STUDY OF STRUCTURAL PARAMETERS AND CATIONDISTRIBUTION OF NICKEL – COPPER SPINEL FERRITES

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Abstract:*Mixed Ni-Cu ferrites having the combination formula $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.0, 0.1, 0.2.) were synthesized by solid state reaction technique using AR grade oxides (NiO, CuO, Fe_2O_3). The formation of mono phase cubic spinel structure of all the samples under investigation have been carried out using X-ray diffraction technique at room temperature.Structural parameters and X-ray intensity ratios were calculated using XRD data for selected planes (220), (400), (440) and compared with the observed intensity ratios in order to obtain cation distribution. 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 copper substituted nickel ferrites.

Keyword:XRD, structural parameters, cation distribution.

1.INTRODUCTION

Spinel ferrites are commercially important materials because of their excellent electrical and magnetic properties. Interesting physical and chemical properties of ferrites arises from ability of these 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 range of applications from microwave to radio frequencies and are of importance from both fundamental and applied research point of view. [1,2]. The twin property of electrical insulator and magnetic conductor makes ferrites useful in many devices such as memory chips, transformer cores, and antenna rod, magnetic recording,microwave devices etc. Compared to other magnetic materials ferrites can be easily prepared, low cost and highly stable. The important electrical and magnetic properties of ferrites depend on various factors which include method of preparation, type, nature and amount of dopants etc [3, 4]. 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 important in order to understand the basic structural, electrical and magnetic properties of spinel ferrites. Among the spinel ferrites, nickel ferrite is having special attraction because of their useful properties such as inverse spinel nature, high saturation magnetization and Curie temperature, high electrical resistivity and chemically most stable. Copper is a Jahn Teller ion with magnetic moment one in the literature very few studies on copper substituted nickel ferrite are reported. Here, we report our results on structural and cation distribution studies of $Ni_{1-x}Cu_xFe_2O_4$ for x = 0.0, 0.1 and 0.2 samples.

2. EXPERIMENTAL

The polycrystalline samples of $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.0, 0.1, 0.2.) were prepared using the standard ceramic 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 carried out for each 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 thepowder of samples compressed into pellets of 10 mm diameter and about 1gm mass using a hydraulic press with pressure 6 ton/inch^2 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 in the 2θ range 20°-80°at room temperature to confirm single phase spinel structure. The cation distribution studies were carried out using X-ray diffraction method.

3. RESULTS AND DISCUSSION
3.1 XRD (X-RAY DIFFRACTION)
Mixed spinel ferrites system of $Ni_{1-x}Cu_xFe_2O_4$ (x = 0.0, 0.1, 0.2.) under investigation has been structurally investigated by X-ray diffraction. The XRD patternsshowed 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(a). It is observed from Table-1(a) that lattice constant increases very slowly with increase in copper content 'x'. The small variation in the lattice parameter with copper substitution can be explained on the basis of very close ionic radii of nickel (0.69Å) and copper (0.72Å) [6]. The ionic radii of nickel and copper are approximately close to each other and hence there is no much variation in the lattice constant.
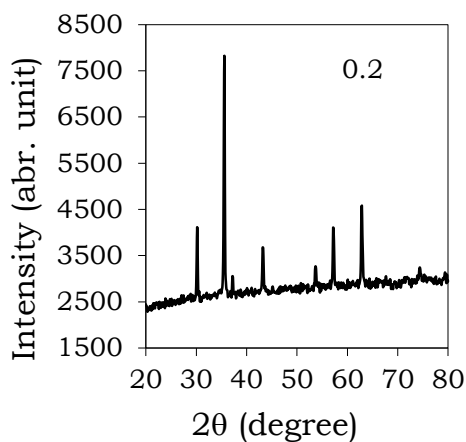

Fig.1 Typical XRD Pattern of $Ni_{1-x}Cu_xFe_2O_4$ for (x=0.2)

3.2 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 inTable1. Fig.2 shows the relation between the hoppinglengths in tetrahedral (A) and octahedral [B] sites asa function of Cu content x. Thedistance

between themagnetic ions increases as the Cu content x increases.This may be explained on the basis of differencein ionicradii of constituent ions Ni^{2+} and Cu^{2+}.
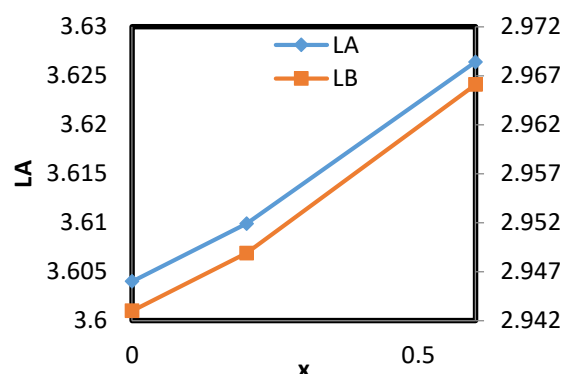

Fig.2 Variation of hopping length L_A& L_B withCu content x of the series $Ni_{1-x}Cu_xFe_2O_4$

3.3 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 B site cations and oxygen ions) have been calculated [9] and are given in Table 1.It is evident from Table 1(a)that the bond length R_A and R_B increases with Cu content x.The increase in bond length can be attributed to the increase in lattice constant 'a' with Cu content.

Table 1(a) Lattice constant (a) Hopping length (L_A, L_B)`Bond length(R_A, R_B) for $Ni_{1-x}Cu_xFe_2O_4$ (x=0.0, 0.1, 0.2)

x	a (Å)	L_A (Å)	L_B (Å)	R_A (Å)	R_B (Å)
0.0	8.325	3.604	2.943	1.888	2.032
0.1	8.328 5	3.609 9	2.946 9	1.89	2.03
0.2	8.374 8	3.626 4	2.958 1	1.9	2.04

Table 1(b)Tetrahedral bond(dAX) Octahedral Bond (dBX), Tetra edge(dAXE), Octa edge(dBXE), for Ni1.xCuxFe2O4 (x=0.0, 0.1, 0.2)

xd$_{AX}$	d$_{BX}$	d$_{AXE}$	d$_{BXE}$ Shared	d$_{BXE}$ Unshared
0.0 1.874	2.040	3.061	2.825	2.944
0.1 1.8753	2.041 3	3.062 4	2.8268	2.9457
0.2 1.8857	2.052 7	3.079 4	2.8425	2.9621

The values of tetrahedral and octahedral bond length d_{AX} and d_{BX} tetrahedral edge, shared and unshared octahedral edge (d_{AXE}, d_{BXE} and d_{BXEU}) were calculated using the experimental values of lattice parameter 'a', oxygen positional parameter 'u' (u = 0.381Å) and equations [10].The values were represented in Table 1(b),It is evident from Table 1 that the tetrahedral edge and octahedral edges all increases as Cu content x increase. This is attributed to the increase in lattice constant with the Cu content.

3.4 CATION DISTRIBUTION

The study of cation distribution in spinel ferrite is important to understand the magnetic behaviour of the samples. In case of the spinel type crystal lattice, the divalent metal ions and trivalent iron ions occupy the tetrahedral (A) site and octahedral [B] site as per the availability of sites. This distribution of ions over these two sites is called as the cation distribution. The cation distribution is strongly dependent of heat treatment, ionic radius, electronic configuration, electrostatic energy, methods of preparation etc. X-ray diffraction [10] Neutron diffraction [11] and Mössbauer [12] are the techniques available to determine the cation distribution. 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 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.

Table2: Cation distribution of $Ni_{1-x}Cu_xFe_2O_4$

x	A-Site			B-Site		
	Ni^{2+}	Cu^{2+}	Fe^{3+}	Ni^{2+}	Cu^{2+}	Fe^{3+}
0.0	0.0	0.00	1.00	1.0	0.00	1.00
0.1	0.0	0.02	0.98	0.8	0.18	1.02
0.2	0.0	0.06	0.94	0.4	0.54	1.06

In this work X-ray intensity ratios of the selected 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) can be calculated using the Buerger's formula [14]. The results of cation distribution data show 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.

4. CONCLUSIONS

Using ceramic technique single phase cubic spinel structured samples of $Ni_{1-x}Cu_xFe_2O_4$ were obtained successfully.Substitution of copper (Cu^{2+}) ions increases the structural parameters of the system.The cation distribution indicates that copper Cu^{2+} and iron Fe^{3+} occupies both tetrahedral (A) and octahedral [B] site where as Ni^{2+} occupies only octahedral [B] site.

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