly been an *ayah* in an orphanage, and that she was a clever, intelligent, affectionate, and a pious woman (*Missing Link*, April 1871: 125). In the first year of her work, Martha visited 13 villages, held mothers' meetings with native Christian

women and conversed with 300 Hindu and Muslim women (*Missing Link*, February 1872: 53). However, according to Kilpin, Martha resigned her job in 1879 because of her failing health (*Missing Link*, October 1879: 312).

Bathsheba: Appointed in 1872 at the Nandyal mission station, Bathsheba was the third Bible woman in the LMS mission in Rayalaseema. She was from the Reddy caste, a dominant caste in Rayalaseema. Her grandmother embraced Christianity in 1855 and her mother did so in the 1860s (ARLMS 1856: 80; *Missing Link*, July 1873: 207). Bathsheba worked in Nandyal town and its vicinity for nine years. In 1881, she was moved to Gooty as the mission station shifted from Nandyal to Gooty. In Gooty station, she worked nearly 27 years under Emma Thomason, the wife of missionary W W Stephenson. Bathsheba married a LMS catechist (*Vivekavathi*, October 1911: 12). For many years, Bathsheba was financially supported by Miss Lees from England (ARLMS 1908: 71; Lewis 1879: 12). Emma Thomason, a missionary, documented that Bathsheba visited the houses of almost every caste and they visited her in her own home, too (MMCLMS 1884: 398). Sometimes, Bathsheba took all the women who visited her to the missionary's house so that these women could see and converse with women missionaries, which was followed by a meeting called "mothers' meeting" (MMCLMS 1884: 398). In 1907, after 36 years of work, she resigned from her job (ARLMS 1908: 71).

Bible Women and Skills

Mary, Martha, and Bathsheba took up the opportunities offered by colonial modernity and missionary Christianity, which introduced Christianity and literacy in their lives. Their knowledge in reading and writing, strong religious faith and association with Kilpin, while she was in Cuddapah, contributed to their appointment as Bible women. They were recruited to evangelise native women. However, their activities contributed towards emancipation and liberation from the oppression they faced as Dalit women. Unlike the later generation of Bible women, they had no formal training.⁵ Initially, they were looked at with suspicion, as fortune-tellers, whose object was to destroy caste, and cause shame and disgrace to those they spoke to (*Missing Link*, January 1875: 26). Nevertheless, the capabilities of Bible women drew the attention of local women, who began asking them to visit their houses. It is important to recognise that despite no formal training, Bible women acquired and used various skills as part of their profession to impart the Christian message.

Reading: Reading was an essential part of the profession of Bible women as they needed to read the Bible. In Rayalaseema, people were astonished to see Mary, Martha and Bathsheba reading (the Bible). When Mary was reading portions from the Bible for female patients in the dispensary, they would exclaim, "How well she reads ... We cannot read a single line" (*Missing Link*, October 1873: 312). When Martha read the Bible to the gathered women in a village, in astonishment they said to one another, "Can women read? ... look at this woman, she

reads without fear or shame" (*Missing Link*, October 1875: 302). The surprise was because a woman being able to read in Telugu society was a new phenomenon. In traditional Indian society, Brahmins maintained the monopoly over education. Dalits and women were denied access to education owing to their caste and gender. Moreover, during this period, women were widely regarded in society as weak, foolish, senseless and the embodiment of evil. Education for women would ruin their lives, bringing shame to their husbands and destroy happiness within families (Acchamamba 1913: 1). In a conversation with Brahmin men, Kilpin was told that "it was not possible for a black [native or Dalit] woman to learn to read," indicating how caste society undermined women, propagating the impossibility of women's literacy (*Female Intelligencer*, September 1864: 189).

However, after mass conversion movements, LMS missionaries established village schools and night schools in *palems*—Dalit settlements, introducing a culture of reading and writing, which was the "threshold of cultural modernity" (Mohan 2015: 10). Bible women took initiative and availed the opportunities provided by missionaries and the colonial state. The advent of education engendered a complex set of changes in the life of Bible women. The act of reading was a new and liberating experience that opened for them a route to get out of the oppressive structures of caste and patriarchy. In a context where education was denied to women in Hindu society, women's knowledge of reading the alphabet not only ensured eligibility to take up the profession of Bible woman but also gave them social respect. Bible women, by learning to read and write, demolished the myth that women were incapable of reading and that only a certain category of people were destined to learn.

Interpreting and contextualising texts: The Bible, the sacred text of Christian religion, occupied a central role in the life of Bible women. For centuries, Dalits were denied access to Hindu religious texts; in addition, they were prohibited from hearing, reading, and reciting Hindu shastras, and if they did, their tongues would be cut off, and molten poured into their ears as punishment. Such was the nature of control Brahmins maintained over the scriptures. Hence, the immense significance of Dalit women accessing the Bible, which was regarded by them as akin to the shastras (*Missing Link*, May 1874: 156). When the Bible was made available in the Telugu language, Dalit converts, especially Bible women, embraced and identified with it. They perceived the Bible as a "Text of Life" and a "Text for Life" (Rajkumar 2018: 121). A certain empowerment came with access to the Bible, as it indicated education. Wherever they went, they carried the Bible. The Bible was viewed as a sacred object that contained divine power. Further, it was integrated into their everyday life. In their world view, the Bible became a powerful "metasymbol" of their culture of literacy (Clarke 2002: 251–54). By memorising and reciting the verses from the Bible, Mary, Martha, and Bathsheba became well versed with the text, developing skills to understand the Bible and appropriate and contextualise it to people's circumstances. Eliza Kent (1999: 138) points out that the ability of Bible women

"to locate on the spur of the moment a particularly appropriate Bible verse or chapter constituted an impressive display of textual virtuosity." When female patients came to the dispensary with various diseases and suffering, Mary Wesley read and explained to them the accounts of people being healed from their diseases and the miracles performed by Jesus Christ in the New Testament (*Missing Link*, October 1873: 312–13). The following extract helps us understand Bathsheba's mastery over the scriptures and her skill in interpreting and appropriating chapters from the Bible according to the context:

a woman being ill sent for her [Bathsheba], told her that she was very ill and wished God would take her. Bathsheba talked to her for some time about the great Physician [Jesus Christ], and read about Christ healing the woman of her bleeding issue ... Two days after, Bathsheba visited her again and read about crucifixion ... and explained that Christ suffered all this for us, and asked her to pray to Him again ... The next time Bathsheba visited her, she was dying, but said: "I am praying to Jesus, will he forgive me?" Bathsheba repeated many texts such as, "Though your sins be as scarlet ... and left her comforted." At her next visit, the woman was dead. (ARLMS 1887: 105)

In the above cited passage, during her dialogue with a sick woman who was about to die, Bathsheba made two references from the Bible which were suitable to the situation. As part of the first reference, she told a story of a woman from the Bible who was suffering from bleeding for 12 years. She was healed when she touched the cloak of Jesus. This illustration highlights that Jesus was a healer who could heal her too. The second reference was made when a dying woman was doubtful about her faith, and who was seeking forgiveness for her sins. Bathsheba read a verse from the book of Isaiah from the Bible: "Though your sins be as scarlet, they shall be as white as snow; though they be red like crimson, they shall be as wool" (Isaiah 1: 18). The story of the healed woman and the verse confirming forgiveness from the Bible certainly appealed to the sick and dying woman.

Through these narratives, Mary and Bathsheba not only addressed the immediate physical need of the sick women but also introduced the Christian god as one capable of healing, forgiving, and meeting their needs. As Sebastian (2003: 16) rightly points out that it was the context of their conversation that is significant, rather than just what was read.

Singing: Mary, Martha, and Bathsheba developed the skill of singing, which was significant for them as they used this skill to disseminate the Christian message to women (ARLMS 1898: 100). In Rayalaseema culture, religious or spiritual matters were transmitted to people in villages through oral traditions of songs. Katta Narasimham, a retired teacher from Cuddapah district, in a conversation with me, recalled that in Rayalaseema it was an age-old custom for the wife and husband or a group to tour the villages, where they present biographical accounts of famous kings and virtuous women through stories and songs. They stay in each village for three to four days telling stories through songs at night and are given grain by the village people.

The singing tradition was very much part of the social life of the villagers in Rayalaseema society. Communicating and

conversing in villages through the medium of songs was common. Women sang songs on occasions, such as childbirth, puberty, and marriage ceremonies, and while working in the agricultural fields, they sang humorous songs, songs on various caste professions, songs about gods and goddess, as well as songs on different social themes (Seeta Devi 2004: 6–7). These oral traditions contributed to Mary, Martha and Bathsheba acquiring singing skills. They learned many of the Telugu Christian songs and employed those to demonstrate the story of a Christian god (*Missing Link*, August 1883: 242). When they were preaching, singing had the power of attracting and holding the audience, making it tremendously significant in the religious and social context they operated within. During her house visits, Bathsheba carried a song book along with the Bible. As Christopher (2015: 157) points out, the song book became a cultural marker that was placed next to the Bible.

Martha and Bathsheba found songs as powerful instruments of enhancing self-expression. During their visits to villages, Bible women sang songs to gain the attention of women. Bathsheba's rendition of songs involved "great expression" which attracted many women (*Missing Link*, August 1883: 242). She was asked to write down the lyrics of the songs she sang, which the women could learn with the help of those who could read (*Missing Link*, August 1874: 251–52). Bible women started their "women meetings" by singing hymns and songs (MMCLMS 1884: 398; ARLMS 1885: 70). Quite often, the gospel story told through the medium of the songs appealed more directly and lingered in the memory of listeners. Over a period, the skill of singing songs became an essential qualification for the job of Bible woman. Sudarasanamma and Vasundaramma, Bible women working currently in Rayalaseema region, revealed to me that along with telling stories from the Bible, singing Christian songs is an essential qualification for a person who wishes to work as a Bible woman.⁶

Bible Women and the Public Sphere

Dalit Women, as Bible women, were engaging in new roles in the public sphere. Jurgen Habermas et al's (1974: 49) notion of the public sphere is an arena of social life where people come together, communicate with each other, exchange opinions and contribute towards the forming of public opinions. The public sphere is open to all people irrespective of caste, gender, and religion differences. However, in traditional Rayalaseema society, the public sphere was the domain of dominant caste men. Women from these dominant castes were confined to the private sphere. In the name of division of labour, these women were expected to perform activities in the domestic space, such as cooking, caring for the elderly, childbearing and rearing, and serving husbands (Christlieb 1930: 41–46). In relative contrast, Dalit women often were required to emerge from the domestic sphere for everyday labour in agricultural fields. However, there were social restrictions on their mobility and public interaction. The patriarchal norms prohibited them from interacting with other men and restricted them to participate in public spaces where men gather. Nevertheless, colonial modernity and missionary Christianity allowed for Mary,

Martha, and Bathsheba to come out as Bible women and into the public sphere. As Jane Haggis (1998: 95) rightly pointed out that while missionary women tried emancipating local women by converting them to Christianity, the Bible women were liberating and elevating themselves from their low caste status, by taking up this profession. Their profession provided them opportunities and enabled their visibility in public sphere. In addition, the profession gave them public roles, such as evangelist, organiser, and teacher. Through these various activities and roles, Bible women commanded religious authority and social respect in the public, which was otherwise denied to those situated in a similar social location. Their visits to the public space and activities they were involved in give us a sense of new gender roles that were being shaped as part of the profession. They found new dignity in public life and a new place in the structure of the missions. Let us examine some of the activities of Mary, Martha and Bathsheba which were carried out in the public sphere.

Touring the villages and visiting houses: The profession of Bible woman enabled Martha and Bathsheba to construct a space where they could move with dignity and freedom. Touring villages was a regular aspect of their work. Inderpal Grewal (1996: 136) argues, the culture of travel and mobility signifies the notion of freedom. While touring the villages as a part of the profession, Bible women not only enjoyed freedom but also overcame traditional gender roles that confined women to the domestic sphere. During village visits, Bible women conversed with women at various places, common among them were public wells and under the shade of large trees. In the traditional village structure, public wells played a significant role. In the colonial period, women from Rayalaseema villages, after finishing household work, went out to public wells to draw water, carrying their pots on their hips (Christlieb 1930: 37–38). The public wells served as a meeting place for women and an opportunity for a chat. It was here that women exchanged village news. During one of her village visits, Martha stood near the village well, leading many women present there to ask her, who she was. When she introduced herself to them, they were in awe of her, and when they learnt that she could read, they asked her to read for them. She read from the Bible and spoke to them about the way of eternal life (*Missing Link*, October 1875: 302).

Gathering under the shade of large neem or tamarind trees was a common feature of rural life in Rayalaseema. During the daytime, particularly elderly men, and women, sat and discussed personal and village matters, while involved in some work such as peeling peanuts or weaving cotton. On one of her visits, Martha reported that she found several women spinning under a tree. Ankamma, who was also present and whom she knew, invited her to sit with them. All the women there, at that time, were from the dominant caste. She sat with them and sang a Telugu hymn. They were astonished to see her reading, singing, and speaking boldly, and said “As for us, we are like slaves, spinning all day long.” She had long conversations with them, read and explained the parable about the Samaritan woman from the New Testament (John 4: 7),

(*Missing Link*, March 1877: 86). Also, Bible women also preached and distributed bible tracts during their travels.

Another important task for Bible women was visiting houses, interacting with women, sharing about the Christian god. Emma Thomason, a woman missionary who Bathsheba worked with in Gooty, reported that Bathsheba visited nearly 60 houses of every caste, read the Bible, and taught them regularly, in one year. Further, she had been received by people of every caste (ARLMS 1885: 70, 1903: 155). Missionary reports show that she visited the houses of Brahmins (ARLMS 1888: 105). In Gooty, a Brahmin woman sent word to Bathsheba to visit her. After a conversation with her, Bathsheba read verses from the New Testament (*Missing Link*, August 1883: 243). Bathsheba’s access to Brahmin women was due to her caste privilege as she was from the dominant Reddy caste, whereas Martha—a Dalit woman, said that due to her caste location she could not speak and approach Brahmin women (*Missing Link*, July 1872: 207). Historically, Madiga and Mala castes were considered untouchables, which could explain this. Moreover, some Brahmin women were not receptive to preaching from Bible women, unlike women from other castes. For instance, Bible woman Elizabeth Joseph from Madanapalli of Cuddapah district reported that some Brahmin women told her that they were not sinners, and they did not care to hear about Jesus (*Missing Link*, January 1875: 26). However, Martha often subverted these caste norms by interacting with different caste people and entering the houses of dominant castes and government officials. Moreover, she visited the houses of Muslims and interacted with Muslim women, too (*Missing Link*, January 1875: 26).

During their house visits, they sang songs, preached the Bible, and offered prayers. Along with this, quite often they also acted as peacemaker in family disputes. They listened to problems of the women in the house, offered prayers for them and their families. In addition, they gave practical hints about health, cleanliness, keeping the house neat, rearing and care of infants and encouraged women to send their children to the mission school (*Harvest Field*, January 1909: 17). Bible women also comforted and supported women in times of bereavement and sickness. At a house where Bathsheba visited, a woman was crying bitterly, because her two children had died recently. Bathsheba calibrated her words according to the context and sang a hymn as well as a reading from the Bible (John 14), which talks about Jesus’s comforting words to the troubled hearts. The portion which she read recognises context and comforts the listener, who responded with, “your words are good; by them I obtain some comfort” (*Missing Link*, June 1876: 180).

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Organising women's meetings: The profession of Bible woman gave Martha and Bathsheba a public role as evangelists and preachers. Preaching about the Christian god and reading the Bible during women's meetings was an important activity which they carried out in the public sphere. Bible women gained this space through these meetings and used this to empower and shape themselves and other women as modern women. The meetings were organised in one of the houses which they visited and sometimes at a missionary's bungalow (MMCLMS 1884: 398). These meetings began by singing songs, as women from the neighbourhood gathered and sat in a circle. Sometimes, the mistress of the house would gather several her neighbours together when she was expecting or had sent for the Bible women (ARLMS 1885: 70; MMCLMS 1914: 221; *Missing Link*, January 1875: 26). After singing, the gathered women were asked to share whatever they remembered from the previous meeting. Then the Bible women read verses from the Bible and explained it to them. Martha and Bathsheba's preaching were characterised by themes that ranged from notions of sin, the birth of Jesus, his crucifixion and resurrection, forgiveness, love of god, and admirable virtues (*Missing Link*, August 1883: 243).

In traditional Rayalaseema society, Dalits and women were kept as illiterates. Reading the scriptures and explaining it to the people was exclusively the domain of Brahmins. Brahmin men alone had the privilege to speak about god and claimed mastery over religious books. For generations, they had the monopoly over religious preaching. Dalits and women were not allowed to hear and read sacred books of the Hindu religion. In this context, reading, reciting, and explaining and preaching the Bible were an empowering experience for the Bible women in the public sphere, as it allowed them to break many caste-based norms. By performing these activities in a public gathering, Bible women proclaimed their equality with Brahmins, and challenged the monopoly of Brahmins. Moreover, as Taneti (2007: 84–85) argues, they established parallel power structures in which they asserted their agency.

Documentation in 1909 suggests that women meetings had been taking place in Gooty town for at least 25 years. In a meeting held in September of 1909, nearly 50 women gathered and discussed topics, such as education, widow remarriage, idol worship and new mothers and children (Vivekavathi, October 1909: 6). Women's meetings opened a new space for socialisation, allowing them to take breaks from their chores, come together, interact with each other, share their problems and happiness, praying and supporting each other, while revisiting previous discussions.

Although the stated purpose of these meetings was redemption from sin, they laid a platform for local women to emancipate themselves from the chains of patriarchy and caste. As they listened to ideas about education, spirituality, and medicine, this ensured a certain exposure to modernity. Also, these meetings helped women build confidence and improve their self-esteem. Through these meetings, mobilising efforts, teaching literacy and scriptures, Martha and Bathsheba created women's networks in Rayalaseema, which

embodied a sense of community, generating incredible social capital among women.

Agent of women's literacy: Martha and Bathsheba took up a public role as agents of women's education; they advocated and encouraged women's education. They introduced women to the reading of the alphabet. Bathsheba's following conversation with a dominant caste woman exemplifies her radical thoughts on women's education. A woman who visited her housewife was astonished to see her reading and said "What! Can this woman read?" In turn, Bathsheba asked her that was not it a good thing to be able to read. The lady replied, "Well, to some extent it may be good thing; but if [girl] children are sent to school they will not learn house-work properly." Bathsheba went a step ahead and argued that if children had a willing mind, they might learn school and housework, too. At the end of her conversation, Bathsheba had read a little book about the advantages which women get if they were able to read (*Missing Link*, August 1883: 243). When Martha was asked by women that "Can women read?" her response was "Yes, we [women] can read and we also can teach others to read" (*Missing Link*, October 1875: 302). Martha and Bathsheba who had experienced empowerment through literacy believed that education was an instrument for betterment of women.

There were prejudices against female education in society. The women folk in the villages were imbued with the notion that "if the women in a house learn to read, the men will die" (ARLMS 1915: 84). Further, they regarded women's reading as a shameful act (*Missing Link*, October 1875: 302). Mary, Martha, and Bathsheba broke these notions by learning to read. In addition, they taught women to break old customs and urged them to send their children to school (*Missing Link*, August 1883: 243). During house visits and women's meetings, apart from religious education, Bathsheba taught women to learn and read the alphabet, sing, and learn and tell stories from the Bible. She encouraged her audience to learn reading so that they could understand the Bible on their own and engage with it better. When women expressed a doubt about their ability to learn, she reassured them that as many others who were learning, they could also (*Missing Link*, August 1883: 243).

Bible women became agents of women's literacy. From their work, it is evident that Mary, Martha, and Bathsheba were instrumental in bringing gender transformation in Rayalaseema society. They believed in the value of education and worked for the enhancement of women's life. By encouraging women to acquire literacy, Bible women challenged the existing caste norms. They used education as a tool for the emancipation of women. Their pioneering work in introducing women to the culture of literacy was a distinctive phase in transforming gender relationships in Rayalaseema.

Conclusions

Ordinary women from Dalit backgrounds availed opportunities provided by colonial modernity and missionary Christianity and became Bible women. By going door to door, reading from the Bible, interpreting it, praying, sharing their own

personal experiences, Bible women became agents of the mission. As Sebastian (2003: 21) argues, Bible women's freedom of movement and their professionalism were signs of the early career woman in South India, and therefore could be termed "liberatory." They became an institution, and their work was indispensable. By acquiring various skills and moving in the public sphere, they crafted themselves as new leaders of social change. Moreover, they mobilised other women to come out from domestic spaces to the public through women's meetings and empowered them by introducing them to the alphabet. This is what conversion meant for women. The modern profession of

Bible woman provided an opportunity to cultivate skills, to empower themselves, to be independent and to defy the older norms under which they were subjugated. Moreover, their endeavour was not only converting, educating women but in that process, they introduced a set of gender models. They mediated between local women and missionary women. In fact, Bible women's work was instrumental to the change of gender roles and spread of Christianity in Rayalaseema. These qualities and achievements, unusual for women at the time, led to the people whom they worked with, to call them as "Teachers of Wisdom" (ARLMS 1904: 166).

NOTES

- 1 Rayalaseema is a contemporary euphemism for what the British, when they ruled India, called "ceded districts" which was part of the Madras Presidency. At present Rayalaseema, one of the regions of Andhra Pradesh state contains four districts, namely Anantapur, Chittor, Cuddapah and Kurnool.
- 2 In colonial and missionary records, they were addressed as Pariahs, Out-castes, Non-castes, Madigas and Malas. In this paper, they are referred as Dalits and their caste names are used wherever necessary.
- 3 Missionary Edward Porter and his wife Martha Kilpin who is often referred in missionary records as "Mrs Porter" were appointed in Cuddapah station in 1844. They worked in that station for 24 years and retired in 1868. Kilpin was known for her efforts for female education in Cuddapah district. She died in 1890 (Sibree 1923: 35; Simmons 1923: 9).
- 4 The other Bible women who worked in Cuddapah district with the financial assistance of BDFM under the instructions of Kilpin were Soovesheyshum, Esther Balchinsoo, Elizabeth Joseph, and Samadhanam (*Missing Link*, January 1874: 30; January 1875: 26; October 1875: 303).
- 5 By 1900, a second generation of Bible women started their work. After passing their primary examination from mission boarding schools, the selected Christian girls were retained in the school and put through a course which trained them to undertake the duties of Bible women. In the Rayalaseema region, from the second decade of the 20th century, three years of theological training was started for Bible women at the Theological Training College of Gooty (Hibbertware 1912: 199; ARLMS 1921: 38; 1922: 43).
- 6 Both of them applied for the job of Bible woman in the diocese. During their interview, they were asked by bishop of the diocese to tell stories from the Bible and sing Christian songs (Personal interview, 22 March 2018).

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Study of magnetic behavior in co-precipitated Ni-Zn ferrite nanoparticles and their potential use for gas sensor applications



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Mössbauer spectroscopy
Magnetcocrystalline anisotropy
Gas sensor

ABSTRACT

A series of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$) were obtained by co-precipitation technique and followed by sintering at 800 °C. The random variation of bond angles resembles possible cation redistribution in the present series of ferrite samples. The cation distributions estimated from Mössbauer analysis are used to find out the net magnetic moment. The magnetic moment (n_B') estimated from Neel's sub-lattice model is not consistent with experimental magnetic moment (n_B). But the magnetic moment (n_B') estimated from the Yafet-Kittel (Y-K) model is in good agreement with the experimental magnetic moment (n_B), supporting the possibility of non-collinear arrangement of spins at B -site. The non-collinear spin arrangement at octahedral (B) site is influencing the magnetization of present series ferrite samples. The increase in saturation magnetization with increase in Ni^{2+} ion concentration is expected due to the decrease in non-collinear spin arrangement at octahedral (B) site. Higher saturation magnetization of 61.32 emu/g was reported for the composition $x = 0.7$. The single domain structure of samples is evident from the hysteresis loops, but interestingly nature of hyperfine interactions can be found from the Mössbauer spectra under spectral line intensities. The increase in the blocking temperature (magnetic ordering) is due to the increase in magnetcocrystalline anisotropy rather than an increase in particle sizes. The composition $x = 0.7$ is showing good sensor response for both LPG and acetone. Moreover, its response and recovery times are less comparing to the other two compositions and therefore it is useful for the sensor fabrication.

1. Introduction

The evaluation of hazardous gas due to industrialization is a major source for environmental pollutions causing many human health diseases. Gas sensors are using widely to detect the harmful gases like CO, CO_2 , SO_2 , NO, NO_2 , NH_3 , etc [1,2]. Different semiconducting oxides of single component oxides (ex: ZnO , TiO_2) and multicomponent oxides (ex: SrFeO_3 , SmCoO_3) have been used for gas sensor applications [3,4]. Now a days spinel ferrites have also been studied for different gas sensor applications. The crystal structure of spinel ferrite belongs to $fd3m$ space group and its unit cell is cubic. Even today, the study Ni-Zn ferrite under nanoscale dimensions for a particular application is very interesting and its general formula unit is written as $(\text{Zn}_{1-x}^{2+}\text{Fe}_x^{3+})_{\text{tetra}}[\text{Ni}_x^{2+}\text{Fe}_{2-x}^{3+}]_{\text{octa}}\text{O}_4$ [5]. In bulk Ni-Zn ferrite as

concentration of Zn^{2+} increases up to the composition $x = 0.5$, the saturation magnetization (M_s) steadily increases due to strengthening of A - B super exchange interaction and after M_s steadily decreases due to decrease in A - B super exchange interaction and increase in the B - B exchange interaction [6]. As the particle size is limited to the metrics of nanoscale, finite size effects come into play influencing the cation distribution between the tetrahedral (A) and octahedral (B) sites. Therefore, the strength of A - B super exchange interaction varied leading to change in the magnetic properties [7]. Moreover, ferrite nanoparticles can exhibit novel properties like superparamagnetism (SPM), single domain (SD) structure, spin-glassy behavior, core-shell interactions [8].

Different values of magnetization were reported for Ni-Zn ferrite prepared by using different methods [9–12]. Kavas et al. [13] prepared

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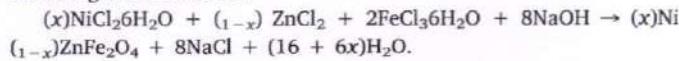
Zn doped Ni-ferrite by PEG-assisted hydrothermal route and observed continuous decrease in magnetization from 80.24 to 3.09 emu/g. Slătineanu et al. [14] in their studies observed that the saturation magnetization is increased from 1.44 to 63 emu/g up to $x = 0.8$ in nickel doped zinc ferrite and there after continuously decreased to $M_s = 43$ emu/g for $x = 1$. Rahimi et al. [15] studied the role of Zn addition in Ni-ferrite and they observed increase in magnetization from 30.93 to 54.97 emu/g up to $x = 0.3$ and after declined to 1.95 emu/g. Moreover, the above literature study that includes the optimum level of higher magnetization is not specific in Ni-Zn ferrites synthesized from wet chemical techniques. Therefore, it can be a more interesting research in ferrite nanoparticles though their physical properties are intensively studied.

In our recent publication [16], we reported structural properties that are evaluated from Rietveld refinement, elastic properties and FTIR spectroscopic studies of present series of ferrite samples. At present, $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ samples are characterized for the magnetic properties and their comprehensive magnetic behaviour was reported in the manuscript. We analyzed the experimental results of magnetic characterization basing on the description of non-collinear spin arrangement in the spinel structure. The ferrite samples were tested for gas sensor applications using different gases like H_2 , SO_2 , LPG and acetone.

2. Experimental methods

2.1. Synthesis

Detailed description about synthesis procedure can be found in our earlier publications [17]. The stoichiometry of present nanoferrite systems obtained from the co-precipitation technique was maintained following chemical route.



2.2. Measurements and characterization

Vibrating sample magnetometer of Lakeshore make, VSM 718 model was employed to evaluate the magnetization measurements at room temperature.

Mössbauer spectrometer operating at constant acceleration mode (triangular wave) in transmission geometry (Co-57 in Rh matrix of strength 50 mCi) has been used to record Mössbauer spectra at room temperature (300 K).

Quantum Design make physical property measurement system (PPMS) was used to obtain magnetization – temperature (M – T) measurements.

2.3. Sensor fabrication

The Ni-Zn ferrite samples were grounded into fine powder using agate mortar. The obtained fine powder was mixed with de-ionized water and made in the form of a paste. The paste was then applied on Al_2O_3 substrate (10 mm length) having a pair of Ag electrodes (separated by 6 mm). It was dried and heat treated at 800 °C for 2 h. Now the sensor is used for different sensor studies. The detailed description of equipment used for different sensor studies was reported in our earlier publication [18]. The sensor response (S) can be evolved using measurements of sensor resistance (R_a and R_g) in air and test gas in the given relation.

$$S = \frac{(R_a - R_g)}{R_a} \quad (1)$$

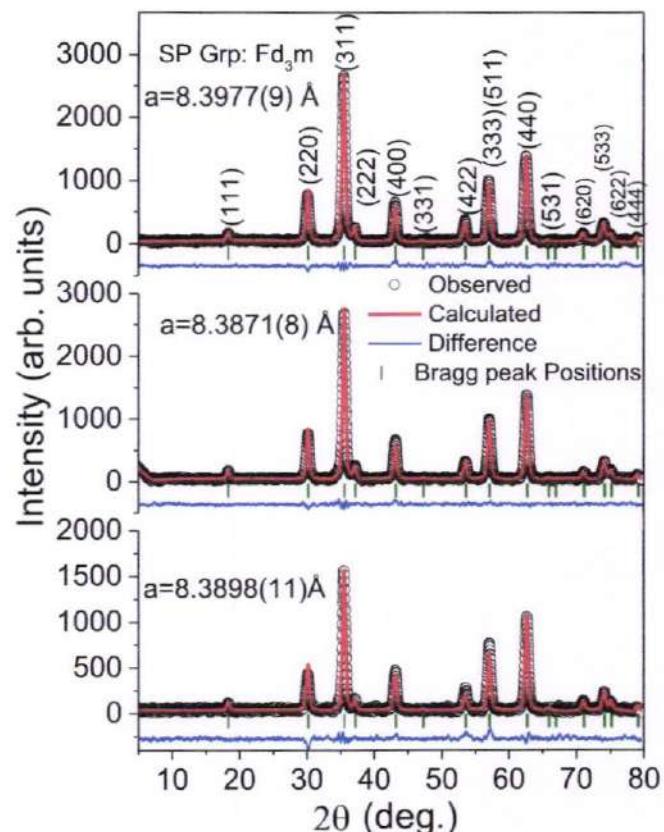


Fig. 1. Rietveld refinement of XRD patterns for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$) [16].

3. Results and discussion

3.1. XRD studies

The Rietveld refinement of XRD patterns of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$) published in our earlier publication [16] are presented again in Fig. 1. These patterns authorized the formation of spinel phase of ferrite samples. The incorporation of different metal ions in spinel structure leads to the extension of tetrahedral (A) and octahedral (B) sites. Generally, the amount of difference in the expansion of A- and B-sites is the ideal oxygen positional parameter (U) and is equal to 0.375 Å. The values of U estimated in the present study are listed in Table 1. The values of U in the present studies are slightly greater than the ideal oxygen positional parameter ($U_{ideal} = 0.375$ Å) and are increasing with the substitution of Ni^{2+} . This is attributed to the change in the cubic symmetry of spinel structure arising from the pinning of O^{2-} ions in the direction of (1 1 1) plane due to cation redistribution at A- and B-sites. The metal–metal (Me – Me) bond lengths, metal–oxygen (Me–O) bond lengths and Me–O–Me bond angles were calculated following the standard procedure reported in the literature [19,20] and are listed in Table 1. The Me–Me and Me–O bond lengths as well as Me–O–Me bond angles are prominent factors to understand the super exchange interactions in spinel ferrites. The calculated values of θ_1 , θ_2 and θ_5 appears to be decreasing, while θ_3 and θ_4 are increasing with the doping level of Ni^{2+} . Chakrabarty et al. [20] reported the establishment of A–B and A–A interactions and fading of B–B interaction basing on the increase of θ_1 , θ_2 , θ_5 and decrease of θ_3 , θ_4 . The estimated values of bond angles in the present study resemble the deteriorating of A–B interaction and escalating of B–B interaction, leading to drop in saturation magnetization. This contrast to the experimental results and we observed an enhancement in M_s . Therefore, an inclusive investigation on the magnetic behaviour of present ferrite systems is

Table 1

Oxygen positional parameter (U), calculated values ion pair bond lengths and bond angles between metal ions.

Comp (x)	U (Å)	Metal-Metal (Me-Me) bond lengths				Metal-oxygen (Me-O) bond lengths				Bond angles					
		b (Å)	c (Å)	d (Å)	e (Å)	f (Å)	p (Å)	q (Å)	r (Å)	s (Å)	θ_1	θ_2	θ_3		
0.5	0.378	2.969	3.482	3.636	5.455	5.143	2.075	1.862	3.680	3.651	124.27	141.24	91.36	124.58	73.95
0.6	0.378	2.965	3.477	3.642	5.448	5.136	2.072	1.859	3.675	3.646	124.28	141.28	91.37	125.59	73.92
0.7	0.381	2.966	3.478	3.633	5.449	5.137	2.048	1.903	3.719	3.663	123.31	139.98	92.79	125.80	72.51

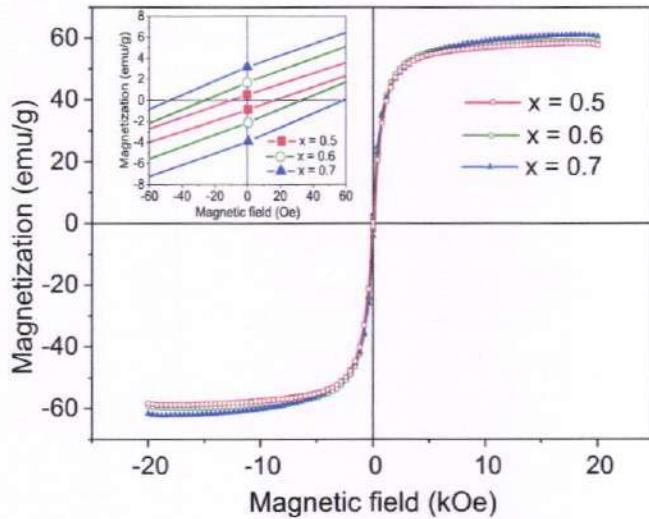


Fig. 2. Hysteresis loops for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$).

needed. However the random variations noted in the bond angles may be related to the variations in structural parameters that is supporting the possible cation redistribution in the present ferrite systems.

3.2. Magnetic studies

The hysteresis ($M-H$) loops (of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$) recorded at 300 K are shown in Fig. 2. The values of saturation (M_s), remnant (M_r) magnetizations and coercivity (H_c) are summarized in Table 2. The $M-H$ loops indicate the soft magnetic character of the ferrite samples. Moreover, unsaturated magnetization even at 20 kOe represents the presence of superparamagnetic clusters those have core-shell morphology. The present values of M_s are less than the magnetization of ferrite prepared by conventional ceramic route (73 emu/g) [21]. It is ascribed to the higher disorder in surface magnetization with frustrated magnetic interactions in ultrafine particles (particles under nanoscale dimensions) due to extensive surface to volume ratio [22]. The plot of variation of M_s , H_c and D_{XRD} against to the concentration of Ni^{2+} is shown in Fig. 3. It can be observed that the value of M_s is increasing with the doping level of Ni^{2+} . Rahimi et al. [15] observed a raise in magnetization up to $x = 0.5$ and after a steady fall in Zn doped Ni-ferrite. They explained this magnetic behaviour basing on the Neel's sub-lattice model. The magnetization in ferrites is governed by $A-B$, $A-A$ and $B-B$ superexchange interactions, but

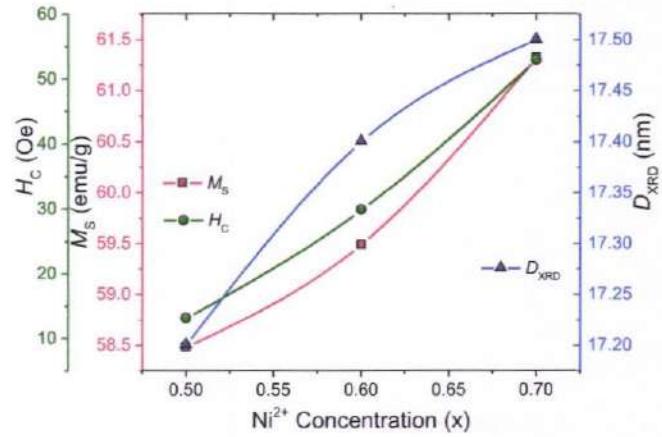


Fig. 3. Variation in crystallite size (D_{XRD}), saturation magnetization (M_s) and coercivity (H_c) with Ni^{2+} concentration.

predominantly due to $A-B$ super exchange interaction compared to $A-A$ and $B-B$ superexchange interactions. Considering that the magnetizations at B - and A - sites as \vec{M}_B and \vec{M}_A , the magnetization of spinel ferrites according to Neel's two sub-lattice model [23] is given as.

$$M_s = |\vec{M}_B - \vec{M}_A| \quad (2)$$

As $A-B$ superexchange interaction increases, the value of \vec{M}_B at B -site increases and the value of \vec{M}_A at A -site decreases leading to increase in magnetization in ferrites. From the Table 1, it was noticed that the values of θ_1, θ_2 and θ_5 are decreased while θ_3 and θ_4 are increased with the substitution of Ni^{2+} . It is attributed to the dilution of $A-B$ and $A-A$ exchange interactions and strengthening $B-B$ exchange interaction. Therefore Neel's two sub-lattice model cannot conclude the magnetic behaviour in the present series of samples. Yafet-Kittel three sub-lattice model may be employed to analyze the variation of magnetic behaviour. In this model the B -site is divided into two sub-lattices which are non-collinear with each other having a canting angle α_{Y-K} [24,25]. This magnetic frustration will determine the magnetic behaviour, for an instant $\alpha_{Y-K} = 0^\circ$, favours in $A-B$ super exchange interaction and $\alpha_{Y-K} = 90^\circ$ favours in $B-B$ super exchange interaction. In the current study, the following relation has been used to estimate α_{Y-K} (canting angles).

$$n_B = (10 - 3x) \cdot \cos \alpha_{Y-K} - 5x \quad (3)$$

where n_B = experimental magnetic moment and x = concentration of Ni^{2+} .

Table 2

Saturation magnetization (M_s), remanent magnetization (M_r), coercivity (H_c) and magnetic moment (n_B). *Crystallite size from XRD (D_{XRD}) and particle size distribution from FE-SEM ($D_{\text{FE-SEM}}$).

Comp (x)	M_s (emu/g)	M_r (emu/g)	H_c (Oe)	n_B	K (emu/cm ³) $\times 10^3$	α_{Y-K} (degree)	$D(\pm 0.1)$ (nm) XRD	$D(\pm 0.1)$ (nm) FE-SEM
0.5	58.48	0.73	13.04	2.48	0.812	54.13	17.2	21.9-39.4
0.6	59.49	1.95	29.82	2.51	1.887	47.78	17.4	27.9-39.4
0.7	61.32	3.58	52.89	2.60	3.450	39.45	17.5	27.2-36.9

*The values of D_{XRD} and $D_{\text{FE-SEM}}$ are taken from our previous reports [16].

The experimental magnetic moments were calculated using the given relation [23] and the values of n_B and α_{Y-K} are listed in Table 2.

$$n_B = \frac{M \cdot M_s}{N_A \cdot \mu_B} \quad (4)$$

where M = molar mass of ferrite sample, M_s = saturated magnetization, N_A = Avagadro's number and μ_B = Bohr magneton.

From the Table 2, it was observed that the values α_{Y-K} are decreasing as Ni^{2+} substitution is increasing. This is ascribed to diminish in non-collinear arrangement of spins at B -site and raise of \vec{M}_B at B -site. This leads to strengthen the A - B exchange interaction resulting to increase in magnetization with the increase in concentration of Ni^{2+} . The non-collinear arrangement of magnetic spins may be explained basing on exchange interactions between the neighbouring spins, the positive exchange integral (J_{ex}) favours collinear spin arrangement, results in ferromagnetism and negative exchange integral (J_{ex}) favours anti-parallel collinear spin arrangement, results in anti-ferromagnetism. Suppose the exchange energy between the neighbouring magnetic spins in B -site varies in between $+J_{ex}$ and $-J_{ex}$ favours non-collinear spin arrangement with a canting angle which substantially determines the B -site magnetization. Pong et al. [26] reported decrease in canting angles in Ni-Zn ferrites. They reported this is due to the increase of the overlapping of wave functions between nearby magnetic ions leading to increase in A - B exchange interaction and decrease in B - B exchange interaction. Though the saturation magnetization (M_s) is increasing with the doping level of Ni^{2+} , but it is marginal. It is ascribed to the dependence of crystallite size of slight growth. Jalaly et al. [27] prepared $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ ferrite by high energy ball milling method and reported a value of saturation magnetization (M_s) of 57.5 emu/g for crystallite size of 18 nm. In the present studies, saturation magnetization of 61.3 emu/g was observed for $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ having average crystallite size of 17.5 nm. It indicates the worth of co-precipitation synthesis to yield ferrite phases possessing higher saturation magnetization. In general the value of M_s is influenced by the cation distribution, crystallite and core-shell interactions.

The low values of M_r and H_c suggests that the ferrite nanoparticles are in SD state. It was observed that the coercivity is increased with the increase in the doping level of Ni^{2+} . The nanoparticles with particle sizes less than a limit D_p exhibits superparamagnetism and particles with sizes greater than D_p and less than a critical size D_c are in SD state. In SD particles, the H_c increases with the increase of particle size up to D_c and above the H_c decreases. For SD particles the H_c decreases with decrease in particle sizes [28] and is given by.

$$H_c = g - \frac{h}{D^{3/2}} \quad (5)$$

where g , h = constants and D = particle size.

The present particle sizes are supposed to greater than D_p and less than D_c , we can conclude that the increase in H_c is according to Eq. (5). On the other hand H_c can be judged by several factors like magnetocrystalline anisotropy, porosity, sizes of the domain, strain, particle size and distribution of particles sizes [29]. The H_c of SD and SPM nanoparticles is given by [28].

$$H_c = \frac{K^4 \cdot D^6}{M_s \cdot A^3} \quad (6)$$

where K = magnetocrystalline anisotropy, D = particle size, A = exchange energy constant and M_s = saturation magnetization.

In the present study, H_c increases and is varied in a manner similar to D , M_s and K . From Eq. (6), H_c is proportional to D^6 , K^4 and inversely varied to M_s , therefore we can expect that the increase in H_c may be attributed to increase in D or increase in K .

3.3. Mössbauer spectroscopic studies

Mössbauer spectra recorded at room temperature for

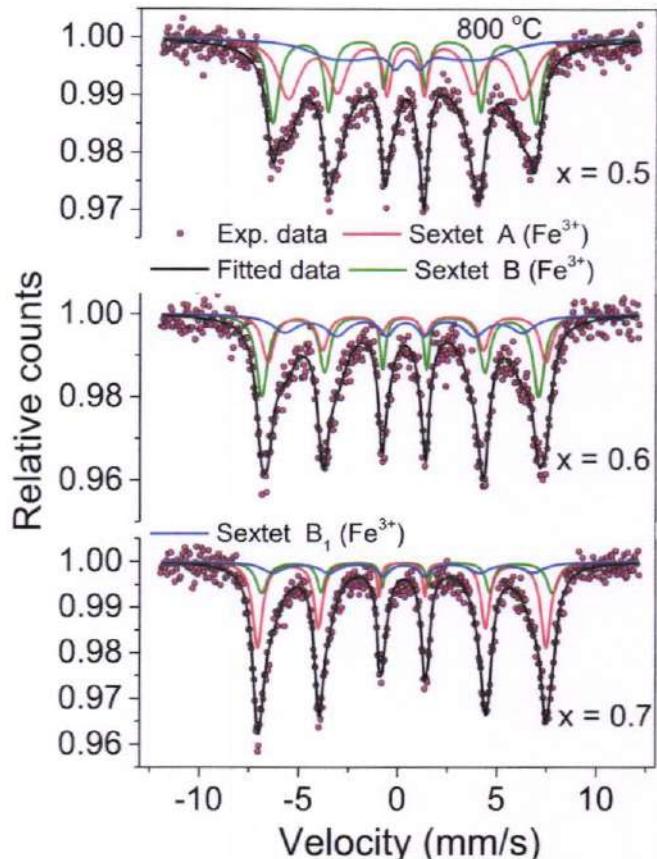


Fig. 4. Mössbauer spectra of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$).

$\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$) are given in Fig. 4. The spectra are analyzed by fitting with a MOSFIT program assuming a Lorentzian line shape. The results of the analysis are relative to Fe metal foil and these are summarized in Table 3. The spectra are characterized by completely resolved sextets out of which the outer sextet is due to iron (Fe^{3+}) ion population at A -sites and inner sextets are due to iron (Fe^{3+}) ion population at B -sites. The B -site spectra consist of two Zeeman splitting (sextets) B and B_1 which is attributed to association of Fe^{3+} ions at two diverse environments in B -site. The assertion of a distinct association of Fe^{3+} ions at B -site is made on the assumption that the particles in nano scale have large surface to volume ratio and therefore distinctions may arise whether the octahedral site in interior to particle or exposed to the surface of the particle. Therefore the sites interior to the particles may have higher fields (sextet B_1) and the sites exposed to the surface of nanoparticles may have lower fields (sextet B). The similar behaviour in nanoferrites has been found in the reported literature [30]. The sextets corresponding to Fe^{3+} ion populations at A - and B -sites in the present studies are assigned based on the isomer shift (δ) values and the corresponding plot of isomer shift is depicted in Fig. 5. The value of δ for A -site is less than that of B -site, because Fe^{3+} ions at A -site are enclosed by six O^{2-} ions and at B -site are surrounded by four O^{2-} ions. Therefore the Fe^{3+} ions at B -site are less shielded by s-electron density resulting to higher value of δ . The range of δ is lower than 0.5 mm/s, indicates only the presence of Fe^{3+} ions and non-existence of Fe^{2+} ions [31] in present ferrite systems. The plot of hyperfine fields (H_f) against to the doping level of Ni^{2+} is shown in Fig. 10. It was examined that H_f of A -site is higher than H_f of B -site and the H_f at A - and B -sites are monotonically increasing with increase in Ni^{2+} ion concentration. The general scenario of increasing trend of H_f indicates the strengthening of A - B exchange interaction. This supports the increasing trend of M_s as reported in VSM studies. Amer et al. [32] reported similar behaviour of hyperfine fields in Mg-doped Cu-nanoferrites. But they reported a

Table 3

Hyperfine magnetic fields (H_f), isomer shift (δ), quadrupole splitting (Δ), line width (Γ) and relative areas (R_A) in percentage of tetrahedral A and octahedral B sites of Fe^{3+} .

Comp (x)	Iron Sites	Hyperfine field, (H_f) Tesla (± 0.1)	Quadrupole splitting, (Δ) mm/s (± 0.04)	Isomer shift, (δ) mm/s (± 0.04)	Outer line width, (Γ) mm/s (± 0.05)	Area (R_A) (%)
0.5	Sextet A (red)	41.1	-0.0003	0.2578	0.68	23.9
	Sextet B (green)	36.7	0.015	0.2943	1.32	37.9
	Sextet B ₁ (blue)	24.05	0.24	0.4228	3.16	38.2
0.6	Sextet A (red)	43.3	-0.214	0.2761	0.68	27.5
	Sextet B (green)	43.5	0.210	0.301	0.72	29.4
	Sextet B ₁ (blue)	37.2	-0.09	0.3647	1.48	43.1
0.7	Sextet A (red)	45.1	0.002	0.2786	0.59	36.8
	Sextet B (green)	45.5	0.09	0.2747	0.69	20.9
	Sextet B ₁ (blue)	40.7	-0.06	0.4165	1.30	42.3

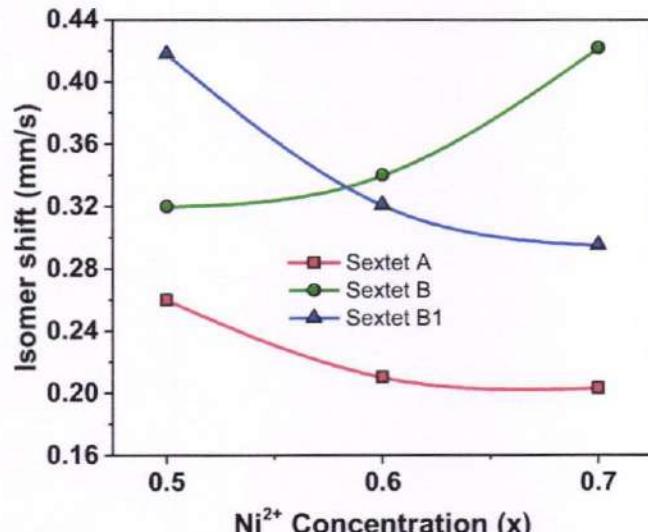


Fig. 5. Plot of isomer shift values against the concentration of Ni^{2+} .

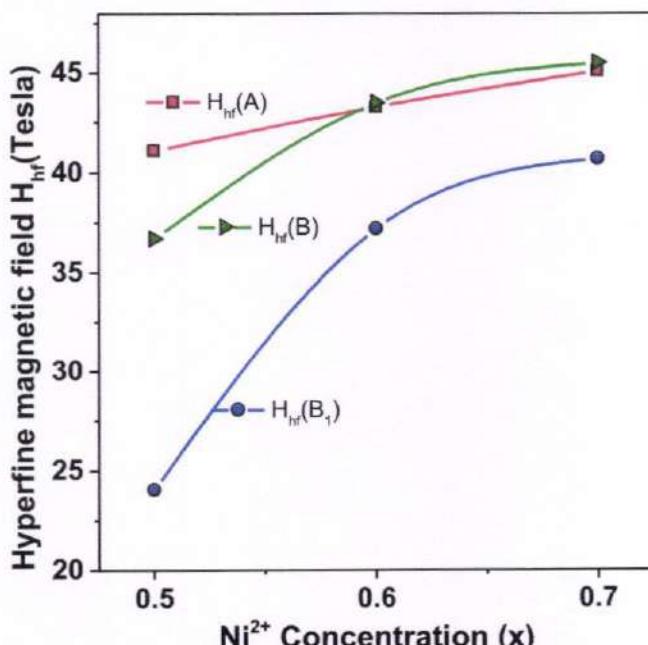


Fig. 6. Plot of hyperfine fields against the concentration of Ni^{2+} .

decrease in magnetization with the substitution Mg^{2+} contrary to the present reports of magnetization. Therefore, a further detailed explanation is required to support the magnetic behaviour in the present series of samples. From the Mössbauer spectra it can be observed that the intensity of sextets is increasing as doping level of Ni^{2+} raises. It is ascribed to the increase of magnetic ordering indicating the increase in hyperfine interaction of ferrite nanoparticles. Kazin et al. [33] reported similar results in Ni-Zn ferrites. They explained the increase in intensity of six line pattern in terms of increase in particle size with substitution of Ni^{2+} . In the present studies also the particle sizes are increasing with substitution of Ni^{2+} , but it is marginal, therefore we cannot expect increases in the intensity of sextets only with the increase in particle sizes. Moreover, the literature reports enable us to point out that the particles with sizes around 17 nm are exhibiting superparamagnetism [34], but in the present study they are exhibiting hyperfine interactions. In this contest, to explain this anomalous magnetic ordering the ratio of areas under Mössbauer spectral line is used to estimate the cation distribution using the relation [35]. Fig. 6.

$$\frac{I_B}{I_A} = \frac{(1 + \lambda)f_B}{(1 - \lambda)f_A} \quad (7)$$

where I_B and I_A = spectral areas under intensity for B- and A-sites, f_B and f_A = recoil free fractions at B- and A-sites, λ = inversion parameter. In the present study, the ratio of f_B to f_A is assumed to be unity [35]. The cation distributions and the values of λ estimated from Mössbauer analysis are listed in Table 4. The estimated cation distributions are consistent with the cation distributions estimated from Rietveld refinement. The magnetic moments (m_B and m_A) at B- and A-sites are calculated using the cation distribution estimated from Mössbauer analysis. These values are used to estimate the net magnetic moment using the below relation [23].

$$n_B = m_B - m_A \quad (8)$$

The obtained values of net-magnetic moment are tabulated in Table 4 as n'_B . The canting angles estimated in VSM studies and the magnetic moments at B- and A-sites estimated from the cation distributions obtained from Mössbauer analysis are used to calculate the values of the net magnetic moment again using the following relation. These values are tabulated in Table 4 as n''_B .

$$n_B = m_B \cos \alpha_{Y-K} - m_A \quad (9)$$

Table 4

Cation distribution, magnetic moments (n'_B and n''_B), inversion parameter (λ) estimated from Mössbauer analysis and blocking temperature (T_B).

Comp (x)	Cation distribution	n'_B	n''_B	λ	T_B (K)
0.5	$(\text{Zn}_{0.26}\text{Ni}_{0.26}\text{Fe}_{0.48})[\text{Zn}_{0.24}\text{Ni}_{0.24}\text{Fe}_{1.42}]\text{O}_4$	5.14	1.81	0.52	133
0.6	$(\text{Zn}_{0.18}\text{Ni}_{0.22}\text{Fe}_{0.55})[\text{Zn}_{0.22}\text{Ni}_{0.33}\text{Fe}_{1.45}]\text{O}_4$	4.62	2.03	0.45	210
0.7	$(\text{Zn}_{0.19}\text{Ni}_{0.07}\text{Fe}_{0.74})[\text{Zn}_{0.11}\text{Ni}_{0.63}\text{Fe}_{1.26}]\text{O}_4$	3.72	1.99	0.26	-

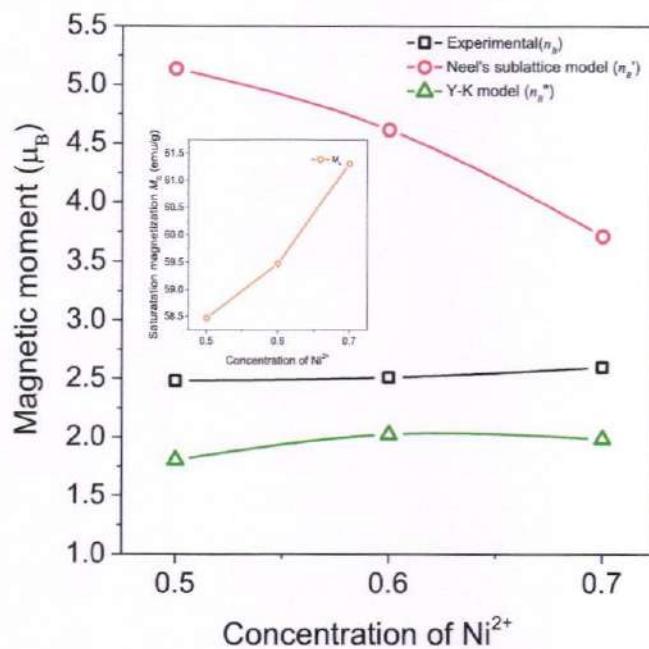


Fig. 7. Plot of magnetic moment against the concentration of Ni^{2+} .

The plot of variation magnetic moment with substitution of Ni^{2+} is shown in Fig. 7 and it was noticed that n'_B is monotonically falling with the doping level of Ni^{2+} . It is ascribed to decrease in magnetic ordering rather than increasing and hence it is not useful for the interpretation. But the values of n''_B being close to the experimental values of magnetic moments n_B and appears to be increasing with the substitution of Ni^{2+} . Therefore, we propose that the possibility of non-collinear collection of magnetic spins at B -site with canting which are affecting the magnetic properties in the present ferrite systems. Alternatively, the magnetic anisotropy is a tendency for magnetization along a preferred crystallographic direction and for an assembly of magnetic particles the magnetocrystalline energy E_A [36] is given by.

$$E_A = k_B T_B \ln \frac{\tau_s}{\tau_o} \quad (10)$$

where τ_s = superparamagnetic relaxation time, τ_o = relaxation time constant, k_B = Boltzmann's constant and T_B = blocking temperature.

The magnetocrystalline energy (KV) which serves as an energy barrier to prevent the change of magnetization direction is less than thermal energy ($k_B T$) above blocking temperature (T_B) and time of relaxation τ_s for nanoparticles is less than τ_o , and hence the internal magnetic field at the nucleus averages to zero and sextets collapse into quadrupole doublet. Such an assembly of ferrite nanoparticles exhibits a state like paramagnetism and is designated as superparamagnetism (SPM). Below blocking temperature (T_B), magnetocrystalline energy (KV) overcomes the thermal energy ($k_B T$) and relaxation time τ_s is more than τ_o then a characteristic Zeeman splitting (sextet) can be observed in the Mössbauer spectrum [37]. Even though the particle sizes are small ($D_{\text{XRD}} \approx 17 \text{ nm}$ from XRD and $D_{\text{FE-SEM}} = 25 \text{ nm}$ from FE-SEM), from the Mössbauer spectra we can observe well resolved Zeeman splitting and therefore we can expect that the values of T_B are near to room temperature or above the room temperature arising from the variation in magnetocrystalline anisotropy. In the present studies, the magnetocrystalline anisotropy is increasing with the doping level of Ni^{2+} that may be responsible for the ascending trend of magnetic ordering in ferrite samples. The plot of line widths (Γ) of B - and A -sites for the compositions against to Ni^{2+} doping is portrayed in Fig. 8. It was observed the values of Γ for B -sites are higher and are decreasing with the substitution of Ni^{2+} . The higher value of Γ of B -sites is endorsed to the canting of magnetic spins at B -sites and its decrement

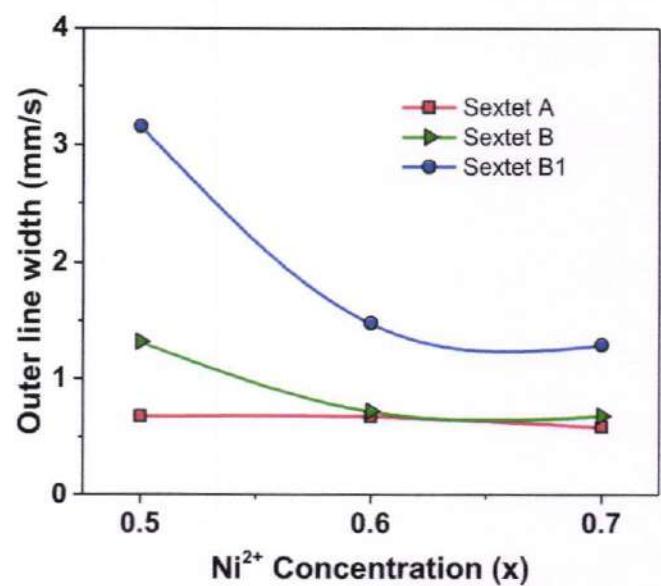


Fig. 8. Plot of line width against the concentration of Ni^{2+} .

reflects the dilution of canting leading to increase in magnetization as reported in magnetic studies. Similar results are reported in nano-ferrites [38]. In bulk ferrites, for a normal spinel $\lambda = 1$ and for inverse spinel $\lambda = 0$. As the dimensions of particles is restricted to the nanoscale, the surface to volume increases, leading to random occupancy of metal ions in the spinel geometry which result in the variation of values of inversion parameter (λ). The inversion parameter (λ) is decreasing with Ni^{2+} ion substitution is ascribed to the gradual transition from normal spinel to inverse spinel. We conclude that the reasonable factors for magnetization and magnetic ordering in the present series of ferrite samples are magnetocrystalline anisotropy, spin canting and crystallite sizes.

3.4. FC – ZFC studies

Mössbauer studies reveal the increases in magnetic ordering though ferrite compositions have nanoparticles are almost of the same size. To check out this behaviour FC–ZFC measurements have been done in the presence of 500 Oe. The magnetization-temperature plots for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6$) are presented in Fig. 9. In the zero field cooling (ZFC), the samples are cooled from room temperature (300 K) to the lowest temperature (5 K). The magnetic field of 500 Oe is applied at low temperature and magnetization is recorded during warming condition. At 300 K the thermal agitation randomizes the magnetic spins, but while cooling in the absence of the magnetic field, the magnetic moments of particles of different sizes is frozen due to their magnetocrystalline anisotropy. The magnetization becomes maximum at a temperature where the magnetic moments don't relax and completes blocked is known as blocking temperature (T_B). Suppose the sample is cooled below T_B , the thermal agitation drastically decreases and the particles of low magnetic anisotropy are blocked and frozen in random orientations. At this low temperature when a field of 500 Oe is applied, then some of the particles with low magnetic anisotropy is tending to align in the direction of the field. As temperature increases the thermal energy frees the frozen magnetic moments and is aligned in the direction of magnetic field resulting increase in magnetization. The magnetization gradually increases and becomes maximum at T_B where thermal agitation energy is balanced with magnetocrystalline energy. Further rise in temperature the thermal energy overcomes the magnetic anisotropy and randomizes the magnetic spins resulting decrease in magnetization. At blocking temperature (T_B) the relation between magnetocrystalline energy (KV) and thermal agitation energy ($k_B T_B$)

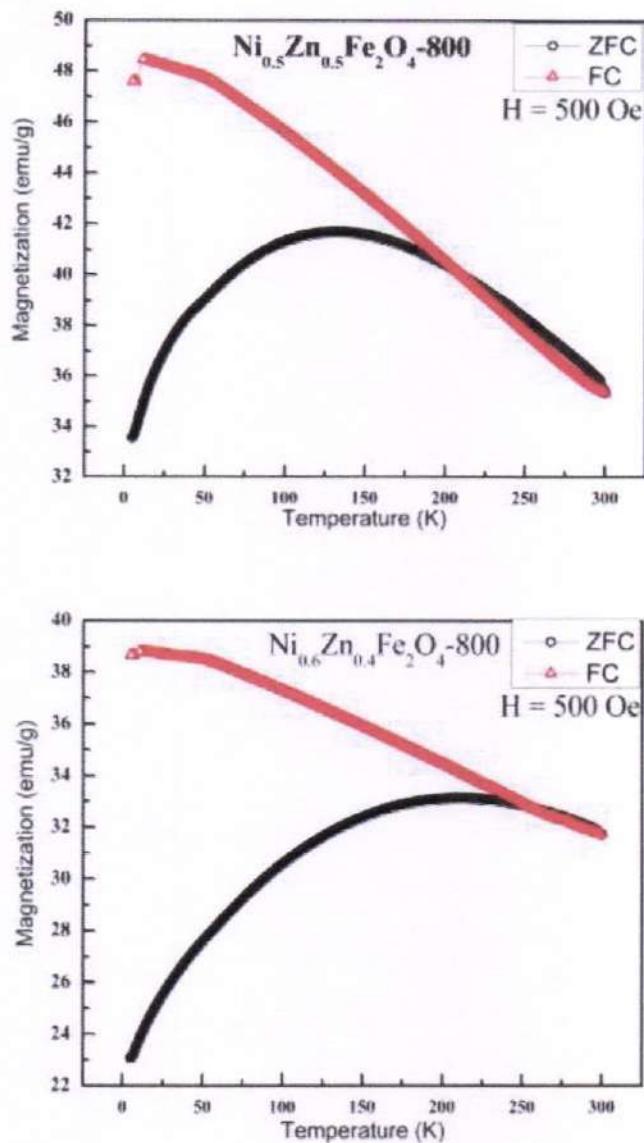


Fig. 9. Magnetization-Temperature plots of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6$).

[39] can be written as.

$$K \cdot V_p = 25k_B T_B \quad (11)$$

where K = magnetic anisotropy constant, V_p = volume of the nanoparticle exhibiting superparamagnetism, k_B = Boltzmann's constant and T_B = blocking temperature.

In field cooling (FC), the samples are cooled in the presence of a magnetic field of 500 Oe and magnetization is recorded from the lowest temperature in the presence of a field. As the temperature is cooled in the presence of magnetic field, the magnetic moments are aligned in the direction of field. At lowest temperature the magnetic moments cope up with the direction of the applied field and therefore the magnetization becomes maximum (less than M_s). As temperature is raised, the magnetization gradually decreases due to randomization of magnetic spins by thermal agitation. The FC and ZFC curves coincide at a particular temperature (T_c) is the transition temperature, which indicates the transition from ferrimagnetic state to superparamagnetic state. The values of T_B are listed in Table 4. It can be noticed that T_B is increasing with increase in the doping level of Ni^{2+} . For a same value of K , as volume (size) of particle (V_p) increases the blocking temperature (T_B) increases. In the present study, suppose the ascending order of T_B is in the accordance of particle size (volume size $V = D^3$) has to get near to

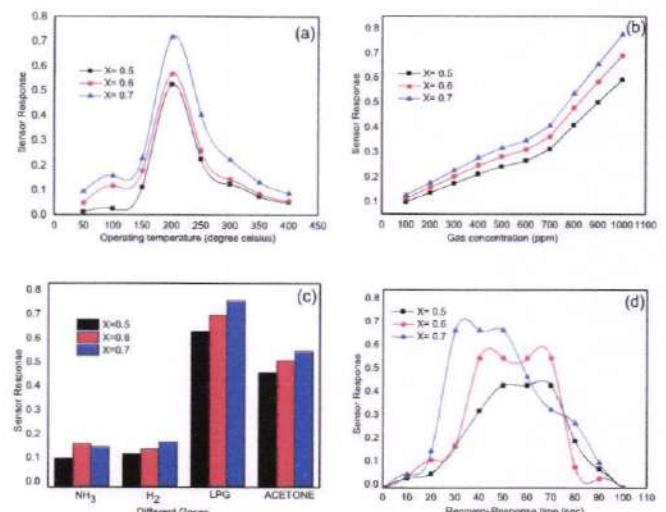


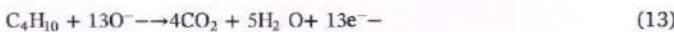
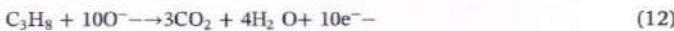
Fig. 10. Sensor characteristics of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6$) nanoferrites: (a) sensor response against to operating temperature (b) sensor response against to different gas concentrations at optimum temperature 200 °C (c) sensor response with respect to different gases at optimum temperature 200 °C and gas concentration of 1000 ppm and (d) sensor response with respect to time at optimum temperature 200 °C and gas concentration of 1000 ppm.

the same values with marginal increment. But the variation in T_B is high with the substitution of Ni^{2+} . Hence the increase in T_B is ascribed to the increase in magnetocrystalline anisotropy (K). The main contributions for K in the present ferrite samples may due to interparticle exchange interactions along with dipole-dipole interactions and surface anisotropy of nanoparticles [36]. Upadhyay et al. [40] reported the cation distribution results in higher magnetocrystalline anisotropy of Ni-Zn nanosized ferrites prepared by co-precipitation method. From Rietveld and Mössbauer analyses, we observed the cation redistribution in the present ferrite systems, which may also another perspective to increase in magnetocrystalline anisotropy. Magnetic nanoparticles are known to be characterized by core-shell morphology [32]. As sizes of the particles is limited to nanoscale dimensions, the probability for laying magnetic spins on their surfaces increases. The spins on the surface have uneven coordination with spin-glassy structure is known as shell (dead layer) and spins in the particle have ferrimagnetic order is known as a core. The exchange interaction among the magnetic spins in the core and shell regions can influence M_s and K of ferrite nanoparticles. The size of the nanoparticles also affects the cation distribution which will change the magnetic parameters.

3.5. Sensor studies

The gas sensor response of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x = 0.5, 0.6, 0.7$) ferrite systems for different parameters are depicted in Fig. 10(a-d). The sensor response typically varies with the operating temperature. Normally, a sensor exhibits very good sensor response at a particular operating temperature for a particular ppm of input gas is the optimum temperature (OT). In order to investigate the sensor applicability, measurements must be taken at high sensor response (sensitivity). Therefore, the identification of optimum temperature (OT) is essential for further gas sensor measurements. The plot of sensor response for 1000 ppm of input LPG concentration as a function of the operating working temperature is shown in Fig. 10(a). The three compositions are showing the similar trend of sensor response variation with respect to the operating working temperature. It can be observed that the sensor response is low at low operating temperature and steadily reaches to maximum with the rise in operating temperature. Thereafter, the sensor response gradually decreases for the further rise in temperature. This is attributed to the changes in the reaction mechanism of input gas with

surface absorbed O^{2-} ions. Initially at low operating temperature, the thermal energy of input LPG gas molecules is low enough to react with the surface absorbed O^{2-} ions of the ferrite systems showing the low sensor response. As operating temperature increases, the O^{2-} ions transformed into O^- ions in the following mechanism $O^{2-} \rightarrow 2O^- - e^-$. This leads to the increase of electron concentration useful for the reaction of test gas. As temperature is raised the test gas reacts with the electron concentration gradient resulting in the increase of conductivity in terms of increase of sensor response to a maximum value. At elevated temperatures the sensor response is decreasing due to the struggling of exothermic reaction for the gas absorption. The samples were showing the good sensor response in between 150 °C and 250 °C of working temperature and were found to be maximum at 200 °C. Therefore, we optimized the operating temperature of 200 °C for the three compositions for further measurements. The sensor response to different LPG concentrations at the optimum temperature of 200 °C is shown in Fig. 10(b). It can be observed that the sensor response is monotonically increasing with increase of input gas concentration (in ppm) and the three samples are showing maximum sensitivity for 1000 ppm. The ferrite composition $x = 0.7$ is showing high sensor response (0.75) comparing to the other two compositions $x = 0.5$ (0.53) and $x = 0.6$ (0.46). The plot of sensor response of three samples for four different gases like LPG, H_2 , NH_3 and CO at concentrations of 1000 ppm and optimum operating temperature of 200 °C is shown in Fig. 10(c). It can be observed that the three samples are showing good sensor response for LPG as well as for acetone. In the present study domestic LPG which is a mixture of propane (C_3H_8) and butane (C_4H_{10}) was used for gas sensor studies. The reaction mechanism for sensor response to input LPG can be expected as.



The reaction mechanism for acetone also follows the above possible reaction. However, the sensor response is relatively low than the sensitivity for LPG. It may be ascribed to difference in the OT of maximum sensor response. In these ferrite systems the composition $x = 0.7$ is found to be showing good sensor response when compared to the other two compositions. Rezlescu et al. [41] observed the similar trend of variation in $Ni_{0.99}Co_{0.01}Mn_xFe_{2-x}O_{4-\delta}$ ($x = 0.01$ and 0.02) for acetone and they reported that this is due to catalytic action of MnO for acetone gas. In the present studies also due to conductive nature of Ni^{2+} than Zn^{2+} , Ni^{2+} may be acted as reactive centers for catalytic reaction to the input gas. Alternatively, the possible reason for the variation of sensor response can be explained in the context of difference in the particle sizes. From the Table 1, it can be observed that the composition $x = 0.7$ has distribution of ferrite nanoparticles of smaller sizes than the remaining two compositions $x = 0.5$ and $x = 0.6$. It was well established that the reduction in size of particles leads to increase of surface to volume ratio [42]. Therefore, the sample with smaller ferrite nanoparticle size has a possibility of expected high sensor response to the input gas. This is due to their higher surface area useful to provide high chemical reaction with the surface absorbed O^{2-} ions of the ferrite sample. It can be observed that the composition $x = 0.7$ is showing good sensor response to both LPG and acetone. However, the sensor response to acetone is less than that of LPG. It is ascribed to difference in OT for acetone and LPG. Generally, response time to the input gas and recovery time when input gas is cut off are very essential to construct a sensor useful for gas sensor application. The response time is the time required to attain 90% of the equilibrium value of conductivity when the test gas is applied. The recovery time is the time needed to get the initial conductivity in air to be established in the sensor. The sensor response with respect to time of exposure of input LPG gas at 1000 ppm LPG for an optimum operating temperature 200 °C is shown in Fig. 10(d). The response time for the three compositions is found 40 s (for $x = 0.7$), 50 s (for $x = 0.6$) and 59 s (for $x = 0.5$) when input gas is

on. The relaxation times are found to be 20 s (for $x = 0.7$), 32 s (for $x = 0.6$) and 45 s (for $x = 0.5$) when the input gas is cut off after reaching the static condition of sensor response. In the present study, on comparison that the ferrite sample with composition $x = 0.7$ prepared co-precipitation method is more suitable for the fabrication of a gas sensor.

4. Conclusion

Pure cubic phase of Ni-Zn mixed spinel ferrites without secondary phases were successfully prepared by co-precipitation technique. Considerable cation redistribution was observed from stoichiometric estimations done with the Mössbauer analysis. The good agreement between the experimental values of magnetic moment (n_B) and the values of magnetic moment (n'_B) calculated from the Y-K model using cation distribution estimated from the Mössbauer analysis supports the spin canting at B -site. Moreover, the higher value of line width at B -site compared to the A -site is also confirming the possibility of spin canting at B -site. The non-collinear spin mechanism at B -site is influencing the magnetic behaviour of present series of ferrite samples. Though particle sizes are small, the present ferrite systems are exhibiting the hyperfine interactions which are expected due to increase in magnetocrystalline anisotropy. The major source for the values of blocking temperature near to the room temperature and their increase increment is also expected due to increase in magnetocrystalline anisotropy rather than increase in crystallite sizes. The composition $x = 0.7$ is showing exceptionally high sensor response to LPG. The response and recovery times for the composition $x = 0.7$ are 40 s and 30 s which are less than other two compositions. Therefore, the ferrite composition $x = 0.7$, suitable for sensor fabrication.

Author contribution

The article is original and has been written by the stated authors, who are all aware of its content and have approved its submission. The article which I have submitted to the Journal has not been previously published, not currently submitted for review to any other journals and will not be submitted elsewhere before a decision is made by this journal.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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7

SMALL SCALE INDUSTRIES IN INDIA OPPORTUNITIES AND CHALLENGES

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ABSTRACT

Small scale industries (SSI) refer to those small entrepreneurs who are engaged in production, manufacturing or service at a micro scale. Small scale industries play a focal role in the economic and social development of India in the post-independence era. Small scale industries constitute the backbone of a developing economy with its effective, efficient, flexible and innovative entrepreneurial spirit. Round the world SSI units have been accepted originator of economic growth and for promoting equitable development. The contribution of SSIs to the Indian economy in terms of employment generation, reducing regional imbalances, promoting intersectorial linkages, magnifying exports and fostering equitable economic growth potential has been quite marvelous. This sector through more than 6000 products ranging from traditional to high-tech, consisting over 36 million units widely dispersed across the country provides employment to over 80 million persons, contributes about 8% to country's GDP beside accounting for 45% of manufactured output and 40% to the export from the country. [1] The SSI sector has the prospective to spread industrial growth round the country and can be a considerable associate in the progress of comprehensive growth. The target of proposed National Manufacturing Policy of enhancing the share of manufacturing sector in GDP to 25% and to create 100 million jobs by end of 2022, as well as to

take India from its present 2 trillion dollar economy to 20 trillion dollar economy can be achieved with the help of SSI units. The paper attempts to discuss the role of small scale industries in developing the economy and explore the various problems faced by it.

Keywords: Small Scale industries, opportunities, challenges, econo.

Introduction:

Small scale industries in India and abroad exhibited considerable robustness and pliability in maintaining an unswerving rate of growth and employment generation during the global recession and economic slowdown. The Indian economy during the current fiscal years has shown considerable growth performance by contributing to create livelihood opportunities to millions of people, in magnifying the export potential and in increasing the overall economic growth of the country. As a catalyst to the socio- economic transformation of the country, the SSI sector distinctly crucial in addressing the national objective of bridging the rural- urban divide, mitigate poverty and generating employment for the admirable community of the country. SSI sector comprises almost about 80% of the total industrial units in the country. In India SSIs occupy 36 million units, contribute to 45% of industrial production, 40% to the export sector through more than 6000 products ranging from traditional to high-tech and provides employment to about 80 million persons. Therefore the small scale industries (SSI) in a developing country like India occupy a special place in the industrial structure. In view of the vast potential of small scale industries, the government has given this sector an important place in the framework of Indian economic planning for economical as well as ideological reasons

Objectives of the study:

1. To study about the opportunities of small scale industries in India
2. To study about challenges faced by small scale industries in India

Methodology of the study:

Secondary data was used for this study, ministry of MSME, RBI reports, various magazines, journals and news papers also used.

Literature review

Although small scale industries continue to straddle the industrial sector round the world, the literature on their varied functioning are not many especially with reference to changing perspectives.

Srinivas K T, (2013) has studied the performance of micro, small and medium enterprises and their contribution in India's economic growth and concluded that MSMEs play a vital role in the inclusive growth of Indian economy.

J. Stately and Michael (1998) in International Marketing under the chapter "Exporting not just for small business show the problems for small exporter and found that

- A relatively large domestic market and lack of exposure to other cultures, making the selection of markets and identification of customers in abroad difficult.
- The lack of managerial capabilities and general resource.
- Controlling the foreign operation, channel, policy and physical distribution.

Different safety and quality standard.

Sumanjeet Singh and MinakshiPaliwal (2017) in "unleashing the growth potential of Indian MSME sector" had concluded that undoubtedly the MSME sector has huge potential for generating innovative entrepreneurship and massive employment but some problems confronting MSMEs are

- Lack of access to finance
- Lack of access to penetrate foreign market
- Lack of skilled manpower
- Lack of reliable and stable infrastructure
- Ineffective marketing network

Dr.Reetu Sharma (2012) in "problems and prospects of small scale industrial units (a case study of exporting and non-exporting units in Haryana) had concluded that SSI units are at a developing stage and more expansion is required but some problems need to be solved

- Underutilization of installed capacity

The marketing activities to be strength for selling SSI manufactured products..

Meaning of small scale industries

A small scale industry is an industrial undertaking in which the investment under fixed assets in plant and machinery or equipment, whether held on ownership term or on lease or hire purchase, does not exceed \square 10 crore for manufacturing enterprise and \square 5 crore for service enterprise. However, the investment limit changes overtime as prescribed by the government.

In accordance with the provision of Micro, Small & Medium Enterprises Development (MSMED) Act, 2006 & the Micro, Small and Medium Enterprises (MSME) are classified in two classes:

1. Manufacturing Enterprises: The enterprises engaged in the manufacturing or production of goods pertaining to any industry specified in the first schedule to the Industries (Development and Regulation) Act 1951 or employing plant and machinery in the process of value addition to the final product having a distinct name or character or use. The Manufacturing Enterprise are defined in terms of investment in Plant and Machinery.
2. Service Enterprises: The enterprises engaged in providing or rendering of services and are defined in terms of investment in equipment.

The small scale industries in India whether in manufacturing sector or service sector are split up into five parts?

1. Manufacturing industries: These units are producing merchantable articles for direct consumption and also for processing industries, example: khadi industries, food processing industries, power looms, etc.
2. Ancillary industries: The ancillary industries produce parts and components for large industries.
3. Service industries: Service industries are known for covering all light repairs shop that is essential to maintain mechanical equipment. These industries completely depend on machinery.
4. Feeder industries: These industries produce certain specialised products like electroplating, casting, welding, etc.

5. Mining or Quarries: These industries cater the demand of different types of stones and minerals of the Indian and foreign market.

Opportunities of small scale industries in India

Small scale industries are the second largest employer of human resource after the agricultural sector and produce a wide variety of products ranging from traditional to high-tech. SSI plays a pivotal role in the Indian economy as of being labour-intensive, helps to generate employment in rural as well as in urban areas. The SSIs had also played a cardinal role in the growth operation of Indian economy since independence despite of drastic competition from the big industrial houses and not immensely enriching support from the government. The following are some of the principal role played by small-scale industries in India.

Origination of employment:

The elemental problem that is confronting the Indian economy is escalating pressure of population on land and needs to create enormous employment opportunities. This problem can be solved to a larger scale by the help of small-scale industries as small scale industries are labour intensive in nature and has shown an outstanding growth in the last decade.

Equitable distribution of income:

Small scale industries trigger the equitable distribution of wealth and income within societies in ways that are economically positive and without being politically turbulent, which is chiefly categorized by more concentration of income and wealth in the organised sector keeping behind the unorganised sector underdeveloped.

Assembling of resources and entrepreneurial skill:
Small scale industries can assemble an adequate amount of savings and entrepreneurial skill from semi-urban and rural areas remain unblemished from the semi-social welfare in the country by identifying hidden talents from the weaker section of the society and investing the intellectual skill for producing or manufacturing commodities

Regional dispersion of industries:

There has been an enormous agglomeration of industries in few metropolitan cities of different states of India. People in search of employment migrate from semi-urban and rural to these developed metropolitan cities to earn a better standard of living which

Ultimately leads to malicious outcome of over-populated, pollution, creation of slums, etc. Small scale industries can overcome this problem of Indian economy by utilising local resources in terms of raw material, investment, intellectual skill, etc, thus brings about dispersion of industries in various parts of the country and promote balance regional development.

Export enhancement: Small scale industries have registered a magnificent growth in export over the years. The value of products exported by the SSIs has increased from 155 crores in 1971-72 to 124417 crores in 2004-05. The SSI units contributes about 40% of India's total export thus this helps India in increasing the foreign exchange reserve and reduces the pressure on country's balance of payment

Supports the growth of large industries: The small scale industries play a pivotal role in serving the

industries by providing accessories, components, small parts and semi finished goods required by big industries.

Better relation between employer and employees:

In small scale industries better industrial relation between employer and employees helps in increasing employee's efficiency and minimise the chance of industrial dispute, leading to comparatively less loss of production and man-days.

CHALLENGES FACED BY SSIs

In spite of expedient contribution by the SSIs towards the Indian economy, SSIs does not get the indispensable support from the concerned Government departments, financial institutions, Banks, credit societies and corporate thus the SSIs are becoming handicap in the face of competition at national and international markets. The major problems faced by the SSIs are discussed below:

Scanty credit assistance

Scanty and timely supply of credit is one of the major problems faced by SSIs in India. Scarcity of finance and weak creditworthiness is the main barrier for the development of SSIs in India. The creditworthiness of these small borrowers is generally weak and therefore they face unwilling creditors who may be persuading to lend only at high rate of interest.

Uneven and poor quality of raw material

SSI units face extreme problems in procurement of raw materials whether from local or international market. The problems arise due to absence of sufficient quantity of raw materials, poor quality of raw material at exorbitant price. The entrepreneur of SSI units has lack of knowledge about the procurement from foreign market. Large scale industries enjoy economies of large scale operation hence can procure the quality raw material at very reasonable

price, thus can sell the products at cheaper price compared to SSIs.

Absence of organised marketing process

SSI units do not have any organised marketing process and even does not appoint any marketing organisation for marketing of products or services as hence their products compare unfavourably with the quality of the products of large scale industries. They have competitive disadvantages in comparison to large scale industries, as large scale industries infuse large amount of money on branding and promotion activities.

Inadequate infrastructure

Inadequate infrastructure is a major problem for the SSI units to grow and prosper. Most of the SSI units are located in semi-urban, urban and rural areas where the power supply is inadequate to run big machines, sometimes power cut off, and poor road connectivity. The absence of adequate infrastructure adversely affects the productive schedule of the enterprise leading to under utilization of capacity. Moreover the machine equipments and technology employed by the SSIs are outdated, where the large scale organisation enjoys competitive advantages.

Beside the above mentioned problems SSI units suffer from a number of other problems also like managerial capabilities, lack of adequate warehousing, free supply of goods, lack of skilled manpower, lack of appropriate information, etc. Due to all these problems the progress and development of Small scale industries could not reach the distinguished stage.

Conclusion:

The furtherance and advancement of SSIs is essential for the development of Indian economy to achieve impartial distribution of income and wealth, economic self-dependence and economic sustainable developments. To boost the SSI sector so that it can take deserved place in the growth mechanism of Indian economy, it is essential to support MSMEs by educating them to make optimum utilization of inbuilt capacity to be successful both under human and economic activity. Some appropriate measures to be taken by the government in providing financial assistance at minimum formalities, a platform to be built by government to help the MSMEs in procurement of quality raw material and train them for organized marketing process.

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DALITS AND THE SPECTACLE OF VICTIMHOOD IN TELUGU CINEMA

Chandra Sekhar

The representation of caste and Dalits in Indian cinema has become a topic of recent interest but there has been no discussion of the depiction of caste in Telugu cinema.¹ In India, the study of the representation of Dalits in popular cinema has been generally limited to the discussion of positive and negative representations. I argue that the issue of representation should not be dealt with at the level of positive and negative representations alone but that one should inquire into how caste discourses shape a film and how a film can reproduce certain caste discourses. This is what this chapter attempts to do, as the movie I will be analysing gives the impression that it represents the issues of caste, and particularly Dalits, in a positive way. This chapter offers a reading of the film *Jayam Manadera: The Voice of Victory* (Victory is Ours, N. Shankar, 2000), a film that adopts complex positions on caste which cannot be regarded merely as positive or negative because the film brings up the question of caste while simultaneously relocating the agency of caste protest and struggle onto benevolent upper castes. *Jayam Manadera* is selected for analysis because it is markedly different from other films which represent Dalits in terms of narrative and language. This movie acquired the reputation among audiences of being a progressive film that explicitly addresses the issues of caste, the empowerment of Dalits and their representation in politics, their temple entry and caste atrocities; furthermore, it was praised by critics for its realistic approach.²

Before analysing the movie, I will provide an overview of how the issues of caste and Dalits were addressed in Telugu cinema before *Jayam Manadera* was released. The Telugu film industry is marked by the realities of caste and its hierarchical nature; filmmakers, producers, writers and artists are almost exclusively from upper castes. Upper-caste domination of the film industry necessarily influences even sympathetic treatments of Dalit issues and ends up effacing the Dalit voice by assigning the role of reformer or leader to upper castes themselves. Such representations have largely been informed by Gandhian reformist discourse, which declares

upper-caste Hindus' practice of untouchability a sin; hence, they have to go through the process of self-purification and a change of heart in order to uplift and accommodate Dalits. The first major attempt to deal with the subject of caste and Dalits was Gudavalli Ramabrahmam's *Malapilla (The Untouchable Girl)*, which was released in 1938.³ Such films in the Gandhian mode are centrally concerned with the question of caste by focusing on a reformist agenda. In most of these movies the hero is from an upper-caste background but portrayed as casteless, progressive, modern and reformed, and a follower of Gandhian ideology. The narratives of these movies are structured around the element of love between an upper caste and a Dalit. As S.V. Srinivas argues, an upper-caste man's love for a Dalit girl is a marker of the upper caste's modernity and the goodness of his heart.⁴ Furthermore, such films want to legitimise the idea of marriage between the upper castes and Dalits; in order to do that these films mediate caste relations by invoking Gandhi and his ideology of caste, quoting *shlokas* from Hindu religious books and consequently reforming Dalits as well as upper-caste communities. In most of these films, women become the symbol for this process of accommodating the Dalit into the upper-caste family. Another element in these films is their open endings or conclusions with *shlokas* from Hindu religious books, statements about the eradication of untouchability, songs about the evil of the caste system or the dedication of the movie to Gandhi.

However, *Jayam Manadera* is different from conventional films even though it was produced by the same industry. This was probably the first instance of the issue of caste being taken up in a movie by a non-upper-caste director. The director Shanker, who came under the influence of a Naxal movement, reads Jyothi Rao Phule and Ambedkar's writings and has a personal experience of poverty and inequality, wants to convey the idea that Dalits and Bahujans need social, economic and, more importantly, political justice and that they will get justice and empowerment only when they enter into politics.⁵ To translate this concept onto the screen, he faced many problems, as film is a collaborative enterprise. In my interview with him, he recalled that when he was contacted by the producer and the hero, who were brothers, and their father, who was also a producer, to narrate the story, he did not tell them that the film was about Dalits; rather he told the story to them in a different way by saying the story was about conflict between two families and conflict arose because the hero's family took sides with poor people and worked towards their betterment.⁶ Shanker stated that

if I say that the movie is about Dalits, no hero accepts to act and no producer comes forward. Being an artist, I have my own limitations because I have to present my concept in a commercial format by having a hero who is from an upper caste (in the film and outside the film also).⁷

Despite these constraints, the film *Jayam Manadera* engages with caste and Dalits in a different way: the filmmaker addresses the following issues on screen: (1) Dalits contesting *panchayat* elections at village level and becoming *sarpanch* (village president), (2) land distribution to Dalits, (3) Dalits' temple entry and (4) atrocities

against Dalits committed by upper castes. In 1985 at the Karamchedu massacre, six Dalits were killed and three Dalit women were raped by upper-caste Kamma land-holders in Andhra Pradesh. After this massacre, as S.V. Srinivas points out, cinema attempted to

render the caste antagonism invisible or to disavow it. The dominant tendency has been to avoid direct references to caste or to underplay them; for instance, in the veiled allusions that were relegated to the comedy track, specific occupations usually marked the comedians as lower caste.⁸

After Karamchedu, many new developments took place in the Dalit movement. In 1991, the Chundur massacre took place where nine Dalits were murdered by Reddys and other upper castes.⁹ The 73rd Constitutional Amendment Act in 1992 brought significant changes by granting seats for Dalits for the post of *sarpanch* in village *panchayats*. Anti-reservation movements demonstrated against upper castes' resentment of Dalits entering into spaces which were regarded by upper castes as theirs. However, from 1980s to 2000 there was no discussion in cinema about any of these developments. Thus the significance of *Jayam Manadera* lies in engaging with some of these issues.

The representation of Dalits in cinema has received some scholarly attention. There are, broadly speaking, three kinds of studies on representation of caste or the Dalit persona in Indian cinema. Firstly, most of the studies attempt to categorise the representations of Dalits as positive or negative. The focus is more on negative representations of the characters, the roles they play and how they are made fun of or how they are given an inferior position in the narrative.¹⁰ Secondly, studies take a biographical approach; they focus on the life of a Dalit actor and the types of roles he has been given in order to analyse how or whether caste plays a major role in the kinds of opportunities given in the industry.¹¹ Thirdly, some studies revolve around the role of caste in the institution of cinema.¹² In all these studies, there is virtually no analysis of Dalits in Telugu cinema and the discourse of caste. This chapter is not only concerned with the representation of Dalits but also on the debate and discussion on how the discourse of caste is generated through cinema. *Jayam Manadera* is examined to illustrate how film narrative attempts to resolve the complex issues of caste conflicts in ways advantageous to dominant castes. I analyse discursive strategies which are representative of strategies adopted by Indian films more widely. I focus on the kind of debate about caste that the film produces, particularly in terms of the characters, story and narrative.

Caste in *Jayam Manadera*

The whole narrative of the film is about an upper-caste hero giving up his life in the process of his struggle for the empowerment of Dalits and how his son fulfils the mission.¹³ There are three sets of characters: (1) Dalits, (2) good upper castes and (3) bad upper castes. Mahadeva Naidu and his son Rudrama Naidu are the good

upper castes.¹⁴ Their relationship to Dalits is reformist and sympathetic. Mahadeva Naidu worked for the empowerment of Dalits and championed the cause of their political representation and their right to enter Hindu temples, and he distributes his lands to them. As he is sympathetic and reformist towards them, Dalits become his followers. The bad upper castes are Narasimha Naidu and his three brothers. Their relationship to Dalits is hostile when they contest elections and want to gain entry into the temple. The relationship of upper castes towards each other is hostile even though they are relatives. Mahadeva Naidu's mingling with Dalits earns him the enmity of Narasimha Naidu. It is this hatred against Mahadeva Naidu for siding with the Dalits that prompt Narasimha Naidu and his brothers to murder Mahadeva Naidu. Upon his murder, Dalit followers want to take revenge on Narasimha Naidu's family and since the Dalit squad does not succeed, Mahadeva Naidu's son Rudrama Naidu takes up the cause of Dalits and avenges the death of his father. The narrative features eight Dalit characters, two good upper-caste men and four bad upper-caste men.

The whole set of caste relations is staged in three scenes. By analysing these scenes and characters, this chapter attempts to analyse how a film, while appearing to speak on behalf of Dalits to foreground the problem of caste, nevertheless reinforces certain existing caste prejudices; further it explores contradictions and looks at the positions allotted to Dalits in the narrative and the stereotypes they reinforce. I will analyse the film from two related perspectives: the first by considering the work as a thesis film, and the second by looking at the rhetoric through which the film conveys its thesis, and matching it with the visuals to see how they relate to one another.

The film as thesis

Jayam Manadera gave the audience the impression that the whole movie is about Dalits by employing long discussions about caste; I call a film that uses this technique a 'thesis film'. I borrow the idea of the thesis film from Steven Maras to help me to read this particular film as propounding a thesis. According to Maras, a thesis film is one which intends to put forth a thesis or a particular kind of theory or conceptualisation. The thesis film makes the theory its content. It is more than just a film with a thesis: the film *is* the thesis. The nature of the thesis is inseparable from its mode of expression.¹⁵ In the present movie the thesis is of caste; the conceptual practice of caste is represented in and by the film. At the thesis level, the protagonist of the film delivers long dialogues or speeches which are seemingly addressed to other characters on the screen but are in fact addressed to the audience. This kind of filmic technique serves a crucial function as it presents the audience with a 'real society' off screen whom the film intends to mobilise into becoming a part of the frame.¹⁶ In this kind of thesis film, the narrative is used to convey the message. In such films, there are typically speeches through which the thesis of the film is conveyed. They are not meant to tell the story of a Dalit person or community but to convey a certain kind of message about caste. In the movie, there are three speeches

by the protagonist through which he intends to highlight the issues of the political representation of Dalits, the importance of land for Dalits, temple entry and the nature of caste system.

The first speech is about the Dalits' political representation. Basavaiah, a Dalit leader, contests the election for the post of *panchayat* president on the encouragement of Mahadeva Naidu. This infuriates Narasimha Naidu's brothers who inflicts physical violence on the Dalits, on Basavaiah and his wife Chandramma. Mahadeva Naidu comes to the rescue of the Dalits. The dialogue between good upper castes and bad upper castes begins. The camera situates the person who asks questions in the corner of the frame and the hero who answers is in a close-up shot occupying the whole screen. Janardan Naidu questions how a Dalit, who is meant to sweep the cattle shed, could contest for the president's post? The protagonist responds with a monologue:

Why can't Dalits contest? With his labour, we increase our wealth, with his sweat we experience luxuries, with his votes we get authority, but why should a weak person be kept away from authority? Votes are theirs, seats are yours, fasting is for them, while positions of power are yours.

Furthermore, when the protagonist is asked by Janardan Naidu, 'who will carry the palanquin if everyone gets into it?', he states that 'the shoulders of the palanquin bearers are tired of the burden; we will know that burden only if we carry it once'.¹⁷

The second speech is at the house of Mahadeva Naidu. After the naming ceremony of Mahadeva Naidu's child, the camera follows Mahadeva Naidu while he is walking towards the balcony carrying his child. Over the shoulder of the hero, the camera tilts up, showing the large crowd of Dalits looking at the camera and chanting 'Long live Rudrama Naidu'. The hero shows his son to Dalits, and says: 'I thank all of you for coming here to bless my child. To have sufficient food like us, to live an honourable life in a society, you have only stomachs but no land. So you need land. The land which I got from my ancestors, I will distribute it to the poor and landless'.

The third speech at the temple is about Dalits' temple entry. Basavaiah becomes the president of the village *panchayat* and according to village tradition, the president has to offer *pattu vastralu* (sacred clothes) to god Rama and Sita in the village temple. But the temple priest refuses to let the Dalit president carry out the ritual saying that the scriptures do not allow a lower-caste person to enter the temple. Mahadeva Naidu tries to convince them by drawing examples from the scriptures (*Sastras*). The argument goes like this between the two parties:

NARASIMHA NAIDU: Mahadeva Naidu, bringing a low caste person into the temple and making him offer sacred clothes to god is against tradition.

MAHADEVA NAIDU: Who says so?

NARASIMHA NAIDU: The *sastras*.

MAHADEVA NAIDU: Which sastras are you talking about? The Holy book Mahabharata, worshipped by Hindus was written by Veda Vyasudu who was born in the Besta caste, Valmiki who wrote Ramayanam is from the Boya caste. Srikrishna who gave us the discourse of Geeta is from the Yadava community. All these people are from backward castes.

PRIEST: Basavaiah is not from a backward caste but belongs to the fifth caste, that is, he is a Dalit.

MAHADEVA NAIDU: (After reciting verses from Geeta) God Sri Krishna says that he has created only four castes; then from where did Dalits come and who created them? Elders who felt that Sudras are outnumbering them, divided people in the name of occupations and castes. Three thousand castes were created.

However, the priest refuses to give a ritual welcome to the Dalit president, which is the custom of the place. The protagonist then brings the sacred thread (*Jhandyam*) from the temple, puts it on Sahadevudu, a Dalit who has learnt the *shlokas*, and asks him to recite the *shlokas*. As a justification for the action of making a Dalit recite the *shlokas*, Mahadevva Naidu recites the verse *Janmana Jayate Shudrah, Sanskaraat dwij uchatye*, which means that at birth everybody is a Sudra, based on one's character, one becomes *dwijah* (twice born). The one who reads the Vedas becomes *Viprudu* (Brahmin) and the one who gains the knowledge of Brahma will become Brahmin. Thus, he makes the point that now Sahadevudu has that eligibility to recite shlokas as he knows the Vedas.

In the three scenes recounted above, the protagonist's speeches arrest the narrative. Every time both parties are engaged in argument, the story does not move forward. The pedagogy about caste is embedded in the protagonist's speeches; he tells the audience about the nature of caste. Caste is equated with the Varna system. It is not determined by birth but by actions and character; this is in accordance with the Gandhian view on caste. One may be a Dalit by birth but one can move up the caste hierarchy. The film seems to convey the message that caste is not an immobile system. Other characters ask questions in order to anticipate the audience's questions. In the first speech, the protagonist is not just arguing for the political representation of Dalits but also gives a detailed justification for his action and tells the audience how to understand caste. The people whom he is ostensibly addressing in the film are actually the audience who need to be convinced or told why and within what framework such an action can happen. In this filmic technique, the action is internal to the film, while the language is the pedagogy of caste reform, directed at the film audience. Hence, the audience gaze becomes an integral part of the film as they are the primary target for this pedagogic and aesthetic project. This technique is used because the audience has to be reasoned with; it is the logic of the film that those who will not listen to reason in the movie will be beaten up. The protagonist will use force to make others listen, at least on screen. The words are meant for the audience, whereas the action is meant for villains or people who do not listen to those words. If actions alone could have solved the whole issue, the protagonist could have started acting, beating up those who disagree; there would

have been no need for him to give those long speeches. However, the speeches are meant to convince the audience, to get them on the side of protagonist, so that whatever he does afterwards will be justified.

Mismatch between rhetoric and action

There is a second level at which the scenes work, a mismatch between rhetoric and action – the rhetoric of the protagonist and the action which follows. In the course of the narrative, the protagonist wins the argument. Each time he puts forth the argument, he wins over his opponents, and, ostensibly, the audience. He wins the argument, but he does not win in the story. In the story, those who supposedly speak for Dalits seem to be losing. Mahadeva Naidu is killed before he sees his dreams for Dalits come true. After his death, Dalits are hunted like animals, their huts are burnt, President Basaviah's wife is stabbed and the whole Dalit community is exiled from the village.

At the level of the story, the film is doing a balancing act: the bad upper caste kicks a Dalit woman and, in return, the protagonist makes her slap him back with her slipper. The bad upper caste cuts out the tongue of Dalit, and in return, his hand is chopped off. There is no clear winner emerging. At the level of the discourse or of the argument, however, the party of Dalits is winning. The rhetoric claims that Dalits and those who stand with/for them are the winners, while that is not something that is taking place on the level of the action.

For instance, in two previously discussed scenes about Dalits' entry into politics and the temple, the protagonist wins the argument and enhances the Dalits' standing; but at the level of action, he does not win on behalf of Dalits as the narrative clearly shows their inferior status and humiliation. The film tries to create an equivalence around action and reaction, but social life does not permit this kind of equivalence when it comes to the atrocity of caste. In the narrative, all the Dalit characters are humiliated. With the protagonist's encouragement, Basaviah contests the president's post and for that reason, his wife and he are beaten up. Since the protagonist asked him to, Sahadeva recites *shlokas* but his tongue is cut off for doing so. And finally, they are hunted by the bad upper castes and exiled from the village. The rhetoric, it seems, does not have any impact at the level of the action. The protagonist still has to beat up the bad upper castes, he still has to create a spectacle through his actions. He is a very progressive, enlightened hero who gives speeches but if we look at the action that follows the speech, there is a complete mismatch. That means the rhetoric is used only for the purposes of enhancing the conflict, for creating the purpose of the conflict. In every scene, the good upper-caste protagonist manages to impress us with his rhetoric, but Dalits are made to pay the price for it.

This rhetoric of Dalit empowerment is in line with Gandhian reform since upper castes reform themselves; it is suggested that there is no need to change the caste order. It can remain intact. Upper castes simply would become more accommodating, bringing Dalits into politics, allowing them to enter into the temples; in that sense the film's discursive strategies are not at all different from Gandhian

discourse. The only difference from Gandhian discourse is that if others do not reform themselves, the hero will be there to teach them a lesson.

I will now problematise a few scenes which reproduce the caste hegemonies. Though the whole story is about Dalits' empowerment, Dalit characters do not have any significant role in the narrative progression. The dominant structures of representation portray Mahadeva Naidu as politically agential. Dalits are perceived as less agential and incapable. They cannot speak for themselves; they never articulate their denial of accessibility to education, to lands and to political power as examples of the practice of caste. They are not capable of articulating their condition as part of the larger social issue. As Jenson Joseph argues, this 'reducing' of Dalit characters to dependents enables the narrative to render the Dalits voiceless and in need of representation by the upper-caste figure.¹⁸ The protagonist has to mediate all the time. Out of his generosity, because he is a modern rationalist and reforming figure, he is willing to do something for them. He is not one of them, but he is willing to work for them. That division is clearly maintained. It is Mahadeva Naidu, the radical reformist figure, who is endowed with the authority to represent the issue of political representation and need for land in the language of rational politics. The protagonist takes proactive roles such as spokesperson, saviour, bestower, teacher and, finally, their representative. In a Gandhian way, he retains the agency of the enlightened upper caste and becomes an object of admiration for Dalits. Dalits have no agency in the narrative. Basaviah, though a president, is never shown as angry, resisting or as a leader – he is voiceless. He is a pacifist and all the anger and protest comes from the protagonist on behalf of them. Even when Dalits form an underground hit squad, their actions are motivated by their love for Mahadeva Naidu, their leader, rather than by their own exploitation. The narrative has given reformist agency to an upper-caste figure who is an enlightened one, in relation to Dalits who are positioned as waiting recipients of enlightened kindness.

The Gandhian visualisation of 'Harijan' is reflected in the representation of Dalit characters by positioning them to be dependent and submissive. A close look at some of the scenes in which Dalits appear on the screen would suggest that their presence within the narrative is expected to show their subservience through their body language, words and physical gestures. I shall try to substantiate this claim by referring to the two scenes in which their subservience has been staged in the narrative. Firstly, when Basaviah's daughter-in-law Ramanamma is crying because of her husband's death at the hands of Narasimha Naidu's people, Basaviah says that he did not die for her sake and his but for their leader. He tells her, 'You should not cry for your husband's death but cry that we haven't got that opportunity to die for our leader'. Secondly, in the scene where Basaviah goes to invite Narasimha Naidu to come to the temple as he is going to give sacred clothes to gods, we find that the language of subservience has been built into his words, as he says:

You are all elders! Greetings to all of you! Babu (Sir), I am the one who is not eligible even to climb the steps of the temple, but it's my luck to offer sacred

clothes to gods Sita and Rama. This is a great thing not only to me but to my entire community.

In the narrative, Dalits are meant *to perform their subservience*. It is not enough for one to merely state their subservience. They actually have to perform it time and time again, and also accept that subservience has to be conveyed in the narrative, that they have no political agency until the protagonist comes and supposedly awakens and speaks for them. In the course of the narrative, characters cannot transform themselves; they cannot become anything except by the intervention of the protagonist.

The protagonist's name *Naidu* suggests that he is Kamma by caste, one of the dominant upper-caste communities in the Andhra region, but he is 'casteless' in the sense that he is seen as transcending his caste identity. Mahadeva Naidu is an enlightened modern reformed Hindu. He is someone who knows Hindu religious books like Mahabharatham, Bhagavadgita, Ramayana and Vedas (as he refers to these in the temple entry scene and teaches Vedas to Sahadevudu). He is a strong devotee of Hindu gods, particularly god Shiva. As a part of his attire, he has a chain of beads around his neck. In fact when he is introduced on the screen, the first cut is to the beads around his neck. His ideology for Dalits' empowerment comes from his knowledge of and devotion to Hinduism. The filmmaker confirmed this during my interview as he said: 'Mahadeva Naidu's generosity towards Dalits comes from his understanding of Hindu Dharma'. Mahadeva Naidu does not question Hinduism, which sanctioned the caste system; rather he is a strong follower and becomes an upholder of it by quoting all those verses from Hindu religious books. In the temple entry scene, the protagonist says that 'The *elders* who thought that Sudras were outnumbering them, had divided people in the name of occupations and castes. Three thousand castes and untouchability between each caste was created'. The above statement absolves the Hindu scriptures of all responsibility for actively sanctioning and endorsing untouchability, notions of purity and pollution and caste hierarchies. The protagonist does not furnish information about these unmarked 'elders' who created the caste system and divided people in the name of caste and who are responsible for discrimination.

The narrative uses the strategy of impersonation to create trust in Dalits on the screen regarding the goodwill of the upper-caste protagonist towards them. Impersonation, as Swathi Margaret argues, is a Gandhian strategy 'through which he reinstalls the privilege of the already privileged twice-born Hindus as icons of social reform'.¹⁹ The movie *Jayam Manadena* succeeds in employing this technique, as manifested in the character of Mahadeva Naidu and later his son Rudrama Naidu. Mahadeva Naidu reiterates his impersonation of Dalits in the narrative through song and speeches which often encourage the caste Hindu orthodoxy to reform. After Mahadeva Naidu announces his land distribution, the song sequence begins with the shot of a camera capturing Dalits beating drums. The song sequence serves the purpose of staging the upper-caste protagonist's characterisation before the mass audience. These sequences are replete with shots of the hero participating in

the festival celebrated by Dalits, playing with Dalits' children, teaching Vedas to one of them, attending a Dalits' wedding at a Dalits' house, as a family dines with them by sitting on the floor (though he is offered a chair). He is always with them as the song describes: 'his smiles made them to utter Vedas, he will come like a relative whenever they call and remember him'. I argue that in the Gandhian imaginary, it is only through the upper-caste impersonation of Dalits that the latter gain 'human' status.

In the narrative, there is clear language and spatial signifiers of difference between Dalits and upper castes. The film shows Dalit characters talking in the 'local' dialect which is associated with the Dalit community, while upper castes speak the formal language. In the *panchayat* elections scene, the camera tilts down to where upper-caste people are beating Dalits on the premises of the *panchayat* office. Basavaiah is dragged outside the gate and the camera frames Basavaiah standing between Janardan Naidu and his brother, behind them the *panchayat* office gate and office building. This shot offers spatial difference that Dalits are not supposed to enter into the power structure, the *panchayat* office. Janardan Naidu's furious dialogues support this idea when he says

how dare you to contest against us? This is our *Panchayat*; either I or my brothers must be the president. How dare you turn against us? (While Janardan Naidu is saying these words, his brother snatches the nomination form from Basavaiah and tears it and Basaviaah is thrown to the ground) I will hack you.

The framing of this scene clearly illustrates the inherited attitude of upper castes about owning political space as their property: Dalits should not dare to enter into that space; if they do, it will result in hacking them down.

The second instance is about Dalits' place in upper castes' houses. In the naming ceremony scene, when Narasimha Naidu's family enters the house of Mahadeva Naidu, there is a cut to the inside of the house where Narasimha Naidu and his brothers want to sit. When they are about to sit, Basavaiah and his friend, who was sitting behind them, greets them. There is a cut to Narasimha Naidu's face which indicates that he is angry to see Basavaiah there (maybe because Dalits are there in that space or because he became president). Basaviah and his friend (Dalit) are sitting in the last row. In fact it is here that we come to know through a comedic character that Basaviah has become the president when he says there is a glow in Basaviah's face. Then the camera employs a wide shot in which the protagonist and his relatives are framed. In this frame, Basaviah and his friend are barely visible as they were sitting in the last row. Except Basaviah and his friend, the whole Dalit community is standing outside; this clearly sends the message that Basaviah is allowed inside because he is a president. And despite the fact that he is president, in upper caste Mahadeva Naidu's house, who is their leader, his seating position is in the last row.

Dalits are incorporated into the mainstream through Brahmanisation, a process by which Brahmanical practices and ideas influence Dalits who assimilate them

as the basis for organising their religious life.²⁰ The narrative depicts Sahadevudu, a Dalit, as someone longing for Brahmanism, not as someone who rebels against Brahmanism, which legitimises his community's oppression in the name of caste. Sahadevudu is shown as desirous of learning the Vedas, and the protagonist makes it possible for him to learn them. In the temple entry scene when the Brahmin refuses to recite *shlokas*, it is Sahadevudu on whom the protagonist puts the sacred thread and makes him recite *shlokas*. According to film scholar Madhav Prasad, it is not the whole Dalit community but Sahadevudu (as an exceptional person because he learned the Vedas) alone who can be admitted into a slightly expanded idea of Hinduism by making him an extraordinary and exceptional figure.²¹

If we do a close reading of the temple entry scene, it provides us with the underlying but clear message that Dalits are not supposed to offer the so-called sacred clothes to Hindu gods. After Mahadeva Naidu puts the sacred thread on Sahadevudu and encourages him to recite *shlokas*, Dalits enter the temple along with Mahadeva Naidu, who stands in front of them as if he is leading them. As Mahadeva Naidu is in front, he first places the Pooja items in front of the Rama and Sita idols and immediately the screen fills with silence; there is no sound of *shlokas* from Sahadevudu. The camera cuts to outside the temple where the villains cut Sahadevudu's tongue off in response to Mahadeva Naidu's argument and judgement. In the whole scene, though Basavaiah enters the temple along with his community, he cannot offer sacred clothes because a Dalit offering clothes to Hindu gods violates the existing norms. And if a Dalit who is regarded as polluted strives to recite *shlokas*, the result must be the cutting off of the tongue and the punishment of muteness for the rest of his life.

Caste configured through gender

This section will examine how caste relations are mediated by gender. We need to observe how the question of caste is interlinked with the question of gender as it is difficult to understand caste without gender. The social relations of caste and gender are based on the exercise of power through the use of force.²² There is one scene in the movie where the narrative reaffirms authority in terms of both caste and gender. In the *panchayat* election scene, Basavaiah is beaten up by Narasimha Naidu's brothers for taking the nomination form for the post of *Panchayat* President; he is tied to a jeep and dragged around the square. Chandramma, Basavaiah's wife, pleads with Narasimha Naidu's brother to leave her husband alone but he rubs a burning cigarette on her shoulders, pushes her to the ground, uses abusive language, kicks her pregnant body, crushes her hand with his foot and asks his brother to drive the jeep over her. While the jeep is coming towards her, suddenly, the camera shifts its focus on the Dalit men's eyes, which look helpless, and on the Dalits who are nodding their heads with sadness (as if it is their fate). She is crying but there is no response from the Dalit men who are standing there. This entire scene draws the attention of the audience towards the increasing violence that imposes the maintenance of order in relations of caste and gender. Dalit women's bodies become a

site of exploitation and violence. As Vasanth and Kalpana Kannabiran argue, gender within caste society is defined and structured in such a manner that the 'manhood' of the caste is defined both by the degree of control men exercise over women and the degree of passivity of the women of the caste. By the same argument, demonstrating control by humiliating women of other castes is a certain way of reducing the 'manhood' of those castes.²³ This is why, while Chandramma is being kicked in public, the men of her caste are standing in silence and cannot stop the upper-caste men because the structure of relations in caste society castrates them through the expropriation of their women. They are denied the right to be men; in relation to the upper-caste protagonist and villains, Dalit men are emasculated. In a sense, Dalits cannot speak; they are waiting to be saved and have to be uplifted by the hypermasculine hero.²⁴

The provocation for the upper-caste men who humiliate Chandramma is twofold: first, while her husband Basaviah is dragged along by the jeep, she asks Narasimha Naidu's brother to leave her husband alone by saying that 'we (Dalits) are brainless as we could not realise that your parents have given birth to the (president) chair along with you'; secondly, by obeying the protagonist Mahadeva Naidu's words to bring another application for nomination. In doing so, Chandramma clearly transgresses the limits of her caste status, which is defined by passivity and submissiveness. Exercising control over the Dalit female body signifies the affirmation of upper-caste men's power. Apart from the violence perpetrated on Chandramma, this entire scene must be seen as an assertion of power over all Dalit men and women. When the protagonist comes, he starts to tell Narasimha Naidu's brother (and the audience) about the importance of 'pregnancy' but not about the importance of 'women'. Generally, in other films, when women are hurt, mistreated or beaten by the husband, the hero speaks about the importance of woman but here the protagonist speaks about pregnancy as if a Dalit woman is not worthy of being considered as a human being. Usually, the hero would say: 'do you know whom you slapped, kicked etc.'; but here, in the case of a Dalit woman, it is not *whom* he kicked but *where*. The focus shifts from the person to the state of pregnancy.

Violence to Dalit women becomes the central conflict in the narrative. The notion that Dalit women can be discriminated against even more than Dalit men has been shown in the scene by positioning her in the narrative to be kicked twice in that scene, and in a later scene, she is stabbed. It portrays the Dalit woman's body as something that can be easily used, abused, tortured and finally disposed of.

Conclusion

Being from the Bahujan community, the filmmaker had to face many obstacles to create a movie on Dalit empowerment. Eventually, when he translated his social concept onto the screen, he could not go beyond the Gandhian reformist framework, which is encoded in the space of mainstream cinema. Neither the domination of upper castes in the industry nor the fact that a particular film is made by a person from a particular caste can directly give us a clue as to the ideology of

the film. The ideology of the film is determined not only by the caste identities of the industry or the filmmaker but also by established ideologies in society and established formats in film. *Jayam Manadera* does nothing to change the discourse of caste; rather, as Jenny Rowena argues, it puts forth a 'pseudo-radical message on the question of caste and reproducing the caste/gender hegemonies'²⁵ by re-allotting the positions to the people within this existing discourse. The protagonist does not question the authority of the Vedas or scriptural sanction of the practice and authority of caste. The film certainly critiques all those who are supposedly not following the caste order properly but the system remains untouched. The enlightened upper-caste protagonist's position is to reinterpret the system in accordance with the somewhat different status of Dalits. Dalits are still voiceless subjects, without self-pride. No leader emerges among them in the film. Even if they do emerge, as with Basaviah and his group, they want to die for their upper-caste leader. The film tries to show the kinds of humiliation that Dalits are subjected to but at the same time the question of who perpetrates humiliation, who protests, who saves and how this whole scenario is staged become important issues. Telugu cinema has dealt mainly with the superficial populist stereotypes of Dalit lives and has hardly entered into the core debate of social realities.

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Notes

- 1 The Telugu Cinema industry, also known as Tollywood, is a part of Indian Cinema and produces films in the Telugu language. It is centred in Hyderabad, in the Indian states of Andhra Pradesh and Telangana. The industry holds the Guinness World Record for the largest film production facility in the world. As per the CBFC report of 2012, the industry is placed second in India, in terms of yearly film production. For an overview of Telugu Cinema see Yves Thoraval, *The Cinemas of India (1896–2000)*, 344–353.
- 2 The discussion generated around the movie in newspapers was that the hero depicts someone who believes that all human beings are equal and fights for social, economic and political justice. The director's announced in the press that Jyothi Rao Phule inspired the hero Mahadeva Naidu's character (Andhra Jyothi, September 3, 2000, p. 4, Vaartha, October 13, 2000, p. 14; Andhra Jyothi, October 13, 2000, p. 4), so many Dalit and Bahujan activists watched the movie and consequently became its advocates. Janga Gautham, a Dalit activist, poet, writer and journalist, criticised the movie: 'the statement that Phule is inspiration for the movie and for the character of Mahadeva Naidu is a trick of director to attract downtrodden people. There is no comparison between Phule and Mahadeva Naidu's character.' I thank Janga Gautham for giving me his unpublished interview of the movie. It was published in one of the Dalit magazines but we could not locate it.
- 3 Other movies on caste are *Pattalu Pattimpulu* (1968), *Kaalam Maarindi* (1972), *Balipeetam* (1975) *Saptapadi* (1981), *Ananda Bhairavi* (1983), *Devalayam* (1985), *Swayam Krushi* (1987) and *Rudraveena* (1988).

- 4 S.V. Srinivas, 'Gandian Nationalism and Melodrama in the 30's Telugu Cinema', *Journal of the Moving Image*, 1 (Autumn 1999), 19
- 5 Shanker was born in the Nalgonda district (the Naxalite Movement was active in this district), Telangana. He belongs to the Darji or Meru caste (tailoring is the occupation of this caste), which is categorised as a backward caste in Telangana. His other films are *Encounter* (1997), *Sree Ramulayya* (1998), *Bhadrachalam* (2002) and *Jai Bholo Telagana* (2011).
- 6 I interviewed him in his office in Hyderabad on February 18, 2018. The interview was carried out in Telugu and I translated his words. I thank Dr. Laxman Aeloy for providing an opportunity to meet the director and I thank director Shanker for giving me his valuable time and sharing with me an unpublished document on this film.
- 7 Shanker said that after narration, the producer and hero accepted the story because they felt this movie had commercial elements, the potential for a mass movie, and gave mileage to the hero. Their father RamaNaidu accepted because by then he was in politics as a member of parliament and he thought that this film could be useful in its appeal to downtrodden people in Andhra region in coming elections. Hence, they had their own intentions to accept this movie.
- 8 S.V. Srinivas, 'Fans and Stars: Production, Reception and Circulation of the Moving Image', Ph.D. diss., University of Hyderabad, 1997, 133.
- 9 For more information on the Karamchedu and Chundur massacres, see the introduction of K. Satyanarayana and Susie Tharu, eds. *From Those Stubs, Steel Nibs are Sprouting: New Dalit Writing from South India Dossier 2* (Noida: Harper Collins Publishers India, 2013).
- 10 See Ravi Srinivas and Sundal Kaali, 'On Caste and Comedians: The Language of Power in Recent Tamil Cinema', in *The Secret Politics of Our Desires: Innocence, Culpability and Indian Popular Cinema*, ed. Ashis Nandy (New Delhi: OUP, 1998), 208–227; Dickens Leonard, 'Spectacle Spaces: Production of Caste in Recent Tamil Films', *South Asian Popular Culture*, 13, no. 2 (2015), 155–173.
- 11 See Sujith Kumar Parayil and Ujith Kumar Parayil, 'Visual Perception and Cultural Memory: Typecast and Typecast(e)ing in Malayalam Cinema', *Synoptique-An Online Journal of Film and Moving Images Studies*, 3, no. 1 (Spring 2014), 67.
- 12 See Vidushi, 'Cinematic Narrative: The Construction of Dalit Identity in Bollywood', in *Media, Margins and Popular Culture*, ed. Einar Thorson, Heather Savigny, Jenny Alexander and Daniel Jackson (New York: Palgrave Macmillan, 2015), 123–135; S.V. Srinivas, *Politics as Performance: A Social History of the Telugu Cinema* (New Delhi: Permanent Black, 2013).
- 13 This movie has been dubbed in Hindi as *Dum: Man of Power* (2000) www.youtube.com/watch?v=EQUgE4EV-YM
- 14 For various techniques that Indian cinema uses to reinstitute the preconceived cultural notions of Dalit castes, see Parayil, 'Visual Perception and Cultural Memory: Typecast and Typecast(e)ing in Malayalam Cinema', 67.
- 15 I use Steven Maras's article 'Notes on a Genre to Come: Screen Writing and the "Thesis-film"' to help conceptualise what the thesis film is, even though Steven Maras explores the thesis film in the context of screen writing.
- 16 S.V. Srinivas calls this kind of filmic technique 'movie mistake'. See *Politics as Performance: A Social History of the Telugu Cinema*, 117.
- 17 All translations are mine.
- 18 Jenson Joseph, 'Revisiting Neelakkuyil: On the Left's cul', *TAPASAM* (April–September 2012), 48–49.
- 19 Swathy Margaret, 'Cultural Gandhism: Casting out the Dalit Woman', *EPW*, XLVIII, no. 18 (May 2013), 87.
- 20 Brahmanisation is the process by which the lower castes seem to adopt the customs and way of life of Brahmins. For a discussion of the notion of Brahmanisation, see M. N. Srinivas's article 'A Note on Sanskritization and Westernization', *The Far Eastern Quarterly*, 15, no. 4 (1956), 481–496.
- 21 My personal conversation with Prof. Madhav Prasad. Similar exceptional Dalit figures can be seen in the films *Malapilla* (the character of Kanchanamala) and *Saptapadi* (the character of Haribabu).

- 22 Rape, harassment, exploitation and abusive language are common atrocities perpetrated on Dalit women in a majority of films. But Dalit women have been given very little space on screen compared to Dalit men.
- 23 Kalpana and Vasanth Kannabiran, 'Caste and Gender: Understanding Dynamics of Power and Violence', in *Life as a Dalit: Views from the Bottom on Caste in India*, ed. Subhadra Mitra Channa and P. Joan (Delhi: Sage Publication, 2013), 288.
- 24 Devon W. Carbado uses the terms emasculation and hyper masculinity to describe the nature of Black male suffering in relation to White men in his article, 'The Construction of O. J. Simpson as a Racial Victim', in *Black Men on Race, Gender and Sexuality: A Critical Reader*, ed. Devon W. Carbado (New York: New York University Press, 1999), 170.
- 25 Jenny Rowena, 'Reading Laughter: The Popular Malayalam "Comedy-Films" of the Late 80s and Early 90s', Ph.D. diss., CIEFL University, 2002, 36.

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Filmography

Telugu

Jayam Manadera: The Voice of Victory (Victory is Ours: The Voice of Victory, dir: N. Shanker 2000).



Rietveld refinement and FTIR spectroscopic studies of Ni^{2+} -substituted Zn-ferrite nanoparticles

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Abstract

Mixed spinel ferrites with stoichiometric equation $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) were synthesized by co-precipitation technique and consequently heat treated at 800 °C for 2 h. EDX spectra concluded the stoichiometry of elemental composition of present ferrite systems. Rietveld refinement of XRD patterns confirms the cubic spinel structure of the ferrite phase belonging to $Fd\bar{3}m$ space group. Lattice parameter (8.398–8.387 Å) is found to be in non-monotonic variation, whereas crystallite size (17.2–17.5 nm) is increased. From FE-SEM studies, the bigger ferrite nanoparticles (range of 27.9–39.4 nm) are found in the sample of composition $x=0.6$. The variation of theoretical tetrahedral and octahedral bond lengths (R'_A and R'_B) is quite opposite to the variation of bond lengths (R_A and R_B) calculated from the Rietveld refinement. The vibrational frequencies in FTIR spectra (ranging from 592 to 385 cm^{-1}) cope with the formation of spinel phase supporting the XRD results. The elastic moduli of present ferrite systems appears to be increasing, but these values are high for the composition $x=0.6$. The isotropic nature of present ferrite systems has been revealed from the same value of Poisson ratio obtained for all compositions.

1 Introduction

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Spinel ferrites are the active magnetic materials in the wide spectrum of applications like transformer cores, high-density magnetic recording, high-frequency absorbers, sensors, photo-catalysts, etc. [1–4]. The physical properties of mixed ferrites like Mn–Zn, Mg–Zn, Ni–Cu, and Mn–Ni have been studied specified for a particular application. Among these ferrites, Ni–Zn ferrite is distinctive due to its important properties such as high resistivity, high saturation magnetization, low eddy current losses, mechanical hardness, etc. [5]. The reconsideration of Ni–Zn ferrite possessing nano-dimension crystallites surely preludes a new approach for biomedical applications like targeted drug delivery, cancer treatment with hyperthermia, etc. [6]. Spinel ferrite has a crystal structure MFe_2O_4 belonging to $Fd\bar{3}m$ space group. M in the spinel structure formula unit represents divalent metal ion like Ni^{2+} , Mn^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , etc. In the spinel structure, O^{2-} anions are crammed into fcc lattice with two co-ordinated interstitial sites, namely tetrahedral (A) site and octahedral (B) site. The occupancy of metal ion (M) in these sites will characterize the spinel structure of the ferrite, in such a way the complete occupancy of the M into the A site

depicts normal spinel and the complete occupancy into the *B* site depicts an inverse spinel structure [7].

It is well established that Ni ferrite is inverse spinel with formula unit $(\text{Fe}^{3+})_{\text{tetra}}[\text{Ni}^{2+}\text{Fe}^{3+}]_{\text{octa}}\text{O}_4$ and Zn ferrite is normal spinel with formula unit $(\text{Zn}^{2+})_{\text{tetra}}[\text{Fe}^{3+}]_{\text{octa}}\text{O}_4$. The combination of these two ferrites will give rise to a mixed spinel with formula unit $(\text{Zn}_{1-x}\text{Fe}_x^{3+})_{\text{tetra}}[\text{Ni}_x^{2+}\text{Fe}_{2-x}^{3+}]_{\text{octa}}\text{O}_4$ [7]. In contrast to this formula unit, cation redistribution may be possible in the spinel structure that influences the structural, magnetic, electrical properties, etc. [8, 9]. Many researchers studied the structural and microstructural properties of different ferrites and mostly reported that these properties are structure sensitive. Recently, we reported structural, microstructural, and elastic properties of $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) nanoferrites prepared by sol-gel autocombustion and co-precipitation techniques [10, 11]. We found that the methods of syntheses and nature of precursors (metal ions) are influencing these properties. Moreover, the secondary phases found in these ferrite systems are affecting their elastic properties. However, a comprehensive study is still to be required for insight understanding of structural and elastic properties even in terms of metal ion sizes and microstructural parameters. In the present study, a series of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6$ and 0.7) ferrite nanoparticles have been produced by co-precipitation technique and heat treatment was carried out at $800\text{ }^\circ\text{C}$ for 2 h. The samples are characterized for structural and microstructural properties. Rietveld refinement has been performed to evaluate the complete structural features of present ferrite systems. In this paper, we reported the results obtained from the analysis of structural, elastic, and microstructural studies.

2 Experimental methods

2.1 Synthesis

Analytical grade nickel chloride ($\text{NiCl}_2\cdot 6\text{H}_2\text{O}$), zinc chloride (ZnCl_2), and ferric chloride ($\text{FeCl}_3\cdot 6\text{H}_2\text{O}$) are considered as initial precursors to prepare $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) ferrite nanoparticles in the present study. The complete description of method of synthesis can be found in our previous publication [12].

2.2 Measurements and characterization

X-ray diffraction patterns were recorded using Phillip's X'pert-PRO X-ray powder diffractometer with a target of CuK_α ($\lambda=1.5406\text{ \AA}$) radiation.

Carl Zeiss Ultra 55 model field-emission scanning electron microscope has been employed to study morphology of the samples and the respective compositional analysis through EDX spectra.

Shimadzu FTIR spectrometer was employed to record IR spectra for the ferrite samples in the range of $250\text{--}4000\text{ cm}^{-1}$.

2.3 Rietveld refinement

The structural analysis for the calculations of lattice parameter, bond lengths, atomic co-ordinates, and site occupancy for the present series of samples has been done by Rietveld refinement on X-ray diffractograms. For the sake of methodology, a brief discussion on Rietveld refinement was presented. First and foremost global parameters such as 2θ -zero and background were refined and after Rietveld refinement of the XRD patterns were performed with the FULLPROF program in the WINPLOTR suite of programs. The quality of fit of the experimental data was checked convoluting the reliability factors $R_{\text{w},\text{p}}$, R_{exp} , and goodness-of-fit χ^2 using the following distribution formulae [13, 14]:

$$R_{\text{w},\text{p}} = 100 \left[\frac{\sum_{i=1,n} w_i |y_i - y_{\text{c},i}|^2}{\sum_{i=1,n} w_i y_i^2} \right]^{1/2}, \quad (1)$$

where y_i and $y_{\text{c},i}$ are the observed and calculated profile intensities and w_i is a suitable weight.

$$R_{\text{exp}} = 100 \left[\frac{N - P}{\sum_i w_i y_i^2} \right]^{1/2}, \quad (2)$$

where $N - P$ is the number of degrees of freedom:

$$\chi^2 = \frac{R_{\text{w},\text{p}}}{R_{\text{exp}}}. \quad (3)$$

Refinements were carried out till convergence is reached for the value of the goodness-of-fit close to 2.

3 Results and discussion

3.1 EDX studies

Energy-dispersive X-ray (EDX) spectra have been recorded to evaluate the elemental composition of present ferrite systems. The EDX spectra of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) nanoferrite systems are portrayed in Fig. 1. The results of analysis corresponding to the calculated atomic weight ratio of Ni:Zn and (Ni, Zn):Fe for the compositions $x=0.5, 0.6, 0.7$ are found to be 0.98, 1.48, 2.29 and 0.49, 0.48, 0.49. These observed composition ratios are consistent with the expected stoichiometry considered under preparation.

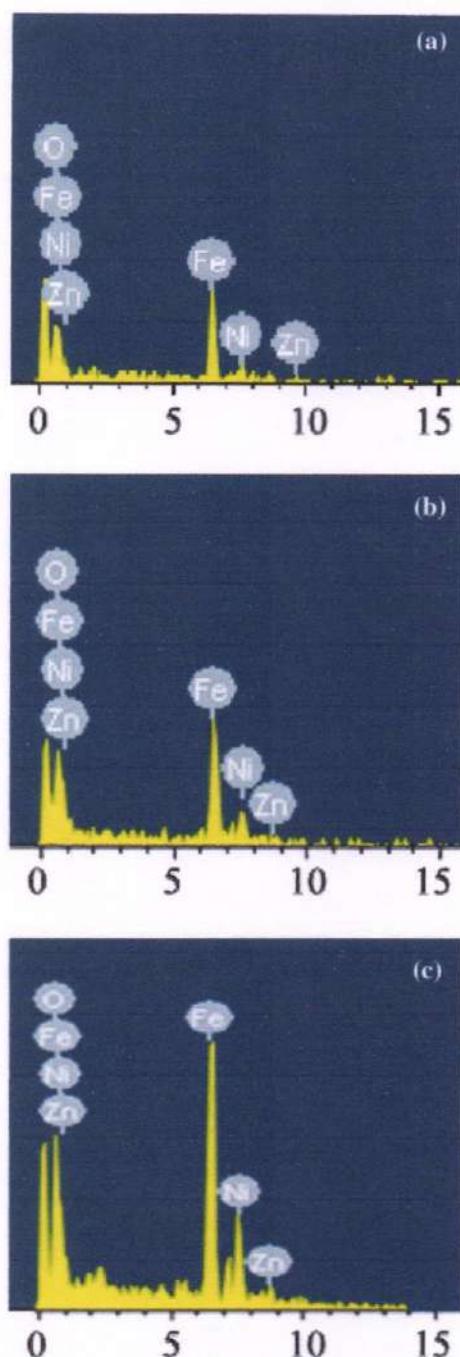


Fig. 1 EDX spectra for **a** $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, **b** $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$, and **c** $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$

3.2 XRD studies

The structural features of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) nanoferrite systems have been investigated through X-ray diffraction. The XRD diffractograms which are refined using Rietveld refinement are given in Fig. 2. The Rietveld refinement revealed the space group of ferrite systems belonging to $Fd\bar{3}m$, and the traces corresponding to the

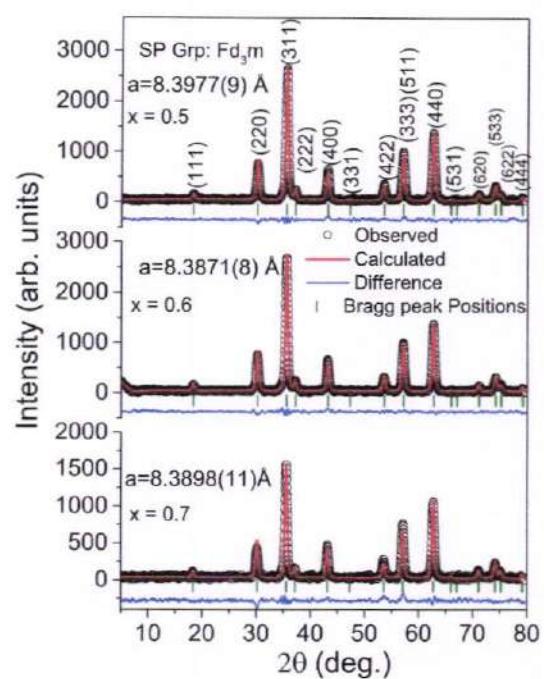


Fig. 2 Rietveld refinement of XRD patterns for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) nanoferrites

secondary phases and unreacted metal oxides are not identified in the diffractograms. The diffraction peaks indexed with (220), (311), (400), (422), (511), (440), (620), and (533) ensure the cubic spinel structure and are consistent with the diffraction peaks of Ni ferrite (JCPDS card no. 86-2276) and Zn ferrite (JCPDS card no. 82-1049). The broadening of the peaks under the observation is an evidence for the presence of ferrite particles having nanoscale dimensions. The reliability of refinement is marked by considering the various R -factors like weighted profile factor ($R_{w.p.}$), expected factor (R_{exp}), and goodness-of-fit (χ^2). The results obtained in the Rietveld refinement performed on the diffractograms of present ferrite systems are listed in Table 1. In general, the weighted profile factor ($R_{w.p.}$) and expected factor (R_{exp}) are known to be structure sensitive [15, 16]. The observed variations of these parameters in the present Rietveld analysis looks to be synonymous for the noticed structural changes in the present ferrite systems, whereas the values of goodness (χ^2) of fit describe the liability of refinement used in the analysis. Comparable Rietveld analyses for Ni-Zn ferrites [17] and

Table 1 Rietveld agreement factors like weighted profile factor ($R_{w.p.}$), expected factor (R_{exp}), and goodness-of-fit (χ^2) for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) nanoferrites

Comp (x)	$R_{w.p.}$	R_{exp}	χ^2
0.5	16.1	7.9	2.03
0.6	15.4	7.8	1.95
0.7	20.4	9.3	2.19

for other ferrites have been reported in the literature [2, 18]. The crystallite size (using Debye–Scherrer formula), theoretical lattice parameter, and X-ray density have been estimated using the following relations [19]:

$$D = \frac{k\lambda}{\beta \cos \theta}, \quad (4)$$

where D , λ , β , θ , and k ($=0.89$) are the crystallite size, wavelength of X-ray beam, full width at half maximum (FWHM), Bragg scattering angle, and shape factor:

$$a_{th} = \frac{8}{3\sqrt{3}} [R_A + \sqrt{3}R_B], \quad (5)$$

where R_A and R_B are tetrahedral and octahedral bond lengths. However, $R_A = r_A + r(O)$ and $R_B = r_B + r(O)$; here, r_A and r_B are the ionic radii of tetrahedral and octahedral sites, and $r(O)$ is radius of oxygen ion (1.32 \AA).

$$\rho_x = \frac{8M}{N_A a^3}, \quad (6)$$

where M , N_A , and a are sample's molecular weight, Avogadro's number, and experimental lattice constant, respectively.

The tetrahedral and octahedral bond lengths estimated from Rietveld refinement are denoted as R_A and R_B . The theoretical tetrahedral and octahedral bond lengths are denoted as R'_A and R'_B . These values are estimated basing on the assumptions that $\text{Zn}^{2+}/\text{Ni}^{2+}$ ions are predominantly

occupying tetrahedral (A)/octahedral (B) sites in the formula unit $(\text{Zn}_{1-x}\text{Fe}_x)[\text{Ni}_x\text{Fe}_{2-x}]\text{O}_4$. For comprehensive understanding, the atomic positions of Ni^{2+} and Zn^{2+} in tetrahedral (A) and octahedral (B) sites for the composition $x=0.5$ are shown in Fig. 3. The values of crystallite sizes (D), experimental lattice parameters (a), and tetrahedral and octahedral bond lengths (R_A and R_B , R'_A and R'_B) are summarized in Table 2. The theoretical lattice parameters calculated using (R_A, R_B) and (R'_A, R'_B) are also listed in Table 2 as a_{th} and a'_{th} . It has been observed that the values of a_{th} and a are consistent with each other, but the difference between a'_{th} and a is about 4.4%. This discrepancy suggests that the metal ions are redistributed between the tetrahedral (A) and octahedral (B) sites against to their normal preferences. The change in tetrahedral and octahedral bond lengths in regard to the concentration of Ni^{2+} is shown in Fig. 4. Moreover, as Ni^{2+} (0.69 \AA) is substituted in Zn ferrite, transfer the Fe^{3+} (0.64 \AA) ions from octahedral (B) site to the tetrahedral (A) site, and hence, we can expect a decrease in tetrahedral bond length (R'_A) and an increase in octahedral bond length (R'_B) as reported in Table 2. However, we observed an opposite phenomenon in case of R_A and R_B estimated from Rietveld refinement, including $R_A < R'_A$ and $R_B > R'_B$ (see Fig. 4) which can suggest that Zn^{2+} and Ni^{2+} are randomly distributed between tetrahedral (A) and octahedral (B) sites in the spinel structure against to their preferential occupancy. The cation distributions in the present series of samples have been done from the intensity ratio of diffraction peaks and using

Fig. 3 Atomic positions of Ni^{2+} and Zn^{2+} in the tetrahedral and octahedral sites for $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoferrite

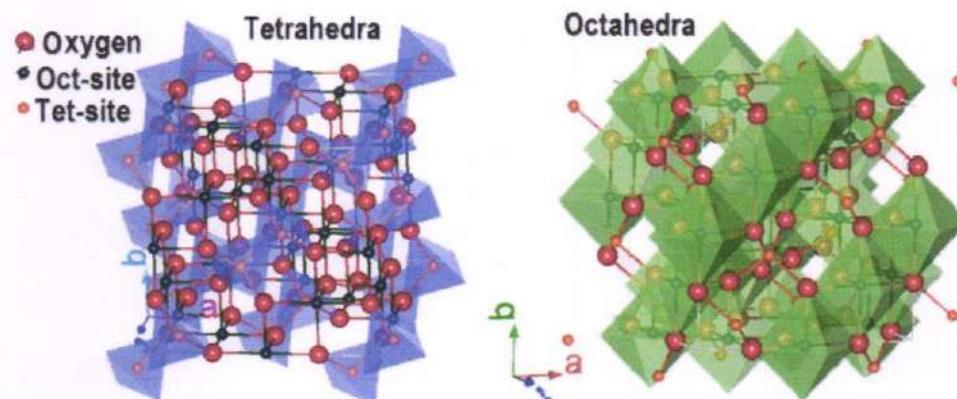


Table 2 Lattice parameter (a), crystallite size from XRD (D), nanoparticle sizes from FE-SEM (D), tetrahedral and octahedral bond lengths (R_A , R_B and R'_A , R'_B), theoretical lattice parameters (a_{th} and a'_{th}), and X-ray density (ρ_x)

Comp (x)	a (\AA)	D (XRD) (nm)	D (FE-SEM) (nm)	R_A (\AA)	R_B (\AA)	R'_A (\AA)	R'_B (\AA)	a_{th} (\AA)	a'_{th} (\AA)	ρ_x (g/cm^3)
0.5	8.398	17.2	21.9-39.4	1.863	2.074	2.01	1.973	8.399	8.356	5.332
0.6	8.387	17.4	27.9-39.4	1.864	2.069	2.00	1.975	8.387	8.346	5.337
0.7	8.389	17.5	27.2-36.9	1.901	2.050	1.99	1.978	8.393	8.339	5.318

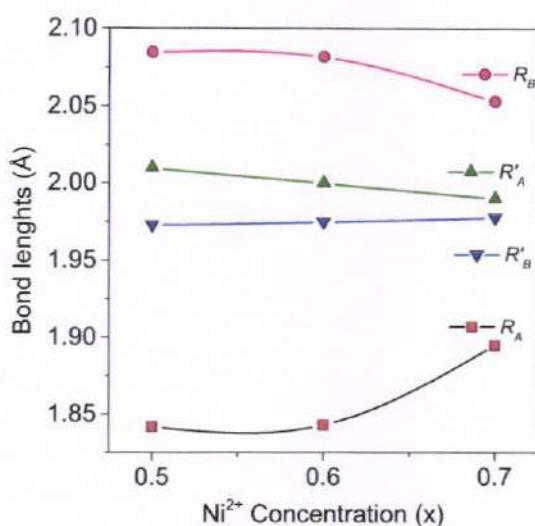


Fig. 4 Plot of variation of bond lengths against concentration of Ni^{2+}

Full Prof program. Initially, the diffractograms are fitted considering the marked occupancy of Zn^{2+} into tetrahedral (A) sites and Ni^{2+} into octahedral (B) sites. However, the observed intensities from the profile fit could not match with the experimental intensities. This enables the possible random occupancy Ni^{2+} and Zn^{2+} into the tetrahedral (A) and octahedral (B) sites. The profiles are refitted, and the results of refinement along with cation distributions estimated from Rietveld refinement are given in Table 3 to support the above argument of cation redistribution. The experimental lattice parameter in the present study appears to be decreased with the increase in Ni^{2+} substitution. This can be explained based on the difference of ionic radii of metal ions. The substitution of smaller Ni^{2+} (0.69 Å) ions for bigger Zn^{2+} (0.74 Å) ions causes lattice shrinkage leading to decrease in the lattice parameter. Similar results have been reported in the literature [20]. However, the lattice parameter for the composition $x=0.6$ is the least and the variation of lattice parameter is found to be in the order $a(x=0.5) > a(x=0.7) > a(x=0.6)$. In

our earlier publication [10] on Mn^{2+} -substituted Zn ferrite, we observed similar variation of lattice parameter and it was explained basing on grain sizes. We reported that the bigger grains may release the tension than the smaller grains causing lattice expansion, resulting to the increase in lattice parameter. In the present study, either the variation of crystallite size (D_{XRD}) or the particle size ($D_{\text{FE-SEM}}$) is not supporting the present trend of variation in the lattice parameter. Therefore, the present variation of lattice parameter can be speculated due to the differences in the cation redistribution of different compositions. It can be seen that the crystallite sizes are almost uniform, but slightly increases with the Ni^{2+} ion doping. Sharma et al. [21] also got uniform crystallite sizes, but the decrease with the increase in Ni^{2+} ion concentration for Zn^{2+} in Mg-Zn ferrite and reported that this is due to substitution of smaller N^{2+} ions. Guo et al. [22] in their studies reported that a decrease in crystallite sizes is due to internal stress produced by the substitution of Sm^{3+} in nickel ferrite nanofibers. In our earlier study [23], Cu^{2+} -doped Ni-Zn prepared under identical conditions, the reported values of average crystallite sizes around to 22 nm are bigger than the present crystallite sizes, and reported that Cu^{2+} enhances the crystal growth. However, its variation is random and is proposed that the substituted bigger Cu^{2+} (0.72 Å) ions may change the thermodynamic stability of Ni^{2+} (0.69 Å) in the spinel structure. We can conclude that the method of preparation adopted in the synthesis may affect structural parameters as well as crystallite sizes. The latent heat liberated during the synthesis [24, 25] may be varied at surface of the nanoparticles in such a way to form nearly uniform crystallites in the present series of samples.

3.3 FE-SEM studies

The FE-SEM micrographs of sintered ferrites of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) at 800 °C are shown in Fig. 5. The spreading range of ferrite nanoparticles in the

Table 3 Atomic co-ordinates ($x=y=z$), site occupancy (g), and cation distribution estimated from Rietveld refinement of XRD for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ nanoferrites

Ions	Wyckoff site	Comp ($x=0.5$)		Comp ($x=0.6$)		Comp ($x=0.7$)	
		$x=y=z$	g	$x=y=z$	g	$x=y=z$	g
$\text{Fe}^{3+}(1)$	8a	0.125	0.48	0.125	0.54	0.125	0.74
$\text{Ni}^{2+}(1)$	8a	0.125	0.26	0.125	0.28	0.125	0.07
$\text{Zn}^{2+}(1)$	8a	0.125	0.26	0.125	0.18	0.125	0.19
Fe^{3+} [2]	16d	0.500	1.52	0.500	1.46	0.500	1.26
Ni^{2+} [2]	16d	0.500	0.24	0.500	0.32	0.500	0.62
Zn^{2+} [2]	16d	0.500	0.24	0.500	0.22	0.500	0.12
Cation distribution		$(\text{Fe}_{0.48}\text{Zn}_{0.26}\text{Ni}_{0.26})$		$(\text{Fe}_{0.54}\text{Zn}_{0.18}\text{Ni}_{0.28})$		$(\text{Fe}_{0.74}\text{Zn}_{0.19}\text{Ni}_{0.07})$	
		$[\text{Fe}_{1.52}\text{Zn}_{0.24}\text{Ni}_{0.24}] \text{O}_4$		$[\text{Fe}_{1.46}\text{Zn}_{0.22}\text{Ni}_{0.32}] \text{O}_4$		$[\text{Fe}_{1.26}\text{Zn}_{0.12}\text{Ni}_{0.62}] \text{O}_4$	

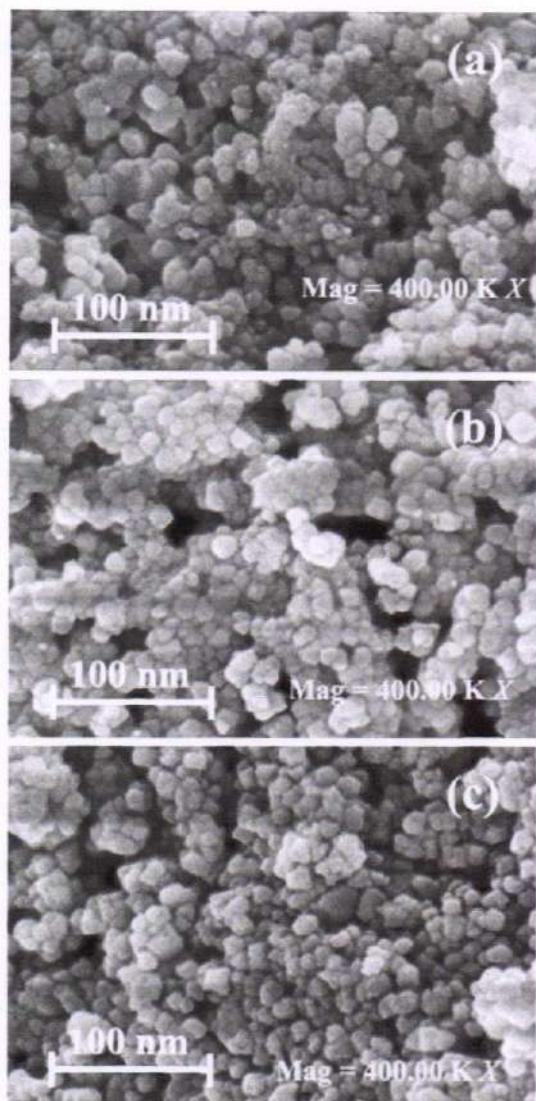


Fig. 5 FE-SEM micrographs for **a** $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, **b** $\text{Ni}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$, and **c** $\text{Ni}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$ with bar scale of 100 nm

present ferrite systems have been estimated using linear intercept method using the following relation [26]:

$$D_{\text{FE-SEM}} = \frac{1.5L}{MN}, \quad (7)$$

where L , M , and N are the total test length, magnification and total number of intercepts.

The corresponding ranges of size of ferrite nanoparticles of the present compositions are given in Table 2. The FE-SEM pictures exposed the spherical shape of nanoparticles possessing just about equal sizes. This may be due to the uniform distribution of surface energy adjacent to boundary regions of grains of different nanoparticles that required for promoting the growth of particles during the sintering process. Similar reports have been found in the literature [27],

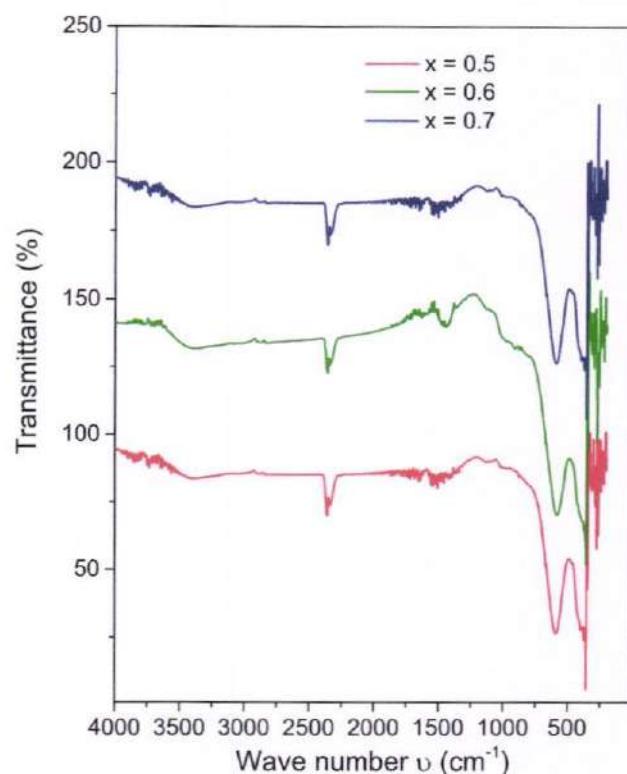


Fig. 6 FTIR spectra of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) nanoferrites

[28]. From Table 2, the ranges of particle sizes indicate the narrow distribution of ferrite nanoparticles in different sizes. Rahimi et al. [29] observed from the micrographs a range of 30–50 nm for particle sizes annealed at 500 °C. Akhter et al. [30] reported a range of 50–90 nm from FE-SEM for particle sizes annealed at 750 °C.

3.4 FTIR studies

Fourier transform infrared spectroscopy is a first-rate technique to probe the structural phase and supplementary elemental groups existed in the ferrite systems. The FTIR spectra of $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) are displayed in Fig. 6. The tetrahedral and octahedral force constants of ferrite systems are dependent on the atomic distances of $\text{Fe}^{3+}\text{O}^{2-}$ complexes and are estimated using the following relation:

$$K = 4\pi^2 C^2 \nu^2 m, \quad (8)$$

where C , ν , and m are light velocity (3×10^{10} cm/s), vibrational frequency of A or B sites, and reduced mass of Fe and O ions (2.601×10^{-23} g), respectively.

The characteristic bands ν_1 , ν_2 , ν_3 , and ν_4 of ferrite systems and force constants K_t , K_o are presented in Table 4. The first three bands are due to metal ion–oxygen complexes at tetrahedral and octahedral sites, whereas the fourth band is due to the

Table 4 Vibrational bonds (ν_1 , ν_2 , ν_3 and ν_4), and tetrahedral and octahedral force constants (K_t and K_o) for $\text{Ni}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0.5, 0.6, 0.7$) nanoferrites

Comp (x)	ν_1 (cm $^{-1}$)	ν_2 (cm $^{-1}$)	ν_3 (cm $^{-1}$)	ν_4 (cm $^{-1}$)	K_t (dyne/cm) $\times 10^5$	K_o (dyne/cm) $\times 10^5$
0.5	583	385	300	272	3.1379	1.3684
0.6	592	390	300	270	3.2355	1.4042
0.7	586	390	300	264	3.1703	1.4042

lattice vibrations [31]. The absorption band due to metal–ion complexes at tetrahedral (A) site is assigned to higher vibrational frequency (ν_1) in the range of 600–500 cm $^{-1}$, and at octahedral (B) site, it is assigned to lower vibrational frequency (ν_2) in the range of 450–350 cm $^{-1}$ [32]. The tetrahedral (A) and octahedral (B) absorption bands given in Table 4 reflect the characteristic bands of cubic spinel structure. It has been observed that the tetrahedral vibrational frequency randomly varies with substitution of Ni^{2+} , indicating random variation in Fe^{3+} – O^{2-} bond length and this is in good agreement with the variation in lattice constant supporting the cation redistribution between tetrahedral (A) and octahedral (B) sites. It is well established that Ni ferrite is inverse spinel in which Ni^{2+} ions occupy octahedral (B) sites and Fe^{3+} ions equally distributed between tetrahedral (A) and octahedral (B) sites, whereas Zn ferrite is normal spinel in which Zn^{2+} ions occupy tetrahedral (A) sites and Fe^{3+} ions completely occupy octahedral (B) sites [7]. The formula unit $(\text{Zn}_{1-x}^{2+}\text{Fe}_x^{3+})[\text{Ni}_x^{2+}\text{Fe}_{2-x}^{3+}]\text{O}_4$ for mixed ferrite system in the present study supports the cation redistribution against their normal preferences and it is attributed to the change in crystal field during the synthesis/ or to the finite size effects arising due to increase in surface to volume ratio at nanoscale. Similarly, the change in (ν_2) reflects the change in Fe^{3+} – O^{2-} bond length at octahedral site. Sridhar et al. [33] observed an increase in tetrahedral vibrational frequency (ν_1) and a decrease in octahedral vibrational frequency (ν_2) in copper-substituted nickel ferrite, and reported that this is due to difference in Fe^{3+} – O^{2-} distances at tetrahedral and octahedral sites. The vibrational bands below 400 cm $^{-1}$ are not clearly visible, probably because of reduced transparency of KBr pellet in this region. However, positions of the IR bands could be located by the shape of the absorption bands in this region. The vibrational band ν_3 in the range 300 cm $^{-1}$ is assigned to octahedral M^{2+} – O^{2-} vibration (where $\text{M}^{2+}=\text{Zn}^{2+}$, Ni^{2+} , and Fe^{2+}). As per the available literature reports [34, 35], the existence of long shoulders to the vibrational bands or possible splitting of ν_2 (octahedral site vibrational frequency band) is stood as an evidence for the existence of John–Teller Fe^{2+} ions. From Fig. 6, either long shoulders or splitting in ν_2 is not observed, and therefore, the probability for the presence Fe^{2+} ions cannot be expected. In the present study, the possibility of ν_3 vibrational band may be due to Ni^{2+} – O^{2-} ion complexes but not due to Fe^{2+} – O^{2-} . The lattice vibration band ν_4 occurring in the frequency range 264–272 cm $^{-1}$ is subjected to the dependent of mass of the

tetrahedral cation. The less intensive vibrational band near 3500 cm $^{-1}$ and intensive vibrational band near 2500 cm $^{-1}$ are assigned to free and absorbed water molecules retained in the samples during the synthesis.

3.5 Elastic properties

Elastic properties of crystalline materials are mainly governed by the potential energy of crystal lattice which is created due to restoring forces of ion network. The interatomic distances/spacing between the different ion complexes influences the potential energy of a particular material system. IR spectroscopy is useful to find the interatomic distances (bond lengths) through the vibrational frequencies obtained in the recorded FTIR spectrum. Stiffness constants and compressibility constants in different crystalline plans are the beneficial parameters to assess the elastic properties of crystalline materials. According to Waldron [32], for the material systems with cubic symmetry possessing isotropic nature (e.g., spinel ferrites), the stiffness constant C_{11} is equal to C_{12} . The stiffness constants (C_{11} and C_{12}) have been calculated by the given relation:

$$\text{Stiffness constant } C_{11} = \frac{K}{a}, \quad (9)$$

where $K = \frac{K_t + K_o}{2}$ and a are the average value of force constant and experimental lattice parameter.

To understand the elastic behavior of present ferrite systems, different parameters like Young's modulus (Y), bulk modulus (B), rigidity modulus (R), and Poisson ratio (σ) have been estimated. The elastic constants of the ferrite samples under investigation have been valued using the following relations reported in the literature [36, 37]:

$$Y = \frac{9BR}{3B + R}, \quad (10)$$

$$B = \frac{1}{3}[C_{11} + 2C_{12}], \quad (11)$$

$$R = \rho_x v_s^2, \quad (12)$$

$$v_s = \left(\frac{C_{11}}{3\rho_x} \right)^{1/2}, \quad (13)$$

$$\sigma = \frac{Y}{2R} - 1, \quad (14)$$

where ρ_x and v_s are X-ray density and shear velocity of elastic waves, respectively.

The calculated values of Y , B , R , v_s , and σ are listed in Table 5. These are the useful parameters to understand the topographic elastic behavior in terms of interatomic interactions and binding forces among the different ion complexes in the spinel structure.

The variation of elastic moduli against to the concentration of Ni^{2+} ion is shown in Fig. 7. It can be observed that the elastic moduli appear to be increasing with the doping of Ni^{2+} , but the increment is not monotonic. This is attributed to the differences of changes in the interatomic distances of the metal ions' complexes present in the interstitial spaces of spinel structure. It has also been observed that the present values of elastic moduli are less than our reported values of elastic moduli for Mn-Zn ferrites prepared by sol-gel auto combustion and co-precipitation methods [10, 11]. It is well known from the literature reports [38, 39] that the lattice parameter depends on the sizes (radii) of metal ions that are substituted in the spinel structure. The incorporation of smaller ions (bigger ions) for bigger ions (smaller ions) in the spinel structure leads to contraction (expansion) of unit cell, leading to the shortening (lengthening) of the bond lengths. In general, we can expect that the values of lattice parameter of Ni^{2+} (0.69 Å)-substituted Zn ferrite is lower than that of Mn^{2+} (0.82 Å)-substituted Zn ferrite. From the Tables 2 and 5, we can see that the present values of lattice parameter (Ni-substituted Zn ferrite) are less than the values of Mn-Zn ferrites prepared by co-precipitation method and greater than the values of Mn-Zn ferrites prepared by sol-gel autocombustion method. Therefore, we can say the sizes of ions are not only the primitive factor for the changes in the structural parameters, but other factors like method of synthesis, porosity, secondary phases, crystallite sizes, etc. may also influence the structural parameters as well as elastic properties of ferrite systems. Since secondary phases are not detected, there might be some other reasonable parameters that are manipulating the elastic performance current ferrite samples. It has been observed that the crystallite sizes in the present ferrite systems are greater than that of our

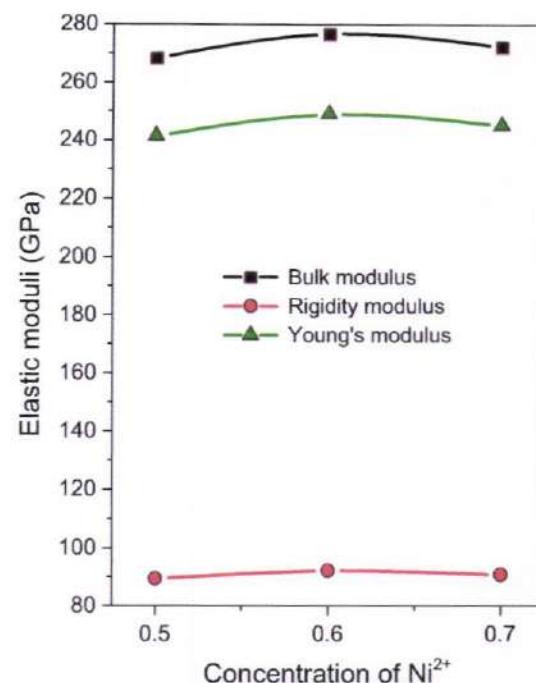


Fig. 7 Plot of elastic moduli (B , R , and Y) with the substitution of Ni^{2+}

reported values of Mn-Zn ferrite systems (see Tables 2, 5). As reported in our earlier studies [11], the bigger crystallites release the tension, resulting in lattice expansion. Therefore, interatomic interactions are weakened showing the low values of elastic parameters when compared to our reported values. The isotropic behavior of present ferrite systems can be visualized from the same of value Poisson's ratio. We can conclude that the methods of synthesis procedure, crystallite size, and cation distribution in the spinel structure are influencing the structural and elastic properties of present ferrite systems.

4 Conclusion

Pure cubic phases of Ni-Zn-mixed spinel ferrites without secondary phases were successfully prepared by co-precipitation technique. Considerable cation redistribution against

Table 5 Shear velocity (v_s) of elastic waves, different elastic moduli (B , R , Y , and σ), and earlier reported values of lattice parameter (a) and crystallite size (D) of Mn-Zn ferrite systems

Comp. (x)	v_s (cm/s) $\times 10^5$	B (GPa)	R (GPa)	Y (GPa)	σ	a (Å) Ref. [10]	D (nm) Ref. [10]	a (Å) Ref. [11]	D (nm) Ref. [11]
0.5	4.0956	268.29	89.43	241.46	0.35	8.355	5.4	8.412	7.2
0.6	4.1562	276.60	92.19	248.94	0.35	8.373	4.5	8.435	7.6
0.7	4.1309	272.26	90.75	245.04	0.35	8.356	5.5	8.438	6.4

to their usual location in the spinel structure was observed from Rietveld refinement of XRD patterns. This cation redistribution highly influences the structural parameters in the present study. The latent heat liberated during the synthesis procedure and grain boundary energy is the reasonable factors for uniform size of ferrite nanoparticles. The nonexistence of Fe^{2+} ions suggested us that the vibrational band ν_3 in the present study is due to $\text{Ni}^{2+}-\text{O}^{2-}$ ion complexes. The cation redistribution and crystallite sizes are the reasonable aspects that are manipulating the elastic behavior of present ferrite systems.

Compliance with ethical standards

Conflict of interest The article is original and has been written by the stated authors, who are all aware of its content and have approved its submission. The article which I have submitted to the journal has not been previously published, not currently submitted for review to any other journals, and will not be submitted elsewhere before a decision is made by this journal and there is no conflict of interests.

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Article

In Search of a Touchable Body: Christian Mission and Dalit Conversions

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Abstract: This paper significantly wishes to unpack the social and cultural impact of the mass religious conversion movements in Rayalaseema society with specific reference to Dalits during the period 1850 to 1880. This paper will use the archival material such as missionary records, magazines, pamphlets, and books written by missionaries; further, it will also utilize oral interviews collected from the field. The mass conversion movements established a relationship between Dalits and missionaries and brought them together. In their efforts to create a new Christian community of Dalit converts, missionaries had interacted with Dalits, shared meal with them, stayed with them and transformed forbidden and “polluted” ghettos into social spaces. The present paper argues that the practices of the missionaries were liberating and humanizing for Dalits. It will examine how these practices led to unintended consequences. It needs to be remembered that the missionaries’ aim was not to abolish caste but to develop Christianity. How did the missionaries contribute to social interaction and build a spirit of solidarity among the Dalit converts? Based on specific situations, incidents, and examples recorded in the missionary archives and oral interviews, the article observes that community conversion movements destabilized the caste structure and brought significant changes in the social life of Dalits in colonial Rayalaseema.

Keywords: caste; Christianity; Dalits; mass conversion movements; Caste; missionaries; social equality; untouchability

1. Introduction

In Rayalaseema, the opportunity of converting into Christianity became available to the Dalits from the second half of the nineteenth century. Rayalaseema is presently one of the regions of the state of Andhra Pradesh in India. The region was called Ceded Districts during the colonial period.¹ The mission organizations which worked in Rayalaseema were the London Missionary Society (hereafter LMS) and the Society for Propagation of the Gospel (hereafter SPG). Missionary operations were first started in Cuddapah in 1822 by John Hands, who was a resident missionary of Bellary. Later, William Howell was appointed to Cuddapah as a resident missionary and Cuddapah was made a separate LMS station in 1824. Howell worked in the town and toured extensively in the district, making use of Telugu language in his preaching (Brackenbury 1914, p. 56; Bolton 1913, p. 31). The

¹ The state of Andhra Pradesh formed in 1956 comprises of three geographical regions known as the Coastal Andhra, Rayalaseema and Telangana. The first two regions were formerly a part of the Madras Presidency until 1st October 1953 when they were detached from it to form separate Andhra state. During the whole period of British Raj, the Rayalaseema region (comprised of the districts of Anantapur, Bellary, Cuddapah and parts of Kurnool) was called Ceded districts as it was ceded to the British East India Company by the Nizam in 1800. After independence, it was renamed as Rayalaseema which presently includes the districts of Anantapur, Chittoor, Kadapa, and Kurnool. In 2014, the Telangana region was declared as a separate state. At present Andhra and Rayalaseema regions remain part of the state of Andhra Pradesh.

SPG Mission was started in Cuddapah in 1842 with a few families who separated from the LMS when their missionary William Howell joined the Church of England. He was accepted as a missionary by the SPG (Hibbertware 1912, p. 51; Pascoe 1901, p. 563). At the initial stage of both these missions, individual conversions happened. The first converts in Cuddapah town were mostly from the Brahmin or dominant castes such as Reddy communities (Lewis 1879, p. 2; Simmons 1923, p. 8).² However, the year 1851 marked the beginning of the increase in the number of converts in the LMS and the SPG missions; these converts were from the Mala community, who approached the missionary first as individuals and later as a group of community.³

The Malas along with Madigas were the lowest in the caste hierarchy. *Manusmriti* (Laws of Manu), an ancient Hindu book is seen as a source for caste inequalities in India. The caste system assigns individuals a certain hierarchical status. In Hindu religious texts the caste system is considered as a system of four *varnas*. Based on their occupations, the Hindu society is divided into Brahmins (priests), Kshatriyas (warriors), Vaishyas (traders) and Shudras (servants). Outside of these four *varnas* are the untouchables or *avarnas*. It is believed that these rigid caste groups originated from the Hindu god Brahma. Brahmins were said to be created from the mouth of Brahma, Kshatriyas came from his arms, Vaishyas were from his thighs and Sudras from his feet (Viswanath 2015, p. 259). The castes at the top of the hierarchy were considered to be pure while those at the bottom were regarded as polluted. *Manusmriti* justifies the caste system as the basis for the order of the society. Furthermore, the book inscribed the violence to be meted out towards lower castes, as can be seen in the following verses:

A low-caste man, who tries to place himself on the same seat with a man of a high caste, shall be branded on his hip and be banished

(*Manusmriti* VIII. 281)

If he mentions the names and castes (gati) of the (twice-born) with contumely, an iron nail, ten fingers long, shall be thrust red-hot into his mouth.

(*Manusmriti* VIII. 270)⁴

The structural cruelty of the *Manusmriti* did not let Malas and Madigas live a life of dignity.⁵ For centuries, they had been despised and degraded; they were in a miserable condition because they were subjected to *antaranitanam* (untouchability), and *chudaranitanam* (unseenability). Their presence and approach were hated by other castes as they were considered impure; even their shadow was believed to be a pollutant. The caste system did not recognize their social value and moreover did not treat them as human beings. The Madigas and the Malas were not allowed to access public places such as temples, schools, and drinking water wells (Cornish 1874, p. 118).⁶

From my readings of the LMS and the SPG reports, it is evident that there were several events of community-based conversion movements from 1851 to 1860 (Missionary Conference 1858, pp. 118–19; Pascoe 1901, pp. 564–65). A visible public Christian community emerged after three decades of missionary work and mass conversions in the 1850s. Dalits became part of the mission through mass conversion movements, and became Christians. The following section will examine the humanitarian and charitable activities of missionaries such as their social interaction with the Dalits, as well as their

² Reddys were the dominant peasant caste in the Rayalaseema region. They comprised half of the population of the region. They were the people who owned lands, monopolized resources, and had control over the villages. Magistrates of the villages were generally drawn from this caste.

³ In missionary texts and colonial administrative records of the Ceded Districts, Dalits were called as pariahs, low castes, non-castes, outcastes, untouchables, panchamas, depressed classes, Malas, and Madigas. The term 'Dalits' is used in this paper to refer to them. The specific caste names are used wherever necessary.

⁴ I have taken these quotes from (Islam 2004, p. 35).

⁵ Dr. Ambedkar burned the text of *Manusmriti* publicly in 1927 as a political act to reject the religious base for untouchability.

⁶ To know more about the everyday life of Madigas and Malas, their social and religious life, refer to (Thurston 1914, pp. 350–51; Henry 1921).

gestures of sharing food and living space in *palems* (Dalit colonies). Further, they changed *palem* into a new location of spatiality where social relations were transformed and a Christian community emerged.

2. Conversion Movements and Social Equality

The conversion movements established a specific form of relationship between Dalits and missionaries. This relationship can be identified as a “contact zone.” According to Mary Louise Pratt, the contact zone is “the space of colonial encounters, the space in which peoples geographically and historically separated come into contact with each other and establish ongoing relations” (Pratt 2007, pp. 6–7). Dalits, who were historically oppressed and were under constant subjugation, and missionaries, who came with a different set of values, came into contact with each other. This perspective helps us to map the relationship between missionaries and Dalits, and how they were constituted in and by their relations to each other. The missionary was a white man, coming from the same community which was ruling the country. There was a connection between the British Empire and missionaries. Missionaries’ association with colonial officials made their evangelizing work easier. They secured protection from the colonial administration and state aid for their work. Missionaries could do what they did and could have some level of impact because of the empire. However, there were times when they had conflicts and ideological chasms with colonial government.⁷ A Missionary would tour villages to preach the gospel; during his visit to villages, people were astonished to see him and they regarded him as a ‘white angel’ (Pandian 1897, p. 205). This might be because of the dress, color, language, and mode of living of the missionary. Further, the missionary had access to power; he was accessible for them and had compassion towards them.

Missionaries as the readers of the Bible were sympathetic to the conditions of existence of Dalits. The Biblical understanding was that all human beings were equal before God and all of them were created in the image of God (Galatians 3:28). The humanitarian worldview of missionaries, which was rooted in the religious conception of the dignity of man, compelled them to seriously acknowledge the social discrimination and inherited inequality of Dalits. The other reason for this was the background of the missionaries. They came from the modern world, with modern ideas and perspectives influenced by the notions of rationality, equality, liberty, and fraternity. In addition to this, several decades earlier, Protestant missionaries worked for the liberation of slaves. They played a prominent role in the worldwide anti-slavery movement, which resulted in the Slave Trade Act of 1807 (Porter 1999). This enabled the missionaries to apprehend the denial of freedom, justice, and rights to Dalits. Missionaries were sympathetic towards Dalits not because they came to help them but because they came from a different world. In the ongoing relationship between missionaries and Dalits, the following activities were carried: turning *palem* into a social space, social interaction, acts of touching, inter-dining, emergence of *badi* and *gudi* and access to public wells.

3. Turning *palem* into a Social Space

The villages in Rayalaseema society were spatially segregated. The social structure of a village was such that it was inscribed with the Hindu caste setup with all the features ordered by Manu.⁸ The village had two types of habitats: *savarnas’* houses and *avarnas’* huts, separated by a distance. The Brahminical Hindu caste society did not allow Malas and Madigas to live in the village among the *savarnas’* houses in order to avoid pollution from untouchables even through wind. They were not regarded as part of the *oor* (village). They lived in a ghetto, a separate place on the outskirts of the village called *geri* or *palem*.⁹ Unlike other castes who lived in mud-roofed houses, the Malas

⁷ For more discussion on missionaries and empire look at (Copland 2006, pp. 1025–54).

⁸ In Hindu tradition Manu is considered as a progenitor of the human race. He was an author of the book *Manusmriti* (Laws of Manu).

⁹ In Tamil, it is called as *ceri* and in Kannad *keri*. Benaiah Cole used the term *palem* (Cole 1916, p. 4) and Francis used the word *geri* (Francis 1905, p. 35.).

and the Madigas lived in huts which were roofed with thatch or Palmyra palm leaves (Cornish 1874, p. 168). Therefore, Dalit localities were considered by village people as impure and polluted. People in the villages avoided visiting *palem*. However, missionaries who were considered by the village people as powerful and superior to them, visited *palem*, stayed there, and interacted with Dalits (Figure 1a,b). Furthermore, they changed this space into a locus of sociality where new spaces of public gathering such as churches and schools were introduced. This new spatiality was the location of social transformation. I substantiate this by illustrating how certain activities of the missionaries contributed to challenge the prevailing caste norms and create new social relations in the village.

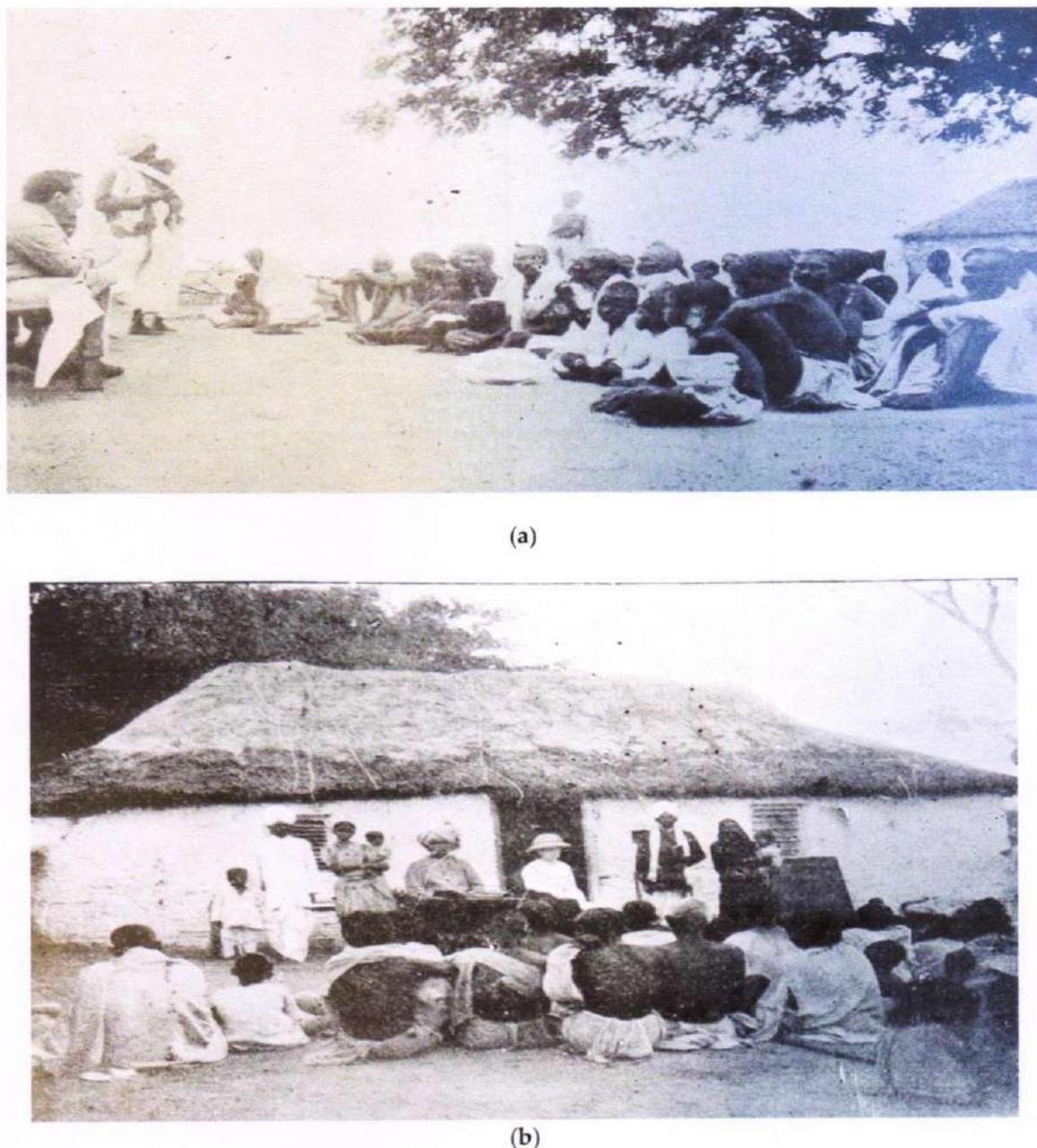


Figure 1. (a,b) Dalits interaction with missionaries in *palem*. Source (Simmons 1923, pp. 7, 12).

3.1. Social Interaction

It is significant to explore the social interaction of missionaries with Dalits. This interaction was characterized as one between the 'white angel' and 'untouchables,' between the powerful and the

powerless. This encounter was very significant in the life of Dalits as it might be the first time in their life that an outsider was interacting with them. Missionaries saw Dalits as human beings with body, soul, feelings, and emotions, unlike dominant castes who saw them as instruments of toil (Mohan 2015, p. 4). By interacting with Dalits, the missionary broke the prevailing notion that Dalits were untouchables and their presence was polluting. In their interaction, the missionaries told the Dalit that "You are the child of God. He made you and cares for you and seeks to save you" (Stanton 1950, p. 136)¹⁰ Till then Dalits were told by Hindu society that they were cursed people, untouchables and *Chandalas* and hence they were incapable of worshipping god. The missionaries, on the other hand, were telling them that they were children of god, they too were created by god and that god takes care of them. These words were appealing and enlightening to Dalits. During their stay in *palem*, missionaries visited each Dalit house and inquired about their problems (Clayton 1890, pp. 243–44).

3.2. Act of Touching

Another significant element that was involved in the relationship between the missionaries and the Dalits was the 'act of touching.' Derrida reflects on 'touch' in Christianity by observing that "salvation saves by touching, and the Savior, namely the Toucher, is also touched ... Jesus the savior is touching, he is the One who touches, and most often with his hand, most often to ... save" (Derrida 2005, p. 100). Thus, touch has a deep significance in Christianity. The discourse on untouchability is articulated around the idea of touch. The Hindu way of life which was codified by Manu conditioned the minds of Dalits to believe that it was a grave sin if they touch caste Hindus. Further, according to Manu's laws caste Hindus touching untouchables was considered as a sin. The Dalit individual's body was considered and treated by caste society as un-touch-able, unclean, and polluted. It was not just the body of the untouchable; even their shadow was regarded as impure. Therefore, they were required to walk in the village only during specific times. Most of the time, they were restricted to remain in the *ceri*. The political theorist Gopal Guru argues that the body of an untouchable person and his/her shadow work in circle to generate a humiliating experience for them. The impossibility of physical closeness performed through the taboo of the shadow of the untouchables removed the potential of human beings ever touching each other. Therefore the real (body) and reflected (shadow) were enfolded in the politics of annihilating untouchables from receiving love and acceptance from society (Guru and Sarukkai 2012, pp. 81–86). Apart from the people of his community, an individual from a Dalit community was never touched by anyone else. It is in this context that the touch of a missionary becomes very significant in the history of Dalits. The untouchable body was acknowledged and touched by the missionaries. Touching is not merely a physical gesture or a pragmatic action. For Dalits who were treated as untouchables, the act of touching is incredibly powerful as it has its own historical and cultural significance. Touching goes against untouchability. The touch established a complex form of connection, as it constituted a relationship between the missionary, the one who is touching and the Dalit, the one who is being touched. An illustration from Telugu literature shows how the missionary touching a Dalit was represented and what did it mean for a Dalit. In the novel, *The Untouchable Spring*, Chinnodu, a Dalit, was called upon by the *Tella Dora* [White Missionary] to go near him. The missionary held Chinnodu's hand and laid another hand on his shoulder. Chinnodu could not believe what had happened when he was thus touched. Until then, he remained untouched by people outside his community. However the missionary touched him; he was not from that village, not from that region; he did not belong to that land. The missionary touched him and said that his body was not untouchable. He did not just utter those words but showed it with his touch (Kalyana Rao 2010, pp. 158–59).

¹⁰ Apart from the LMS and the SPG missions, the American Baptist Mission (ABM) also worked in the Rayalaseema region. William Arthur Stanton was a missionary from ABM.

The missionaries telling Dalits that their bodies were touchable was beyond the imagination of Dalits. It could be argued that the touch of the missionaries provided comfort, empowerment, acknowledgment, and affirmation of humanity to Dalits. As Christopher argues, "The act of touching restored the human dignity to the body that was otherwise despised, loathed, and feared" (Christopher 2018, p. 7). The touch of the missionaries was liberating and humanizing for Dalits who were treated and made to believe for centuries that their body, presence, and shadow was untouchable and impure. Generally, Dalits were made to believe that, in their presence and with their touch, even the (Hindu) gods became polluted (Neelakantha Sasthri 1935, p. 15). However, the god of the missionaries was not contaminated by the presence of Dalits. The touch of the missionaries had a profound effect on the lives of Dalits as it broke the stigma that their bodies were not worthy of being touched.

3.3. Inter-Dining

The interaction between missionaries and Dalits was brought even closer through the act of sharing a common meal. A common meal draws people together and gives them a sense of community. The Brahminical Hindu social order and its culture prohibited inter-dining, particularly sharing food with Dalit communities. Hindus regarded that inter-dining was offensive to their beliefs and doctrines, which they considered as sacred. It is widely believed that eating food prepared by Dalits and eating food with them polluted the dominant caste people. It was not only the body and presence of Dalit, which was regarded as polluting; even the food cooked by Dalits was stigmatized as impure and polluted. It was in this context that the significance of the practice of inter-dining with Dalits becomes even more evident. Missionaries shared meals with the Dalit converts in their thatched huts. Missionary Todman from Cuddapah, during his tours in villages, had meals with Dalit converts where they sat on the ground together and were seen "eating in local fashion with fingers." In one of the villages, after taking baptism, Dalits invited Todman and his wife for lunch. They shared their meal with the baptized family. The missionary Dorothea Smith of Anantapur had a meal with a Dalit family, all seated on a mat. After eating all of them gathered around and discussed some chapters from the Bible (MMCLMS 1922, p. 237; 1934, p. 7).¹¹

As Shuman observed, "the act of eating together and sharing meals is known as commensality, an activity that not only preserves the physical body but also creates and strengthens social bonds" (Shuman 2003, p. 501). Eating the food cooked by Dalits, which was served on common plates used by Dalits, was an expression of community bonding. Missionaries eating in the huts of Dalits symbolically expressed that the former was part of Dalit community. The feelings of love, joy, and community sense, which emerged from sharing food with the missionaries, were significant for Dalits. Further, it brought them into closer contact and allowed them to converse together as brothers and sisters.

3.4. Emergence of Badi and Gudi

After conversion movements, little thatched huts emerged in every Dalit *palem*. During the fieldwork, Dalits said that this thatched hut was their *badi* and *gudi* (school and temple).¹² This was a school and a church, both at the same time; school by day and church by night. The school and temple are public spaces. In traditional Rayalaseema, caste played a significant role in gaining access to these public places. Dalits were denied their right to access these spaces. However, the public sphere was formed around spaces such as churches and schools in Dalit *palems*. Dalit Children gathered in the school in washed and cleaned dresses. They were taught to read and write and listen to stories about Jesus and Christianity (Stanton 1950, p. 122). The school and church thus became new locations

¹¹ The *Missionary Magazine and Chronicle of the London Missionary Society* (MMCLMS 1820–1940) was a monthly magazine of the LMS Mission. It was published in London. This magazine contains the monthly reports from LMS missionaries from various parts of the world. This is one of the important sources which I used. I have collected copies of this magazine from 1820 to 1940. Whenever this magazine is referred to in this article, the abbreviation MMCLMS will be used.

¹² Personal Interview from 2 November 2016.

for public gathering. It was here that men and women gathered every night and learned to sing, pray, and worship God and hear Christian preaching. Missionaries preached to them in those huts about God, sin, repentance, salvation, and devotion. Dalits oriented themselves to the teachings of the Bible and engaged with the ideas, meanings, and symbols related to it. In a course of time, a new consciousness emerged through what they heard during these Bible classes. The dynamic force of the Word—the written word (the Bible) and the spoken word (from missionary)—worked powerfully in the hearts of Dalit listeners; in Sanal Mohan's words, it worked as an "oppositional knowledge." Such oppositional knowledge became a source of enlightenment to Dalits to nurture themselves and cultivated in them new behaviors, new habits, a sense of morality, and a new understanding of themselves (Mohan 2015, p. 49).

The beginning of a new life, transformation, empowerment in Dalits began in these thatched huts. As missionary William Stanton states, "Here light is beginning to dawn on minds long bound in the prison-house. Here new hopes, desires and aspirations are born" (Stanton 1950, p. 122). For the missionary, this little thatched hut was "the nursery of the Kingdom and home of Religion" but for Dalits, it was a door to a new life and a center for their community. A new world was opened up to children and elders in these huts. By entering into the *palem*, staying there, and establishing the school-cum-church in the *palem* missionaries brought this otherwise forbidden and ostracized space into the folds of public space and transformed it into a space for knowledge and community gathering.

3.5. Access to Public Wells

Dalits were excluded from enjoying the right to access public wells in the villages. Caste rules were very strict about wells. The practice of untouchability was related to 'touching' water. When Dalits went to the well, they were supposed to wait for the other caste people to give them water. If Dalits drew water from wells, those wells were considered polluted. They were denied access to water because of their caste. Missionary Christlieb from Anantapur says that one may see a [dominant caste] man drive his oxen down to a water tank and give them a good wash down, or wash his soiled loin cloth in it, but people from the Mala and the Madiga castes were not allowed to dip their vessels in the tank to take home the household water for cooking (Christlieb 1930, p. 38). However, missionaries put in efforts to help Dalits to dig wells for themselves and to own their wells of drinking water. In Mutyalapadu village of Cuddapah district, even today there is an old well in the *palem*, which is built with stones. Among the stones, a slate was engraved with the following letters in old Telugu language—John Clay, 1857 (Figure 2a,b). John Clay was one of the prominent SPG missionaries who worked in Mutyalapadu station. In the same village, there is another well in the *palem* which was a well dug by the missionary Richard Dendi Shepherd.¹³ In fact, during famines, one of the relief works which missionaries organized for Dalits was the digging of new wells and repairing old wells (ARLMS 1898, p. 105).¹⁴

¹³ Jayaraju. Personal interview. 5 November 2016.

¹⁴ *Annual Reports of the London Missionary Society (ARLMS 1826–1950)* was an annual report of the LMS Mission. It was published in London. It contains information about the mission work in each mission station from Rayalaseema along with the information from other parts of the world. I have collected copies of these reports from 1826 to 1950. This is one of the major sources which I used for my research. To refer to this report in the article, I use the abbreviation ARLMS.

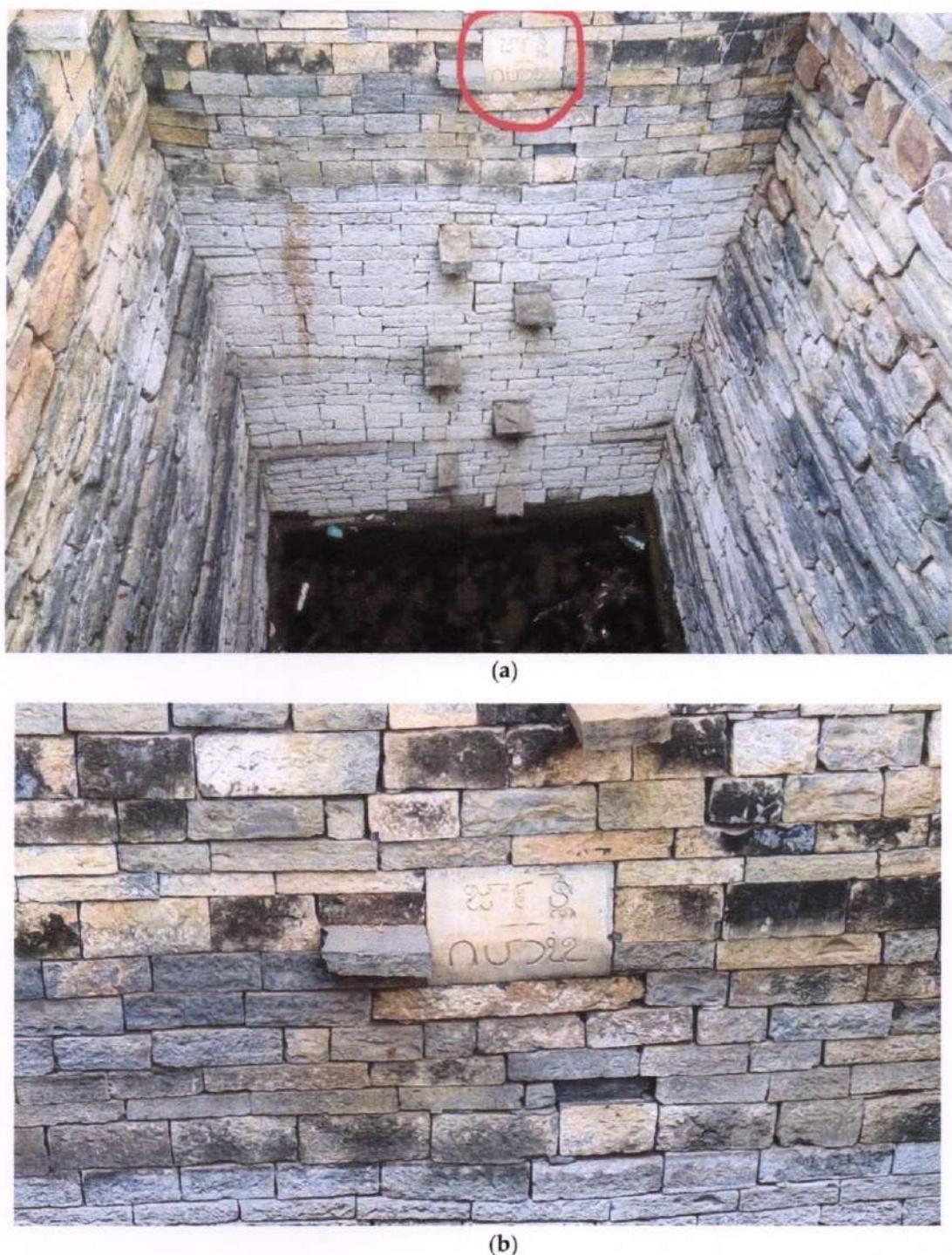


Figure 2. (a) Drinking water well dug by Missionary John Clay; (b) in the well, inscription of missionary name (John Clay) and year (1857) in Telugu language (Photo by the author).

4. Taking Sides with Dalits

Missionaries took a political stand when they saw Dalits were denied lives of dignity as human beings and individuals. They opposed caste violence perpetuated by dominant castes over Dalits. Missionary F. L. Marler from Gooty wrote in a report:

Could we make an example of some of these scoundrels [dominant caste Reddys], others might be held in check. I do not forget that I came here to preach to all men, and to bring the

Gospel of Christ and His righteousness to the most hardened of men; but it seems to me that, if we could by championing the cause of the oppressed, show men that we hate injustice, and will fight against it with all our power, we should create an impression that must tell for the Gospel in the end.

(MMCLMS 1893, p. 244)

Missionaries could not tolerate injustice and therefore supported Dalits in their cause. There are incidents in the missionary reports where missionaries challenged the practice of bonded labor which was one of the essential aspects of the structure of caste system. In the southern Indian missionary conference of 1879, missionary Jacob Chamberlain presented such a case. In one of the villages, ancestors of eleven Dalits whom the missionary referred to as slaves, had obtained some money from a Reddy, agreeing to work for him along with their children, until the debt was paid. The Reddy had been very careful and ensured that the Dalits would never be able to clear the debt. When the Dalits converted to Christianity, the Reddy demanded that as Dalits were his workers, they had to work for him on Sundays as well as on other days. One Sunday, during worship at the mission house, a message came to Chamberlain that the Reddy had inflicted violence on the Dalits. Some of their houses were burnt down, and some people were beaten up. That night, Chamberlain and his colleagues went to the village and demanded a meeting with the Reddy. Chamberlain warned the Reddy against such violence. It was said that the missionary and six of his colleagues dismounted in front of his door. This had an impact on the Reddy and he agreed to have a meeting with them. In the meantime, the missionary met all Dalit families and asked them to tell him the circumstances. During this meeting, Reddy mentioned that the Dalits were in bondage to him. They had obtained money which they never paid back. If they would pay off this debt he would at once give them their freedom. The missionary found that the amount, owed by all those eleven Dalit families put together, with all their ancestral debts, was 71 rupees. Missionary Chamberlain and his colleagues paid that money and freed the Dalit families (Missionary Conference 1879, pp. 64–65).

Bonded labor was linked with caste. In Rayalaseema, Dalits were landless, economically dependent on the dominant caste Reddys. Many of Dalit families worked for Reddy landlords day and night without being paid and were always available to the Reddy and his family. As missionary Nicholson claimed, “each birth, each sickness, and each death plunges them deeper and deeper into the slough of debt, in which they have been ever since their birth” (ARLMS 1904, p. 163). Many of them, having borrowed money from Reddys, were bound to work for Reddy landlords for generations together. The interest kept increasing for such a loan. Furthermore, given their illiteracy, Reddys robbed and cheated these Dalit families in every way. They wrote down on the notarized paper larger sumsthan what the Dalits had initially borrowed (Goffin 1913, p. 51). In the description provided by Chamberlain, the Reddy perpetrated violence on Dalits when they asserted their individuality by not working in his fields on Sundays and attending the church against the wishes of Reddy. The Reddy could do that since he held these bond papers as evidence for the loan. Reddy was afraid when missionaries questioned him given the latter’s knowledge of law. Missionaries confronted bonded labor, an old caste-practice, by questioning Reddys and releasing Dalit families by paying the debt.

In Jammalamdugu vicinity of the Cuddapah district, even today people recall how missionaries helped their (Dalit) communities during atrocities. Benhar, a pastor from Pulivendula remarked in a conversation with me that in the Nemmaladinne village, a Mala convert was tied to a tree and beaten up by the Reddys. Some Malas made a long journey to Jammalamdugu which was a mission station and reported to the missionary about what had happened. The missionary reached the village by horse and went to the place where the Mala person was tied up. Still sitting on the horse, he asked the people to untie the Mala. He then expressed his anger to the Reddys, took a coin from his pocket, bent it and threw it at the Reddys. He declared “these are my people. You bring this coin into the original shape and meet me at Jammalamdugu.” Benhar further said that “the coin was not easy to bend, and when

the missionary bent it, it showed how angry he was at Reddys and his love towards us [Malas].”¹⁵ Sikhamani, an elderly man from Chinna Venturla village remembered in one conversation that

We had a thatched hut school in our *palem*. Hanumanta Reddy and Venkata Reddy came to the *palem*, destroyed the school and took all the equipment with them. The same night elders of the church, which included my grandfather, went to Jammalamadugu and reported the events to the missionary. Upon hearing this, the missionary came to the village and warned the Reddys. He ordered them to return whatever they had taken. By the evening of the next day, they returned all the articles.¹⁶

In matters of justice, missionaries supported Dalits. On many occasions when justice was denied to Dalits, missionaries took up the cases. Missionary Clayton tells a story of what happened in one of the villages of Tamil Nadu in the Madras Presidency to understand how Dalits were discriminated, cheated upon by the dominant castes and how Dalits got justice with the intervention of the missionary. According to Clayton, in one of the villages, a Dalit woman was caught by Velu Mudaliyar, one of the landlords from the dominant castes in the village, while she was plucking fruits in his farm. The angry Velu abused her and struck her so hard that she died on the spot. Following such unexpected consequences, Velu approached the village headman Sundara Mudaliyar whose name and fame was great in that area. Velu took the headman to the place where the Dalit woman had died and expressed his fear of imprisonment. The headman assured him security and sent a man to bring Chellan, the husband of the dead woman. When Chellan approached the headman, he was asked to choose between going to jail and taking ‘compensation’ of a few silver coins, equivalent to ten rupees. When Chellan inquired further the headman told him that somebody had struck Chellan’s wife and she was lying dead on Velu’s land; the headman then made false allegations against Chellan blaming him for his wife’s murder. When Chellan started crying, he was told by the headman that nobody knows who killed her; since her body fell in Velu’s land, Velu would pay the ten silver coins to perform the funeral. Further, he said that it was a better option to take the ten white coins and to take a new wife than going to jail and be hanged for killing her. Besides, the headman threatened him that if Chellan were not willing to agree to his terms, he would be seized by Velu. Further, a complaint would be registered that Chellan killed his wife and the former would present himself as a witness to the crime. Since there was no other option, Chellan accepted the money and took the body of his wife. The landlord who was the murderer and the headman were greatly relieved. On the evening of the fourth day, the headman heard from his grandson that the missionary had come and was staying for the night with Dalits. Hearing about the missionary was like a thunderclap to the headman. As he predicted, the missionary came to know about the death of a woman through Chellan. That midnight, three police came, arrested Velu and imprisoned him in Chingleput (Clayton 1890, pp. 229–44).

The above incident, gives insights into the life of Dalits—how it was not considered worth living; and how easily they could be killed and disposed of. They had no power to question the murderers who belonged to the dominant castes. If they dared to ask, they would be accused as murderers. Given the fear of colonial law, they were afraid of their crime and negotiated with Chellan. When the missionary intervened, law was implemented. Punishment meted out to the dominant castes was a new reality in society, a significant indicator of social change. Therefore the presence of missionaries empowered Dalits so that they could use the law and challenge the power and authority of the Reddys.

5. Hostility from the Dominant Castes

The involvement of missionaries in the lives of Dalits and their support for Dalits in matters of justice led the dominant castes to look at them with contempt. Mission records and oral accounts

¹⁵ Personal Interview on 16 July 2015.

¹⁶ Personal Interview on 11 July 2016.

demonstrate incidents of growing animosity of the dominant castes towards missionaries. After the conversion of Dalits, following the instigation of village magistrates and Karunams, the Reddys of Vanipenta and Mutyalapad villages of Kurnool district attacked the missionary Uriah Davies and violently drove him out of the villages (Colonial Church Chronicle 1856, p. 95; Hibbertware 1912, p. 54).¹⁷ In Kadiri, a group of dominant caste people planned to attack the missionary. One night, they sent nearly twenty people to the missionary's bungalow. They however could not find him or his family and left after plundering and pillaging the bungalow (Samuel 1923, pp. 234–35). During my interview with Sunil Varakumar, he recollected an incident he was told by his elders. In the Talamanchipatnam village of the Cuddapah district, the Reddys resisted the entry of the missionary to the village and let their dogs loose upon his horse. The missionary fell off the horse and was beaten up by the dominant caste mob¹⁸. Sujiv from Mutyalapadu and Leelamma from Rudravaram village recalled what they were told by their grandparents that the missionary R.D. Shepherd from Mutyalapadu station was attacked by *palegars* on account of treating Dalits well¹⁹.

6. Dalits Writing Missionaries into Their Household and Community Histories

Dalits remember the missionaries to the present day for their involvement in improving the lives of their communities. One of the LMS missionaries, Edward Porter came to Cuddapah in 1844, and worked till 1868 (Figure 3). It is significant to mention Porter here because mass community conversion movements took place during his time. Based on my oral history accounts, I infer that he left a deep mark in the hearts of Dalits. Before his retirement, Dalit converts from many villages in the Cuddapah district came and gathered at the mission church in Cuddapah to give their farewell to the Porter family (Porter 1885, pp. 65–66). Benaiah Cole, a Dalit convert from Cuddapah characterized Porter's time in Cuddapah as “Edward Porter's Era.” He wrote in his book that, “Vikramarka established his era by squandering away all the Royal Treasures; Shalivahana by war and bloodshed; but Father Porter's was established by *love and piety*”. Further, he said

Ah! Venerable shades of Porter! What a mine of confidence of his name was to these poor people [Dalits]. I have seen the cubs of lions roar for hunger but I have not ever heard of Porter's converts to know what hunger was. He was a man of prayer therefore he fed his children with bread, butter, and kisses

(Cole 1916, pp. 25–28).

After fourteen years of Porter's departure, in 1882, Henry Stanley Newman visited villages in the Cuddapah mission station; he witnessed converts remembering Porter with “intense affection.” Dalits told Newman with tears in their eyes that “He was more than father to us” and Porter's portraits were hung on the walls of their little huts (Newman 1876, pp. 123–24).

Missionary J.I. Macnair from Cuddapah wrote that though it was nearly forty years since Porter left Cuddapah, his name was still a household word among many Dalits. Porter's stay in Cuddapah was a watershed moment, a red mark on the calendar so to speak, in a country where time was remembered by events and not by years. “I was baptized in Porter-dorah's²⁰ time,” “In Porter-dorah's time I was five years old”—these and such expressions were common” (MMCLMS 1905, p. 238). Benaiah Cole provides ethnographic observations about Porter's love towards Dalit converts in Cuddapah. After his retirement, Porter left a bungalow behind him as his private property. Many years later, when the question of selling the bungalow was referred to him, he sent a long list of names as a reply. In that list,

¹⁷ The Colonial Church Chronicle was a missionary journal published by the SPG Mission. It was an annual journal printed from London. This journal contains the information of the SPG Mission stations and reports of missionary work across the globe.

¹⁸ Personal Interview from 11 December 2016.

¹⁹ Personal Interview from 5–6 November 2016.

²⁰ In Telugu language *Dorah* means “lord” or “sir” or “master.” It is used to address both the white missionary as well as the local feudal lords.

each Christian's name in Cuddapah station was entered and opposite to it was mentioned, the amount they should get from the sale-proceeds of that bungalow; the smallest amount paid to the lowest of the Christians was rupees twenty. "In this way, he was the only one who used Home Christian Charities over poor Christian people for Christian purposes" (Cole 1916, p. 28). Porter died in 1882 in England. When missionary Bacon announced the news of his death in the Cuddapah church, the entire congregation was in tears. At the close of the church service, a proposal was made that a marble tablet should be placed in the chapel in memory of Porter (Porter 1885, p. 73). This tablet is still there in the Cuddapah town church building which was erected in 1884. (Figure 4).

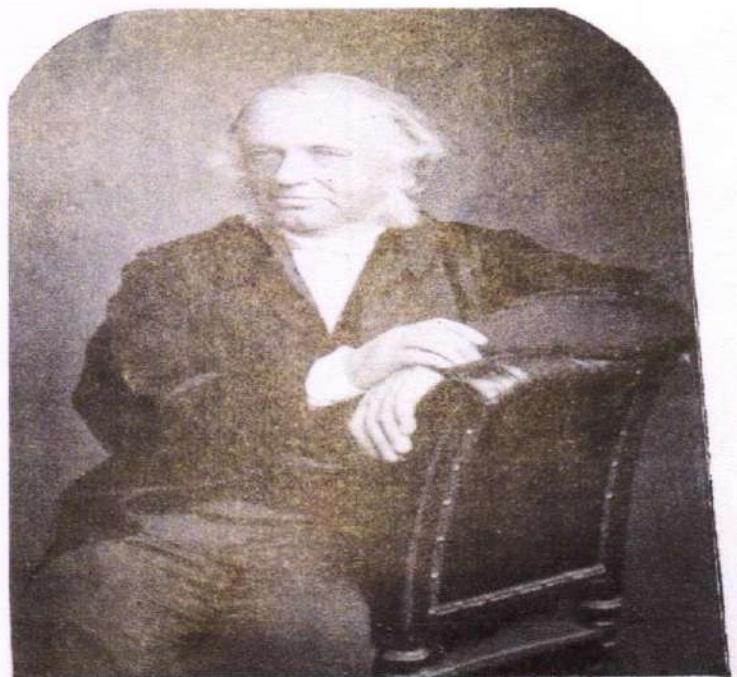


Figure 3. Missionary Edward Porter (Source: (Simmons 1923, p. 8)).

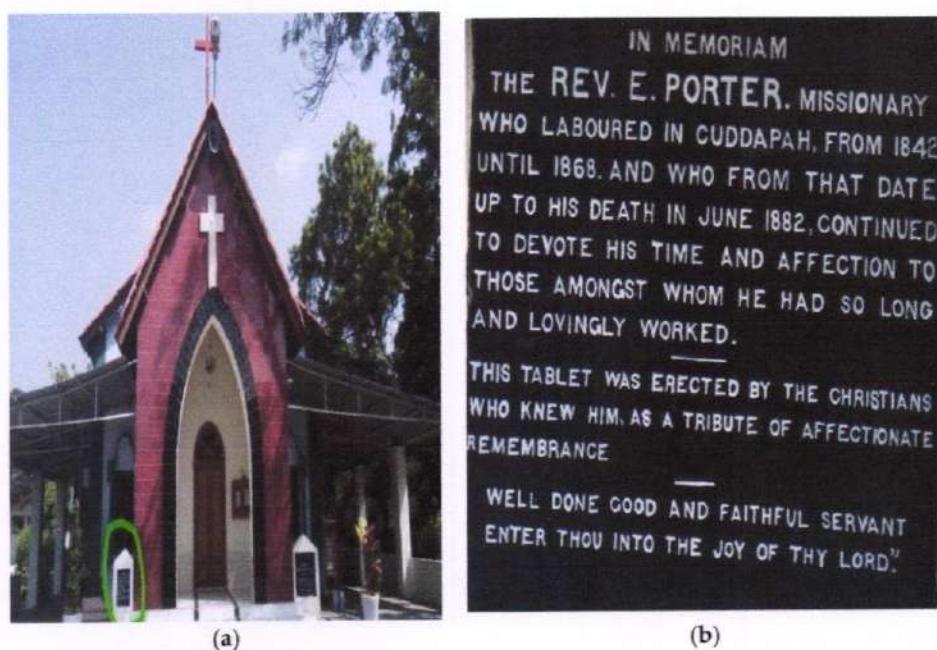


Figure 4. (a,b) Tablet which is erected in 1884 in the church building in memory of missionary Edward Porter (Photo by the author).

In remembrance of missionaries who worked among them, Dalits named their children after the names of missionaries. In Mutyalapadu village, Joseph named his son Satyananda Dendi Shepherd John Clay²¹. Sujiv who is a teacher from the same place named his son Richard. John Clay and Richard Dendi Shepherd were SPG missionaries and worked at the Mutyalapadu station²². In Jammalamadugu as Martha Yesudas remarked, a Christian lady named her child Peggy and another lady Smith. Peggy Hawkins was a lady missionary who worked in that area and Smith was a medical missionary in Campbell hospital at Jammalamadugu²³.

7. Conclusions

The above discussed evidence and oral accounts show how Dalits were treated as untouchable and were made to live in a ghetto. Nobody touched them, or ate with them. They were not treated as equals and were attacked. Nobody came to/for them and they were denied access to the most basic necessities, including drinking water. I have argued in this paper that Dalits conversion and their relationship with missionaries brought a remarkable social change among Dalits in Rayalaseema society. In the process of making Dalit converts as a Christian community, the missionaries questioned the hierarchical principles of caste-based society in India. Dalit converts experienced social equality which was expressed in the form of social interaction through community dining, accommodation, and dialogue with people outside their community.

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²¹ Personal Interview from 5 November 2016.

²² Personal Interview from 5 November 2016.

²³ Personal Interview from 8 November 2016.

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Proto historic and Prehistoric studies in recent times

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ABSTRACT

This essay explores recent developments in prehistoric and protohistoric studies in India, focusing on the interdisciplinary approach, human-environment interaction, technological advancements, exploration of new sites, and an emphasis on public outreach. The protohistoric period, marked by the emergence of written records, is characterized by the use of epigraphic data to reconstruct the history of ancient societies and the study of ancient trade networks. The trends discussed highlight the significant progress in understanding India's prehistoric and protohistoric past, facilitated by innovative methodologies and collaborative research.

INTRODUCTION

The prehistoric period is the period in human history before written documents were created. People at this time were not cultured. Only archeological evidence is used to study this era's past. Three sections make up this time frame:

1. Paleolithic Period (from early period to around 8000 B.C.)
2. Mesolithic Period (around 8000 B.C. to around 4000 B.C.)
3. Neolithic Period (around 4000 B.C. to around 2500 B.C.)

The time between prehistory and history is known as proto-history, and it lasts for about 2500 B.C. During this time, no culture or civilization has yet perfected writing, but other cultures have already acknowledged its presence in their own writings. until about 600 B.C.

The study of the remains of human civilizations, typically discovered through excavation, is known as pre- and protohistory (prehistoric and historic archaeology). As a result, it advances knowledge about the best era in human history. There are several ongoing trends in protohistoric, and prehistoric research in India.

PROTO HISTORIC AND PREHISTORIC STUDIES IN RECENT TIMES

Actually, Prehistoric and Protohistoric studies have been an important area of research in India for several decades. Prehistoric studies focus on the period before the invention of writing, while protohistoric studies deal with the period when writing began to be used. In recent times, there has been significant progress in these fields due to the adoption of new methodologies and interdisciplinary approaches. In this essay, we will discuss prehistoric and protohistoric studies in recent times in India.

Interdisciplinary approach: Protohistoric, and Prehistoric research in India has become more interdisciplinary, combining archaeological, geological, biological, and environmental data to create a more comprehensive understanding of the past. Archaeologists are now working with experts from other disciplines such as geology, biology, and environmental science to study the prehistoric past of India. This approach has enabled researchers to obtain a more comprehensive understanding of prehistoric cultures and their relationships with the environment. For example, by combining archaeological and geological data, researchers have been able to reconstruct the paleoclimate and vegetation of different regions of India, helping them understand how prehistoric people adapted to environmental changes.

Focus on human-environment interaction: There is an increasing emphasis on understanding the complex relationships between people and their environment. Researchers are looking at how humans adapted to environmental changes, used natural resources, and transformed landscapes. For instance, archaeologists are studying how prehistoric people used natural resources such as water, forests, and minerals and how they transformed landscapes for their needs. This focus on human-environment interaction has provided new insights into the prehistoric past of India and has highlighted the importance of sustainable resource use.

Technological advancements: The use of advanced techniques such as radiocarbon dating, DNA analysis, isotopic analysis, and high-resolution imaging is becoming more prevalent in research. These techniques are helping researchers to reconstruct past human behavior, migrations, and cultural interactions. Technological advancements have revolutionized prehistoric research in India. For example, DNA analysis has enabled researchers to reconstruct the genetic history of ancient populations and identify their relationships with modern populations. Isotopic analysis has helped researchers understand the diet and mobility patterns of prehistoric people.

Exploration of new sites: Research in India is expanding its geographic scope, with new sites being discovered and excavated in different regions of the country. These sites are providing new insights into the re-examination of existing data: Protohistoric, and Prehistoric research in India is also focusing on re-examining existing data and revisiting old hypotheses. This approach is helping researchers to question past assumptions, identify gaps in knowledge, and generate new research questions.

Emphasis on public outreach: Protohistoric, and Prehistoric research in India is increasingly emphasizing public outreach, with efforts to communicate research findings to a wider audience. This approach is helping to promote public awareness and appreciation of India's rich prehistoric heritage.

The studies in India have also seen significant progress in recent years. The protohistoric period in India is characterized by the emergence of written records, which provide valuable insights into the political, economic, and social systems of ancient societies. One of the major trends in protohistoric studies in India is the use of epigraphic data. Epigraphy is the study of inscriptions, and it provides valuable information about the languages, scripts, and socio-political systems of ancient societies. Researchers are now using epigraphic data to reconstruct the history of ancient kingdoms and empires in India.

Another trend in protohistoric studies in India is the study of ancient trade networks. Trade was an important aspect of protohistoric societies, and researchers are now using archaeological and epigraphic data to reconstruct ancient trade networks. For example, the discovery of Roman coins in southern India has shed light on the trade links between India and the Roman Empire.

CONCLUSION: In conclusion, prehistoric and protohistoric studies have seen significant progress in recent times in India due to the adoption of new methodologies and interdisciplinary approaches. These trends have enabled researchers to obtain a more comprehensive understanding of the prehistoric and protohistoric past of India, and they are likely to continue shaping research in these fields in the future.

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