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“STUDY OF STRUCTURAL PARAMETERS AND CATION DISTRIBUTION OF Cu^{2+} IONS SUBSTITUTED NICKEL FERRITES”

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ABSTRACT

Objective: To prepare and study the Cu^{2+} ion substituted nickel ferrites with reference to structural parameters and cation distribution

Materials and Methods: The samples of Cu^{2+} substituted nickel ferrites having the composition formula $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.4, 0.8$) were prepared by solid state reaction technique using AR grade oxides. The formation of mono phase cubic spinel structure of all the samples under investigation have been carried out using XRD technique at room temperature. X-ray diffraction data were used to calculate structural parameters and X-ray intensity ratios were calculated for selected planes (220), (400), (440) and compared with the observed intensity ratios in order to obtain cation distribution.

Results: The results of the cation distribution indicate that Cu^{2+} and Fe^{3+} occupy both sites whereas Ni^{2+} occupy octahedral B site. In this work we report our results on structural parameters and cation distribution of mixed Ni-Cu spinel ferrites.

Conclusion: The structural parameters of nickel-copper system increases with Copper ions.

Keywords: XRD, structural parameters, cation distribution.

INTRODUCTION

Excellent electrical and magnetic properties of spinel ferrites make them commercially important materials. Interesting physical and chemical properties of ferrites arises from ability of those compounds to distribute cations amongst the available tetrahedral A-site and octahedral B-site and magnetic A-A, B-B and A-B interactions. Ferrites fulfill the wide selection of applications from microwave to radio frequencies and are of importance from both fundamental and applied research point of view. [1,2]. The dual property of electrical insulator and magnetic conductor makes ferrites useful in many devices like transformer cores, antenna rod, and memory chips, microwave devices, magnetic recording etc. Compared to other magnetic materials ferrites can be easily prepared, low cost and highly stable. The important electrical and magnetic properties of ferrites rely upon various factors which include method of preparation, type, nature and amount of dopants etc [3, 4]. Usually, spinel ferrites are prepared by ceramic technique. The electrical and magnetic properties are greatly influenced by the occupancy of cations at tetrahedral (A) and octahedral [B] sites. Thus, the study of cation distribution is very important in order to know the essential structural, electrical and magnetic properties of spinel ferrites. Among the spinel ferrites, nickel ferrite has special attraction due to their useful properties like inverse spinel nature, high saturation magnetization and Curie point, high electrical resistivity and chemically most stable. Copper may be Jahn Teller ion with magnetic moment one within the literature only few studies on copper substituted nickel ferrite is reported. We have prepared a series of copper substituted nickel ferrite with the formula $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) using ceramic technique. Here, we report our results on structural and cation distribution studies for $x = 0.0, 0.4$ and 0.8 samples.

MATERIALS AND METHODS

The polycrystalline samples of $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.4, 0.8$) were prepared by solid state reaction technique [5]. A.R. grade oxides of corresponding ions (NiO , CuO and Fe_2O_3) were mixed in stoichiometric proportion. Grinding using agate mortar (4 h) was dispensed for every sample. The samples were pre-sintered at 1293 K

for 12 h. The sintered powder is again reground and sintered at 1353 K for 14 h. Then the powder of samples compressed into pellets of 10 mm diameter and about 1gm mass mechanical press with pressure 6 ton/inch² and sintered at 1273K for 12 h. The samples were furnace cooled to room temperature. The prepared samples were characterized by X-ray powder diffractometer within the 2θ range 20°-80° at room temperature to substantiate single phase spinel structure. The cation distribution studies were carried out using diffraction method.

RESULTS AND DISCUSSION

XRD (X-ray diffraction): Mixed spinel ferrites system of $\text{Ni}_{1-x}\text{Cu}_x\text{Fe}_2\text{O}_4$ ($x = 0.0, 0.4, 0.8$) under investigation has been structurally investigated by diffraction. The XRD patterns showed in fig. 1 indicate that the samples have single phase cubic spinel structure. The Bragg's peaks are sharp and intense. The lattice parameters are calculated using XRD data and are given in Table-1. It's observed from Table-1 that lattice constant increases very slowly with increase in copper content 'x'. The little variation within the lattice parameter with copper substitution will be explained on the idea of very close ionic radii of nickel (0.69Å) and copper (0.72Å) [6]. The ionic radii of nickel and copper are approximately near one another and hence there's not much variation in the lattice constant.

Hopping length

The distance between magnetic ions, hopping lengths (L_A and L_B) in tetrahedral A-sites [7] and octahedral B-sites [8] is estimated and values are given in Table 1. Fig. 2 shows the relation between the hopping lengths in tetrahedral (A) and octahedral (B) sites as a function of Cu content x. The distance between the magnetic ions increases because Cu content x increases. This may be explained on the idea of difference in ionic radii of constituent ions Ni^{2+} and Cu^{2+} .

Bond length

The bond length R_A (is the shortest distance between A site cations and oxygen ion) and R_B (is the shortest distance between

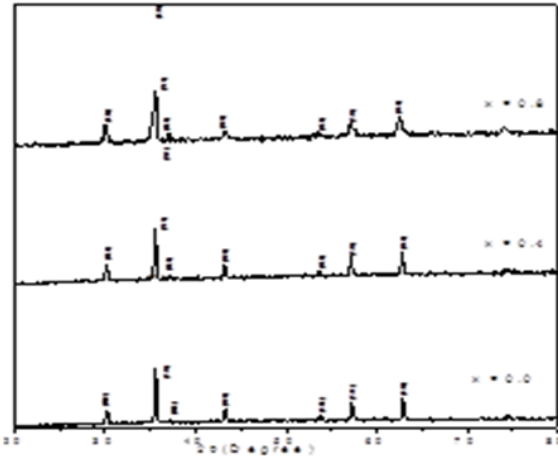


Fig.1: XRD Pattern of Ni_{1-x}Cu_xFe₂O₄

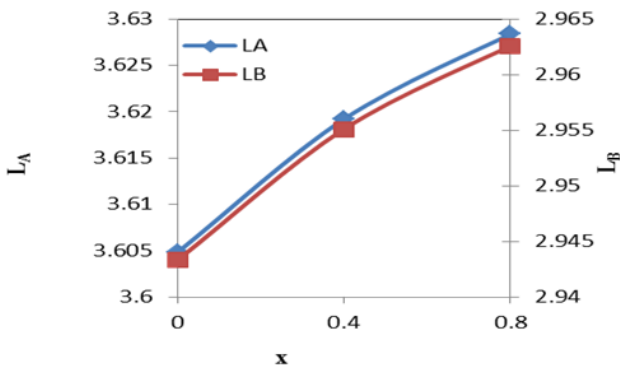


Fig.2: Variation of hopping length LA & LB with Cu content x of the series Ni_{1-x}Cu_xFe₂O₄

B site cations and oxygen ions) are calculated [9] and are given in Table 1. It is evident from Table 1 that the bond length RA and RB increases with Cu content x. The increase in bond length will be attributed to the increase in lattice constant 'a' with Cu content.

Table 1a: Lattice constant (a), Hopping length (LA, LB), Bond length (RA, RB) for Ni_{1-x}Cu_xFe₂O₄ (x=0.0-0.8) prepared by ceramic technique.

x	a (Å)	LA (Å)	LB (Å)	RA (Å)	RB (Å)
0.0	8.325	3.604	2.943	1.888	2.032
0.4	8.328	3.619	2.955	1.896	2.040
0.8	8.379	3.628	2.962	1.901	2.045

Table 1b: Tetrahedral bond (dAX), Octahedral bond (dBX), Tetra edge (dAXE), Octa edge (dBXE) for Ni_{1-x}Cu_xFe₂O₄ (x=0.0-0.8) prepared by ceramic technique.

x	dAX	dBX	dAXE	dBXE	
				Shared	Unshared
0	1.874	2.04	3.061	2.825	2.944
0.4	1.882	2.048	3.073	2.836	2.956
0.8	1.886	2.053	3.081	2.844	2.963

The values of tetrahedral and octahedral bond length dAX and dBX tetrahedral edge, shared and unshared octahedral edge (dAXE, dBXE and dBXEU) were estimated using the experimental values of lattice constant 'a', oxygen positional parameter 'u' (u = 0.381Å) and equations [10]. The values were represented in Table 1. It's evident from Table 1 that the tetrahedral edge and octahedral edges all increase as Cu content x increases. This is often attributed to the rise in lattice constant with the Cu content.

Table 2: Cation distribution of Ni_{1-x}Cu_xFe₂O₄

X	A-Site			B-Site		
	Ni ²⁺	Cu ²⁺	Fe ³⁺	Ni ²⁺	Cu ²⁺	Fe ³⁺
0	0	0	1	1	0	1
0.4	0	0.04	0.96	0.6	0.36	1.04
0.8	0	0.08	0.92	0.2	0.72	1.08

Cation distribution

The study of cation distribution in spinel ferrite is very important to know the magnetic behavior of the samples. Just in case of the spinel type space lattice, the divalent metal ions and trivalent iron ions occupy the tetrahedral (A) site and octahedral [B] site as per the provision of sites. This distribution of ions over these two sites is termed as cation distribution. The cation distribution is strongly dependent of warmth treatment, ionic radius, electronic configuration, electrostatic energy, methods of preparation etc. Diffraction [10] Neutron diffraction [11] and Mössbauer [12] are the techniques available to see the cation distribution. In the present work diffraction method has been used to study the cation distribution. In diffraction method, X-ray intensity ratios of a particular plane were calculated and compared there for intensity 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.

In this work X-ray intensity ratios of the chosen Bragg reflections (220), (400), (440) were calculated and compared them with the observed intensity ratios as these planes are structure sensitive [13]. The X-ray intensity (I) for a given reflection (hkl) will be calculated using the Buerger's formula [14]. The results of cation distribution data shows that even after substitution of copper, nickel ferrite retain its inverse spinel nature. Copper and ferric ions occupy both tetrahedral and octahedral sites whereas nickel can occupy only octahedral [B] site.

CONCLUSIONS

Using ceramic technique single phase cubic spinel structured samples of Ni_{1-x}Cu_xFe₂O₄ were obtained successfully. Substitution of copper (Cu²⁺) ions increases the structural parameters of the system. The cation distribution indicates that copper Cu²⁺ and iron Fe³⁺ occupies both tetrahedral A and octahedral B site where as Ni²⁺ occupies only octahedral B site.

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