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Mössbauer and Structural Study of Co^{+2} Substituted Zn-Ferrite

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Abstract: *A complete system of polycrystalline spinel ferrite, $Zn_{1+x}Co_xFe_{2-2x}O_4$ (where $0.0 \leq x \leq 0.6$ in the steps of 0.1) have been synthesized by standard ceramic method and studied by using X-ray diffraction (XRD). The XRD dataconfirmed the single-phase formation of the samples. The lattice constant and Cation distributions were studied by using XRD analysis. The Mossbauer spectroscopy suggests the two oxidation states corresponding to Fe^{3+} andFe^{2+} ions.*

Keywords: X-ray diffraction, Query Temperature, lattice constant, Cation distributions, Mossbauer spectroscopy

I. INTRODUCTION

The ferrites have been studied from Several decades extensively because of their importance in the basis as well as in applied research.[1-3] The spinel ferrite having general formula $\mathbf{MFe_2O_4}$, (M = a divalent cation) is belongs to an important class of magnetic material because of their remarkable magnetic properties particularly in the radio frequency region, high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization, high Curie temperature, mechanical hardness and chemical stability.[4] The important magnetic and electrical properties of ferrite mainly depend on the methods of preparation, type and amount of dopant, cation distribution etc.[5] On the basis of crystal structure, ferrites are grouped into three important classes, namely spinel ferrite, garnet and hexa-ferrite[6]. The crystal structure of spinel ferrite consists of two interstitial sites, tetrahedral (A) and octahedral[B] sites, in that cations are occupied.

The mixed ferrites of zinc with tetravalent substitution Sn^{4+}, Ge^{4+}, Ti^{4+}, Sn^{4+}, and Co^{4+} ions form a very important class of magnetic semiconductor materials which are widely used in many technological applications. The effects of divalent and trivalent metal ions on the structural, magnetic, and electrical properties of zinc ferrite were studied by many researchers.[7,8] Few reports are available to show effect of tetravalent substitution ions on the properties of zinc ferrite.[9] However, yet cation distribution and their correlation with magnetic properties not been studied in detail. When two Fe^{3+} ions are replaced by Co^{4+} ions in combination with divalent Zn^{2+} ions, may result in improved magnetic as well as electrical properties of zinc ferrite. The aim of this work is to synthesize zinc ferrite with Co^{4+} substitution with the chemical formula $Zn_{1+x}Co_xFe_{2-2x}O_4$, and the study of structural, and Mössbauer spectral studies.

II. EXPERIMENTAL SECTION

The Zinc oxide (ZnO), cobalt oxide (CoO_2), and ferric oxide (Fe_2O_3) were mixed in stoichiometric proportions to prepare a series of polycrystalline spinel ferrite $Zn_{1+x}Co_xFe_{2-2x}O_4$, in the step of 0.1. The samples were prepared by using standard double sintered ceramic technique[10]. The stoichiometric calculations were carried out by using the equation,

$$\mathbf{(1+x)\ ZnO + xCoO_2 + (1-x)\ Fe_2O_3 \longrightarrow Zn_{1+x}Co_xFe_{2-2x}O_4}$$

Each sample was ground for 3 hours using agate mortar. The samples were pre-sintered in a muffle furnace at 950°C for 10 hours. The pre-sintered samples were reground and compressed into a disc shaped pellet form by using hydraulic press with a pressure of 6 ton per $inch^2$. These pellets weresintered at 1110°C in air for 24 hours and were slowly cooled to room temperature. X-ray diffraction (XRD) patterns were recorded at room temperature in the 2□ range of 20^0 to80^0 to confirm the formation of single-phase cubic spinel structure. The cation distribution was estimated through X-ray

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diffraction technique. Mössbauer spectroscopy measurements were carried out at room temperature for the prepared sample.

III. RESULTS AND DISCUSSION

X-ray diffraction (XRD) analysis

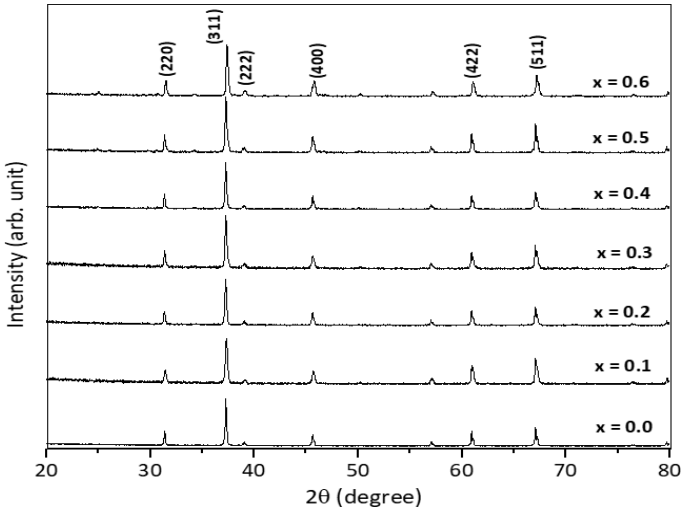

Fig.1: X-ray diffraction pattern for $Zn_{1+x}Co_xFe_{2-2x}O_4$

Fig.1 illustrates the room temperature powder XRD pattern for the spinel ferrite $Zn_{1+x}Co_xFe_{2-2x}O_4$ system. The XRD pattern shows the presence of (220), (311), (222), (400), (422) and (511) peaks. All the Bragg reflections correspond to cubic spinel structure. No extra peak other than cubic spinel phase observed in the XRD pattern. The analysis of XRD pattern reveals the formation of single-phase spinel ferrite.[10] The XRD pattern also shows slight shift in peak position towards higher 2 angle due to substitution of Co^{4+} ions in zinc ferrite. The inter planer spacing 'd' values for the recorded peaks were calculated according to Bragg's peaks. The lattice parameter 'a'of the spinel ferrite $Zn_{1+x}Co_xFe_{2-2x}O_4$, (0.0 Θ x Θ 0.6) system was calculated with an accuracy of Θ 0.002. where, d- inner planner spacing, N = $(h^2+k^2+l^2)$; (h, k, l) being the Miller indices. The variation of lattice constant with Co^{4+} content x is given in Table.1. It can be observed from Table.1, that the lattice constant of $Zn_{1+x}Co_xFe_{2-2x}O_4$ increases from x = 0.0 to x = 0.1, beyond x = 0.1 the lattice constant decreases with Co increase in content x. The decrease in lattice constant with Co increase in content x is attributed to the difference in ionic radii of constituent ions i.e., Zn^{2+}, Fe^{3+} and Co^{4+}. In the present series $Zn_{1+x}Co_xFe_{2-2x}O_4$, two Fe^{3+} (0.61Å) ions are replaced by combination of Zn^{2+}(0.72Å) ions and Co^{4+}(0.52Å) ions, thereby decreasing the lattice constant of the system. A similarresult of variation of lattice constant in tetrahedral substitution is observed in the literature[11]. The decrease in lattice constant is almost linear and obeys Vegards law.[12]

Cation distribution

The study of cation distribution in spinel ferrite is important to understand the magnetic behavior of the samples. There are different techniques available to determine the cation distribution in a given spinel ferrite. The cation distribution of spinel ferrite can be studied by using X-ray diffraction method[13], magnetization[14], Mossbauer[15] and neutron diffraction technique.[16-19] In the present work, X-ray diffraction method has been used to study the cation distribution. In X-ray diffraction method, X-ray intensity ratios of a selected plane were calculated, and the calculated intensity ratio is then compared with the observed intensity ratios. The intensity ratios were calculated for various distributions of cations at tetrahedral (A) and octahedral [B] sites. The structure factor, multiplicity factor and Lorentz polarization factor were taken from the literature and the calculated intensity ratio and observed intensity ratio were compared for several combinations of cations, distributed at (A) and [B] sites using computer software. Details of the intensity ratio calculation method used for obtaining cation distribution in spinel ferrite were reported by Qiang-min Wei et al.[20]. In the present work (400), (422), (440) planes were considered to calculate intensity ratio. These planes are assumed to be

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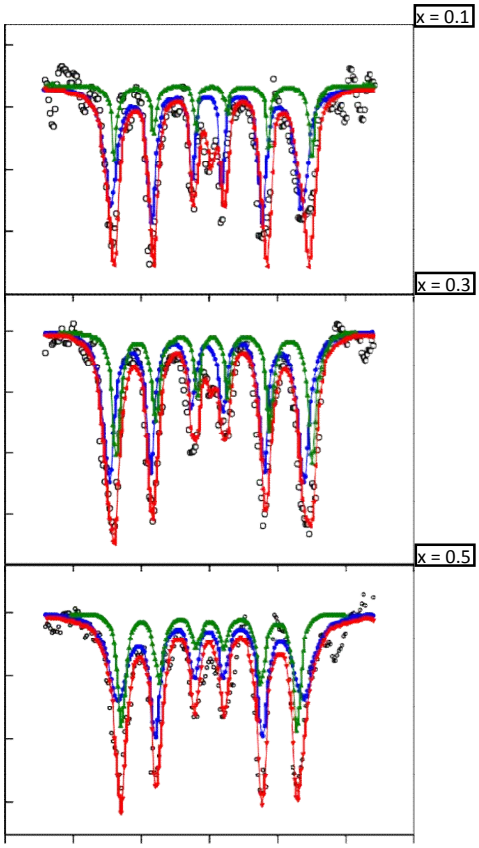
sensitive to the cation distribution. The cation distributions calculated from X-ray intensity ratio calculation is illustrated in Table1. The table shows that Zn^{2+} occupies octahedral [B] sites whereas Co^{4+} and Fe^{3+} both occupy tetrahedral (A) and octahedral [B] sites.[21-23]

Table.1: Lattice constant, and cation distribution for the $Zn_{1+x}Co_xFe_{2-2x}O_4$,

Co content'x'	Lattice constant 'a' Å	Cation distribution	
		A-site	B-site
0.0	8.441	(Co0.0 Fe1.00)	[Zn1.00 Fe1.00]
0.1	8.665	(Co0.06 Fe0.94)	[Zn1.1 Co0.04 Fe0.86]
0.2	8.351	(Co0.14 Fe0.86)	[Zn 1.2 Co 0.06 Fe0.74]
0.3	8.349	(Co 0.18 Fe0.82)	[Zn 1.3 Co 0.12 Fe0.58]
0.4	8.321	(Co 0.24 Fe0.76)	[Zn 1.4 Co 0.16Fe0.44]
0.5	8.235	(Co 0.30 Fe0.70)	[Zn 1.5 Co 0.20Fe0.30]
0.6	8.512	(Co 0.36 Fe0.64)	[Zn 1.6 Co 0.24Fe0.16]

Mössbauer Spectra Analysis



The Mössbauer spectrums of typical sample x (=0.1, 0.3, 0.5) for $Zn_{1+x}Co_xFe_{2-2x}O_4$ ferrite were obtained at room temperature is shown in Fig 2 Mossbauer spectrums have been fitted with two. typical sample two separate six-line Zeeman splitting (sextets) corresponding to iron ions at tetrahedral (A) and octahedral [B] site. Mössbauer data suggests that the isomer shift varies with Co content x indicating that the electron charge distribution is negligibly influenced by substitution. The quadrupole shift (Qs) in the Zeemansextet is very much less for A and B sites which is a

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general observation for a spinel ferrite system. The small positive values of 'Qs' indicate that Zn^{2+} ions extensively preferred [B] site. Co^{4+} ion opposes to Zn^{2+} ion due to super exchange interaction between Zn^{2+} and Co^{4+} ions occupy both sites. This suggests that cubic symmetry of these two sites has not been disturbed. The values of hyperfine field decrease with increase in Co content x. The Hyperfine field is less in tetrahedral (A) than that of octahedral [B] site. This is a general observation observed in another ferrite[21]. The Co^{4+} ions replace Fe^{3+} ions at octahedral B-site only, which causes a reduction in the number of active linkages between A and B sites and thereby reducing hyperfine magnetic field. The isomer shift 'Is' values in millimeter per second in the small range. These values are typical for that of Fe^{3+} ions octahedral (A) sites of spinel ferrite. This means that 's' electron charge distribution of Fe ions is negligibly influenced by Co^{4+} substitution. The values of isomer shift indicate that the reported sextets for all the samples are due to the Fe^{3+} ions only.[22-23,24-29]

IV. CONCLUSION

The finding of experimental results on structural and Mössbauer spectrum properties of tetravalent Co4+ substitution in Zinc ferrite is, that the ferrite system Zn1+xCoxFe2-2xO4 are prepared in a single-phase cubic structure. The value of lattice constant decreases beyond x=0.1 shows that, two Fe3+ ions are replaced by combination of Zn2+ions and Co4+ ions. Cation distribution data and Mössbauer spectrum analysis suggest that Zn2+ prefer to occupy octahedral [B] site, Co4+ and Fe3+ occupy both tetrahedral (A) site and octahedral [B] sites.

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