Structural investigation of aluminium substituted zinc ferrites

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Abstract

Aluminium doped zinc ferrites $ZnAl_xFe_{2-x}O_4$ with $0.0 \leq x \leq 0.4$ were synthesized solid state reaction route. The single phase formation of the ferrite samples were confirmed by X-ray diffraction measurements. The lattice parameter is found to decrease linearly with aluminium ion substitution due to smaller ionic radius of aluminium. The experimental and theoretical lattice parameter, X-ray density, bulk density and porosity have been determined. The cation distributions have been estimated from X-ray intensity calculations. The present studies indicating that the zinc ferrite exhibits a normal spinel structure when diluted with aluminium ions

1. Introduction

Spinel ferrites are the most widely used in many applications including magnetic recording, ferofluids, magnetic resonance imaging (MRI) [1]. Zinc ferrite has a normal spinel structure with a tetrahedral A-site occupied by Zn^{2+} ions and octahedral B-site by Fe^{3+} ions [2]. The magnetic properties of these ferrite systems depend on the type of cations and their distribution among the interstitial sites i.e. tetrahedral (A) and octahedral (B)-sites. Additions of diamagnetic ion in single or mixed ferrites have received a great deal of attention over the past few years. The addition of non-magnetic ions in a spinel ferrite is found to alter their magnetic properties. The cation distribution in aluminum substituted spinel ferrites have been already estimated by several workers [3-5]. The present work deals with the synthesis and estimation of cation distribution in aluminium substituted zinc ferrites by using X-ray diffraction measurements.

2. Experimental Details

The ferrite system; $ZnAlxFe2_{-x}O_4$ for x = 0.0, 0.1, 0.2, 0.3 & 0.4 were synthesized using standard solid-state reaction route reported earlier [4]. To ensure the single-phase formation of the ferrite system, the powder X-ray diffraction studies were made using Cu-K_α radiations of wavelength 1.5406 Å.

3. Results and Discussion

The X-ray diffraction pattern of $ZnAl_xFe_{2-x}O_4$ ferrite system for x = 0.0, 0.1, 0.2, 0.3 & 0.4 are displayed in Figure 1.

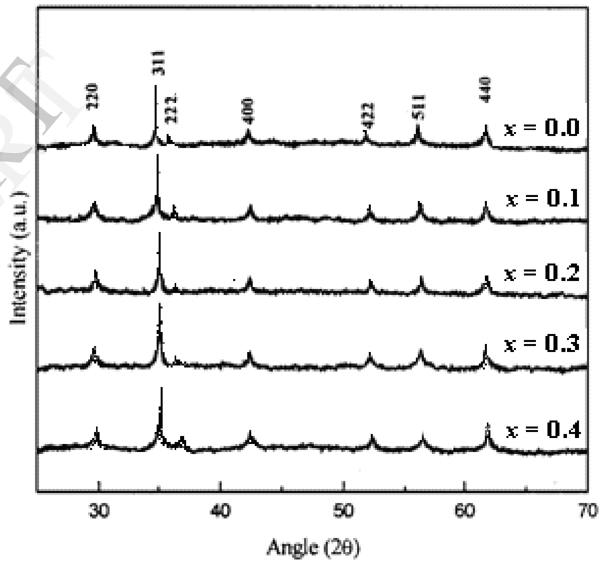

Figure 1: X-ray diffraction pattern of $ZnAl_xFe_{2-x}O_4$ system

The indexing of diffraction lines from various planes was assigned using JCPDS file No. 22-1012. All the samples were found to be face cantered cubic (fcc) with Fd-3m (227) space group. The values of lattice constant a_{ob} (Å) for all samples from X-ray data are listed in Table 1. The lattice parameters 'a_{ob}' decreases linearly with increase in aluminum content (x) is attributed to the replacement of Fe^{3+} ions of radius 0.67 Å by Al^{3+} ions of radius 0.51 Å, causing the shrinking in the unit cell dimensions.

Table 1: Lattice parameters for $ZnAl_xFe_{2-x}O_4$ system.

Composition (x)	Lattice constant (±0.002) a_{obs}	a_{th}	X-ray density (±0.002)(gm/cm^3) d_x	d	Porosity P (%)	Volume 'Å^3'
0.0	8.443	8.316	5.326	5.102	7.264	601.85
0.1	8.432	8.293	5.283	5.002	6.983	599.50
0.2	8.421	8.271	5.237	4.732	6.857	597.16
0.3	8.408	8.248	5.199	4.691	6.790	594.39
0.4	8.397	8.226	5.154	4.613	6.810	592.09

The bulk density of the each sample was determined by Archimedes's principle, while the X-ray density was calculated from the values of the lattice parameter using the formula

$$dx = \frac{ZM}{Na3} \qquad (1)$$

where 'Z' represents the number of molecules in a unit cell of the spinel lattice, M, the molecular weight of the ferrite samples, N, the Avogadro's number and a, the lattice constant of the ferrite system. It is observed that X-ray density d_x decreases with increasing aluminium content 'x', this is because the decrease in mass overtakes the decrease in volume of the unit cell. The percentage porosity of each sample was calculated by the following equation

$$(p\%) = [1 - \frac{d}{dx} \times 100] \qquad (2)$$

where, d_x is the X-ray density and d is the bulk density of the samples. The observed values of porosity lie with in the range, which are generally observed in ferrites. The X-ray intensities of (220), (400) and (440) planes are sensitive to the cations on tetrahedral (A) and octahedral (B) sites, therefore, the intensities of these planes were used to determine the cation distribution. The X-ray intensity were calculated using formula [6]

$$I_{hkl} = |F_{hkl}|^2.P.L_p \qquad (3)$$

Where I_{hkl} is the relative integral intensity; F_{hkl} the structure factor; P is the multiplicity factor; Lp the Lorentz factor. The structure factors were calculated by using the equation suggested by Porta and Furhashi et al [7-8]. The multiplicity and Lorentz factors were taken from the literature [9]. The ionic scattering factor reported in international tables for X-ray crystallography [10] is used for the calculation of structure factor. It is well known that the intensity ratios (I_{220}/I_{440}) and (I_{400}/I_{440}) are considered more sensitive to the cation distribution [11]. The intensity ratios of these planes were calculated for various cation distributions using the following relation reported earlier [4]

$$(I_{hkl}/I_{h'k'l'})_{Expt.} = (I_{hkl}/I_{h'k'l'})_{cal.} \qquad (4)$$

The decrease in lattice parameters 'a' and the shift of peaks towards higher angle with increasing aluminium contents suggest that aluminium atoms have been incorporated into the spinel structure [3]. Fig. 1 shows that with increasing aluminium concentration, the intensities of these reflections as compared to (311) peak, decreases indicating that Al^{3+} ions enter in octahedral site. Based on the above, intensity ratios for these planes were calculated for various cation distributions and that closet to experimental data are given in Table listed below

Table 2: Cation distribution data calculated from XRD pattern of the $ZnAl_xFe_{2-x}O_4$ system.

Composition (x)	Cation distribution	X-ray Intensity $I_{(220)}/I_{(440)}$ Exp.	Cal.	$I_{(400)}/I_{(440)}$ Exp.	Cal
0.0	$(Zn)^A[Fe_{2.00}]^B O_4$	0.9846	0.9973	0.4904	0.4632
0.1	$(Zn)^A [Fe_{1.9}Al_{0.1}]^B O_4$	0.9758	0.9517	0.4926	0.4705
0.2	$(Zn)^A [Fe_{1.8}Al_{0.2}]^B O_4$	0.9403	0.9635	0.4863	0.4819
0.3	$(Zn)^A [Fe_{1.7}Al_{0.3}]^B O_4$	0.9582	0.9576	0.4574	0.4420
0.4	$(Zn)^A [Fe_{1.6}Al_{0.4}]^B O_4$	0.9726	0.9698	0.4738	0.4285

On the basis of estimated cation distribution, the theoretical lattice parameter a_{th} can be determined using the following relation

$$a_{th} = \frac{8}{3\sqrt{3}}(rA + ro) + \sqrt{3}(rB + ro) \qquad (5)$$

where r_A & r_B are the radius of the A & B-sites respectively. and r_o is the radius of the oxygen ion O^{2-} (1.48 Å). The calculated values of theoretical lattice parameter (a_{th}) are nearly equal to experimental observed values of lattice parameter (a_o) which confirm that the estimated cation distribution is correct one. These results are similar to those reported earlier [12].

4. Conclusion

Aluminium substituted zinc ferrites have been synthesized by usual double ceramic route. The unit cell parameter decreases linearly with the increase of aluminium concentration (x) due to small ionic radius. The experimental and theoretical lattice parameter, X-ray density; bulk density and porosity were found affected on addition of aluminium ions. The cation distribution obtained from X-ray intensity calculations suggests that the present ferrite system exhibits a normal spinel structure.

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