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STRUCTURAL PROPERTIES OF ZINC AND ALUMINUM SUBSTITUTED CUPPER FERRITE PREPARED BY CERAMIC METHOD

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Abs tract:-The samples of $Cu_{0.6}Zn_{0.4}Al_xFe_{2-x}O_4$ ferrite system with ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) were prepared by the usual doubled sintering conventional ceramic technique. The powder samples were annealed at $900^\circ C$ for 24 hours and the samples were pressed into pellets of 10mm diameter are sintered at $1100^\circ C$ for 36 hours. The samples were studied by means of X-ray diffraction. The X-ray analysis showed that all the samples had single-phase cubic spinel structure. The variation of lattice constant with Cu^{2+} , Zn^{2+} and Al^{3+} concentration deviates from Vegard's law. The cation distribution estimated from X-ray intensity ratio calculations suggest that, Zn^{2+} ions occupies tetrahedral (A) site and Al^{3+} , Cu^{2+} ions at octahedral [B] sites..

Keyw ords:Ferrite, Ceramic Method, Lattice constant.

1.INTRODUCTION

Crystalline Cu-Zn spinel ferrites have been investigated extensively due to their potential application in non resonant devices, radio frequency circuits, high quality filters, rod antennas, transformer cores, read and write heads for high speed digital tapes and operating devices [1]. Studies on structural, electrical and magnetic properties of Cu-Zn ferrite been reported by many workers [2-6]. The variation of magnetization and Mossbauer study of Cu-Zn ferrite with different Zn concentration has been carried out recently by Rezelescu [7], Cuciurenau [8] related Curie point to cation distribution in Cu-Zn ferrites Evans et.al.[9] have studied magnetic properties of Cu-Zn ferrites by Mossbauer spectroscopy. From these studies on Cu-Zn ferrites, the ferrite having the composition $Cu_{0.6}Zn_{0.4}Fe_{2-x}O_4$ have been taken as a base for investigation for the present work, as it shows a maximum value of magnetization for $Cu_{1-x}Zn_xFe_2O_4$ system.

The aim of the present paper is to look into the effect of substitution nonmagnetic Al^{3+} on the structural and magnetic properties of $Cu_{0.6}Zn_{0.4}Al_xFe_{2-x}O_4$ system with ($x=0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) prepared by conventional double sintering ceramic method. The structural studies and phase purity of the samples have been investigated using powdered X-ray diffraction data. The unit cell parameters were determined and the respective X-ray densities were calculated for all the samples of the present system. The intensities of Bragg peaks have been used to determine the most probable cation distribution.

2. EXPERIMENTAL:

The polycrystalline samples of Al^{3+} substituted

$Cu_{0.6}Zn_{0.4}Al_xFe_{2-x}O_4$ system ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0) were prepared by conventional ceramic technique. The starting materials were Fe_2O_3 , CuO , ZnO , Al_2O_3 supplied by E-Merck. The oxides were mixed thoroughly in stoichiometric proportions to get the desired composition and wet ground using acetone as the medium. The mixture was dried and pressed it to form pallets. The pellets were fired at $900^\circ C$ for 24 hours and cooled slowly to room temperature. The samples were again finely powdered and pressed into pellets of 10mm diameter by applying a pressure of 5 tones per sq. inch. The pellets were finally sintered at $1100^\circ C$, for 36 hours and were cooled to room temperature in air using the temperature controlled carbolyte furnace. The pallets were found to be crack free, flat and hard.

The x-ray powder diffraction data were recorded at room temperature using Cu-K radiation on Philips X-ray diffractometer (model PW 3710). The x-ray diffraction patterns exhibit sharp Bragg peaks corresponding to single phase spinel structure for all the samples and which thus confirmed the phase purity for all the samples prepared. The x-ray diffraction data were recorded between the 2θ range 0° to 80° with a rate 0.50° / minute at room temperature. The lattice constants were determined and their respective x-ray densities were calculated.

3. RESULTS AND DISCUSSIONS:

XRD analysis:

The room temperature X-ray diffraction patterns showed sharp lines corresponding to single phase structure for all the samples. Fig (1) represent the X-ray diffractograms for $x=0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 samples. The values of lattice parameter are determined from X-ray

data with an accuracy of $\pm 0.002 \text{ \AA}$ and are summarized in Table 1. The lattice parameter decreases linearly with increase in Al^{3+} concentration as shown in Fig 2 This variation of lattice parameter 'a' with 'x' can be explained on the basis of ionic radii of substituted ions [10]. The observed decrease in 'a' with x is due to the replacement of large ionic crystal radius of Fe^{3+} (0.64 \AA) by smaller Al^{3+} (0.50 \AA). The X-ray density 'd' for all the samples was calculated using the ion [11].

$$d_x = ZM / NV \quad (1)$$

where, Z is the number of molecules per unit cell ($Z=8$), M is the molecular weight, N is the Avogadro's number and V is the volume of unit cell ($V=a^3$). The values of X-ray density 'd' represented in table 1 shows a linear decrease in 'dx' with increase in Al^{3+} concentration. This is due to decrease in mass overtakes the decrease in volume of the unit cell. The Table 1 also represents the percent porosity 'p%' for the system. The cation distribution in spinel ferrites can be obtained from the analysis of X-ray diffraction [12], Mossbauer effect [13] and Magnetization [14]. In the present work the cation distribution is estimated from magnetization (300 K) and X-ray intensity analysis. In order to determine the cation distribution, X-ray intensity calculations were carried out and compared with observed data. The ratio of intensities of reflections due to the planes (220) and (440) has been chosen as a criterion to determine the cation distribution. The X-ray intensities were determined according to the formula suggested by Burger [15]

$$I_{hkl} = |F_{hkl}|^2 P.L_p \quad (2)$$

where I-is the relative intensity, F-is the multiplicity factor for plane hkl and L_p is the Lorentz polarization factor.

$$L_p = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \quad (3)$$

The formulae for structure factors for the planes (hkl) given by Furahashi et.al [16] have been used. The formulae for the multiplicity factor and Lorentz polarization factors are taken from literature [17]. In the present system $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{AlFe}_{2-x}\text{O}_4$ of ferrites variation of Al^{3+} concentration 'x' results in replacement of $x\text{Fe}^{3+}$ ions by $x\text{Al}^{3+}$ ions. In accordance with the site preference energies, Zn^{2+} occupy (A) site Cu^{2+} , Al^{3+} occupy [B]- site and Fe^{3+} ions shows no definite site preference [18]. The distribution of the divalent and trivalent cations amongst tetrahedral (A) and octahedral [B] sites in the as $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{AlFe}_{2-x}\text{O}_4$ determined from the intensity ratio of X-ray diffraction lines. The results of X-ray intensity calculation for various possible models have been tried and were compared with observed intensity ratios. The cation distribution estimated from the X-ray diffraction intensity ratio calculation are summarized in Table 2 showing the occupancy of Al^{3+} , Cu^{2+} ions at octahedral [B] site, where as Zn^{2+} ions occupy tetrahedral site. A-site

concentration of Fe^{3+} ions remains unaffected by the substitution of Al^{3+} in $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{AlFe}_{2-x}\text{O}_4$

The ionic radii r_A and r_B are the ionic radii of tetrahedral (A) and octahedral [B] site ions respectively. These r_A and r_B are used to calculate the theoretical values of lattice parameter a_{th} as

$$a_{th} = \frac{8}{3\sqrt{3}} (r_A + R_0) = \sqrt{3} \cdot (r_B + R_0) \quad (4)$$

The particle size 't' is given by

$$t = \frac{0.9}{B \cos \theta} \quad \text{with } B^2 = B_a^2 = B_b^2 \quad (5)$$

Where, t - is diameter of crystal particle, λ - is wavelength of the X-ray radiation, θ - is Bragg's angle, B - is measure of broadening of diffraction due to size effect B and B_a, B_b are full width at half maxima of the XRD line of the sample and standard specimen respectively.

4. CONCLUSION

Conventional ceramics method plays an important role in governing the properties of the ferrite system. The samples show single phase cubic structure. The X ray patterns were used to determined lattice parameter and structure factors were used to develop the cation distribution for these systems. The results obtained are in good agreement with theoretical results obtained.

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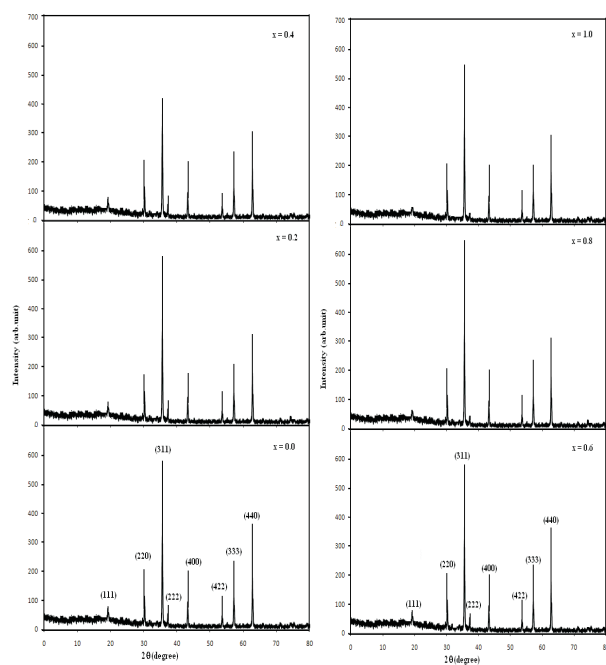


Fig. 1: The X-ray diffraction pattern for the $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{AlFe}_{2-x}\text{O}_4$ system ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0)

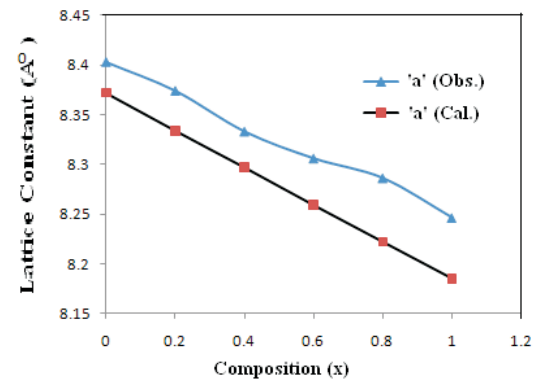


Fig 2: Variation of observed and calculated lattice constant with Al^{3+} concentration of the system $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{AlFe}_{2-x}\text{O}_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0)

Table 1: Lattice constant 'a', X-ray density 'd_x' and porosity P% for the $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{AlFe}_{2-x}\text{O}_4$ system

x	Lattice Constant a (Å)		X-ray density d _x (gm/cm ³)	Porosity p%	Particle size t (Å ⁰)
	a (Obs) (Å)	a _h (Cal.) (Å)			
0.0	8.403	8.372	5.37	14.7	213
0.2	8.374	8.334	5.30	13.8	192
0.4	8.333	8.297	5.24	17.3	439
0.6	8.306	8.259	5.16	17.9	358
0.8	8.286	8.222	5.06	21.1	185
1.0	8.246	8.185	5.00	32.0	185

Table 2: Cation distribution and comparison of X-ray intensity ratios for the $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{AlFe}_{2-x}\text{O}_4$ system.

(x)	A-site	B-site	I(400)/I(440)		I(400)/I(422)		I(422)/I(440)	
			Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0.0	(Zn _{0.4} Fe _{0.6})	[Al _{0.0} Cu _{0.6} Fe _{1.4}]	0.44	0.43	1.92	1.96	0.23	0.22
0.2	(Zn _{0.4} Fe _{0.6})	[Al _{0.2} Cu _{0.6} Fe _{1.2}]	0.42	0.56	1.75	1.33	0.24	0.41
0.4	(Zn _{0.4} Fe _{0.6})	[Al _{0.4} Cu _{0.6} Fe _{1.0}]	0.39	0.37	1.56	1.26	0.25	0.29
0.6	(Zn _{0.4} Fe _{0.6})	[Al _{0.6} Cu _{0.6} Fe _{0.8}]	0.38	0.42	1.41	1.37	0.27	0.30
0.8	(Zn _{0.4} Fe _{0.6})	[Al _{0.8} Cu _{0.6} Fe _{0.6}]	0.33	0.59	1.25	1.61	0.26	0.36
1.0	(Zn _{0.4} Fe _{0.6})	[Al _{1.0} Cu _{0.6} Fe _{0.4}]	0.31	0.45	1.13	1.35	0.27	0.33

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