



Cation distribution in nanocrystalline Al³⁺ and Cr³⁺ co-substituted CoFe₂O₄

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ABSTRACT

CoAl_xCr_xFe_{2-2x}O₄ spinel ferrite systems (where $x = 0.1$ to 0.5 in steps of $x = 0.1$) were synthesized by wet chemical co-precipitation technique, aiming to study the relationship between cation distribution and concentration of the simultaneous substitution of Al³⁺ and Cr³⁺ ions. The Al³⁺ and Cr³⁺ site occupancies show nearly linear composition dependence. The obtained results show, that both Al³⁺ and Cr³⁺ ions predominately occupy the octahedral B-site. This is consistent with their preference for large octahedral site energy. The concentration of Al³⁺ and Cr³⁺ ions in octahedral sites increases while that of Fe³⁺ ions decreases linearly.

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1. Introduction

Magnetic ferrites are a group of technologically important magnetic materials. Synthesis of nanocrystalline spinel ferrite has been investigated intensively in recent years due to their potential applications in high-density magnetic recording, microwave devices, and magnetic fluids [1]. The interesting properties of ferromagnetic spinels of the general formula AB₂O₄ originate mainly from the magnetic interactions between cations with magnetic moments that are situated in the tetrahedral (A) and the octahedral [B] sites.

The properties like cation distribution and magnetic interactions play an important role in determining the utility of these materials and as such have their scientific importance. Determination of cation distribution between the tetrahedral and octahedral for spinel ferrites has been a subject of many studies [2–4], since theoretical interpretation of the chemical and physical properties (e.g. magnetic, semiconducting, catalytic, etc.) of these compounds rests on the sites assigned to the cations. The cation distribution in spinel ferrite can be obtained by X-ray diffraction. The Bertaut [5], Furuhashi [6], and Baltzer [7] methods are all based on a comparison between the diffraction intensities observed experimentally and those calculated for a large number of hypothetical crystal structures. Additionally, thermoelectric measurements [8], neutron diffraction [9], and electron spin resonance [10] are also used to study the cation distribution.

In our previous report [11] we prepared cobalt aluminum chromium ferrites by double sintering technique. It was concluded that, magnetization measurements exhibit non-collinear ferrimagnetic structure for $x > 0.3$. Nakatsuka et al. [12] calculated cation distribution and bond lengths in CoAl₂O₄ using Rietveld analysis and found that CoAl₂O₄ is largely inverse spinel, local bond length on A-site abnormally long and repulsion between B-site cations considerably large.

The present work reports cation distribution study from X-ray diffraction patterns for the spinel system CoAl_xCr_xFe_{2-2x}O₄ ($x = 0.1$ to 0.5 in steps of $x = 0.1$), where a large number of cations have been selected in which some of the cations are neighbours in the periodic table. For such systems XRD is the most suitable method for the determination of the exact cation distribution and other crystallographic parameters. The progressive substitution of Fe ions by Al and Cr ions introduces changes in the cation distribution in the spinel compounds.

2. Experimental

The samples of the CoAl_xCr_xFe_{2-2x}O₄ systems ($x = 0.1$ to 0.5 in steps of $x = 0.1$) were prepared by wet chemical co-precipitation method. Mixed oxide powders were produced from aqueous solution containing Co, Al, Cr and Fe sulphates. The starting solution prepared by mixing 50 ml of aqueous solutions of FeSO₄·7H₂O, CoSO₄·7H₂O, Al₂(SO₄)₃·16H₂O, Cr₂(SO₄)₃·6H₂O in stoichiometric proportions. Here for $x = 0$, Co and Fe are in the 1:2 ratio. In the present work we have assumed the molarity of Co as 0.25 M and hence the molarity of Fe is 0.5 M. A 2 M solution of sodium hydroxide was prepared as a precipitant. The starting solutions were added into the precipitant because of the cation is exceeded and sequential precipitation of the hydroxides can be avoided. The suspension (pH = 11) containing dark green intermediate precipitant was produced. The two solutions were mixed with stirring and maintaining the temperature at 60 °C for about 1 h. Simultaneously H₂O₂ was

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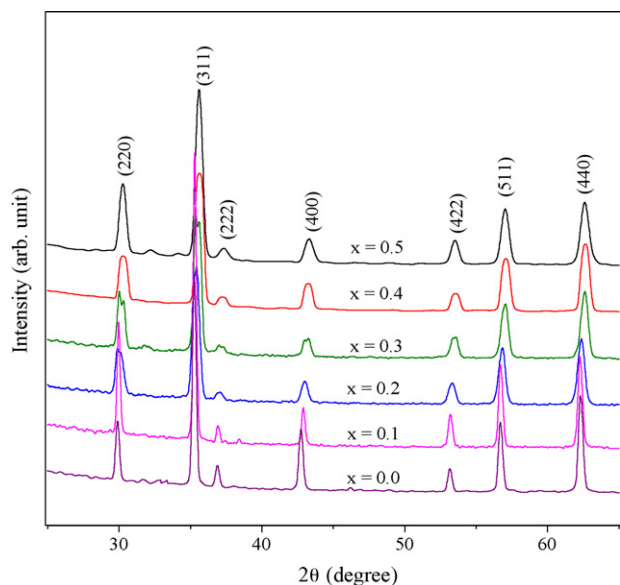


Fig. 1. XRD pattern of $\text{CoAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$.

added in order to bubbling of oxygen into suspension and to promote the oxidation reaction, until all the intermediate precipitates change into the dark brownish precipitates of the desired spinel ferrite. The samples are filtered, washed by distilled water several times and by acetone and dried at 150°C under vacuum. The wet samples of Co–Al–Cr–Fe ferrites were annealed in air at 800°C for 24 h.

The powder X-ray diffraction (XRD) pattern for all the samples were recorded at room temperature on Philips X-ray diffractometer (Model 3710) using $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$). The scanning (2θ) range was $20\text{--}80^\circ$ with a step size of 0.02° and 4 s per scan. The X-ray generator was operated at 40 kV and 30 mA. A specially processed Si powder sample was used for instrumental standard. The (1 1 1) reflection of Si at around 28.5° indicates that the instrumental broadening is very small (0.5 \AA).

3. Results and discussion

The X-ray diffractogram of all the samples are presented in Fig. 1. The presence of planes (2 2 0), (3 1 1), (2 2 2), (4 4 0), (4 2 2), (5 1 1) and (4 4 0) in the diffractograms confirms the formation of cubic spinel structure. The values of lattice parameter 'a' were determined using XRD data with an accuracy of $\pm 0.002\text{ \AA}$. It is observed that lattice parameter goes on decreasing from 8.391 \AA ($x = 0.0$) to 8.291 \AA ($x = 0.5$) with increasing Al–Cr content x . The decrease of 'a' with increase in x is because of the fact that the larger ionic radii of Fe^{3+} (0.67 \AA) are replaced by smaller ionic radii of Al^{3+} (0.51 \AA) and Cr^{3+} (0.63 \AA) simultaneously. The particle size calculated using the Scherrer equation ($t = 0.9\lambda/\beta \cos \theta$) and it is in the range of 18–30 nm. The mean ionic radius of the tetrahedral (A) and octahedral [B] site (r_A and r_B) can be calculated by the following relation

$$r_A = (1 - (x - y - z))r\text{Fe}^{3+} + (x - y - z)r\text{Cr}^{3+} + z\text{Al}^{3+} \quad (1)$$

$$r_B = (1 - (x - y - z))r\text{Fe}^{3+} + yr\text{Cr}^{3+} + r\text{Co}^{2+} + (y - z)r\text{Al}^{3+} \quad (2)$$

where y and z are the concentration of Cr^{3+} and Al^{3+} ions, respectively.

Using the values of 'a', the radius of oxygen ion $R_0 = 1.32\text{ \AA}$ and r_A in the following expression, the value of the oxygen positional parameter 'u' can be calculated using the following relation [13]

$$r_A = \left(u - \frac{1}{4}\right)a\sqrt{3} - R_0 \quad (3)$$

The relation between oxygen position parameter (u), mean ionic radius of the A-site (r_A) and of the B-site (r_B) with Al–Cr is shown in

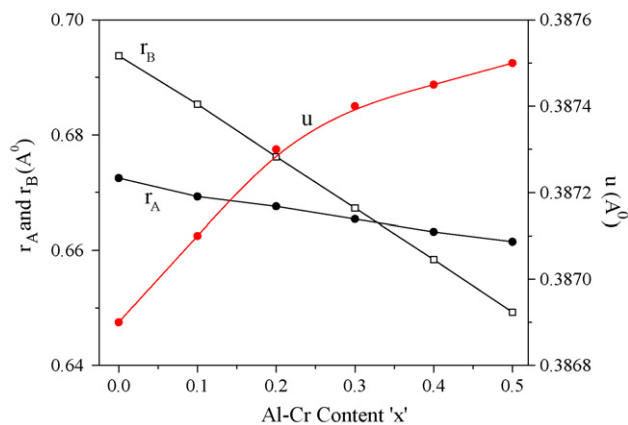
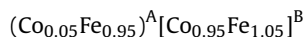


Fig. 2. Variation of ionic radius (r_A and r_B) and oxygen parameter 'u' with Al–Cr content x .

Fig. 2. The decrease in ' r_B ' may be due to the increasingly occupation of the smaller ionic radii of Al^{3+} (0.51 \AA) and Cr^{3+} (0.63 \AA) ions to the B-sites instead of Fe^{3+} (0.67 \AA) ions. The slow decrease in r_A is due to the addition of Al^{3+} instead of Fe^{3+} ions and migration of Co^{2+} from B-site to A-site. 'u' increases as a function of x . This observation may be due to the correlation between the ionic radius and the lattice parameter.

Since cobalt aluminates (CoAl_2O_4) is partially inverted spinel, Al^{3+} can occupy both tetrahedral (A) and octahedral [B] sites. On the other hand cobalt chromate (CoCr_2O_4) is normal spinel, Cr^{3+} occupy only octahedral [B] site, as Cr^{3+} has strong preference for octahedral site. Fe^{3+} ions can occupy both tetrahedral A and octahedral B sites. Comparing the site preference energy of the constituent ions [14], the cation distribution for pure cobalt ferrite (CoFe_2O_4) has been accepted as,



The cation distribution in the present system was obtained from the analysis of X-ray diffraction patterns. In this method the observed intensity ratios were compared with the calculated intensity ratios. In the present study Bertaut method [5] is used to determine the cation distribution. This method selects a few pairs of reflections according to the expression

$$\frac{I_{hkl}^{\text{Obs.}}}{I_{h'k'l'}^{\text{Obs.}}} \propto \frac{I_{hkl}^{\text{Calc.}}}{I_{h'k'l'}^{\text{Calc.}}} \quad (4)$$

where $I_{hkl}^{\text{Obs.}}$ and $I_{hkl}^{\text{Calc.}}$ are the observed and calculated intensities for reflection (hkl), respectively.

In this method the best information on cation distribution is achieved when comparing experimental and calculated intensity ratios for reflections whose intensities (i) are nearly independent of the oxygen parameter, (ii) vary with the cation distribution in opposite ways and (iii) do not differ significantly.

In the present work the reflections (2 2 0), (4 0 0), (4 4 0) were used to calculate intensity ratio. These planes are assumed to be sensitive to the cation distribution [15–17]. These planes are assumed to be sensitive to the cation distribution. The temperature and absorption factors are not taken into account in our calculations as they do not affect the intensity calculation. If an agreement factor (R) is defined as in Eq. (5), the best-simulated structure which matches the actual structure of the sample will lead to a minimum value of R and the corresponding cation distribution is obtained for each hkl and $h'l'k'$ reflection pair considered.

$$R = \left| \left(\frac{I_{hkl}^{\text{Obs.}}}{I_{h'k'l'}^{\text{Obs.}}} \right) - \left(\frac{I_{hkl}^{\text{Calc.}}}{I_{h'k'l'}^{\text{Calc.}}} \right) \right| \quad (5)$$

Table 1
Observed and calculated X-ray intensity ratio of $\text{CoAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$.

x	Intensity ratio					
	I_{220}/I_{440}		I_{400}/I_{440}		I_{220}/I_{400}	
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.
0.0	0.251	0.512	0.396	0.496	0.596	1.069
0.1	0.260	0.594	0.420	0.502	0.619	1.183
0.2	0.413	0.626	0.250	0.453	1.652	1.381
0.3	0.436	0.600	0.263	0.461	1.659	1.300
0.4	0.487	0.642	0.455	0.477	1.071	1.346
0.5	0.692	0.649	0.539	0.472	1.282	1.376

The intensities of these are nearly independent of the oxygen parameters. The calculations were made for various combinations of cations.

To determine the cation distribution and its variation with composition, it is necessary to calculate for each composition the above mentioned intensity ratios expected for given arrangements of the cations and compare them with the experimental values. For the calculation of the relative integrated intensity of a given diffraction line from powder specimens as observed in a diffractometer with a flat-plate sample holder, the following formula is valid

$$I_{hkl} = |F_{hkl}|^2 P \cdot L_P \quad (6)$$

where F is structure factor, P is multiplicity factor, L_P the Lorentz polarization factor and

$$L_P = \frac{1 + \cos^2 2\theta}{\sin^2 \cos 2\theta} \quad (7)$$

The atomic scattering factor for various ions was taken from the literature [10].

It should be added that the calculated integrated intensities are valid at 0 K. Since the observed values are obtained at room temperature, a suitable correction is in principle necessary for the precise comparison. However, the spinels are high-melting compounds, the thermal vibration of the atoms at room temperature should not differ greatly from that at absolute zero. Therefore, in our intensity calculations no temperature correction was deemed necessary.

The intensity ratios have been calculated for various combinations of cations and were compared with observed intensity ratio and those agree are compiled in Table 1. The cation distribution for each concentration and the site preferences of cations distributed among tetrahedral A-site and octahedral B-site showing the fraction of Al^{3+} and Cr^{3+} ions on either sites are listed in Table 2. It

Table 2
Cation distribution of $\text{CoAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$.

x	Cation distribution	
0.0	$(\text{Co}_{0.05}\text{Fe}_{0.95})^A$	$[\text{Co}_{0.95}\text{Fe}_{1.05}]^B$
0.1	$(\text{Co}_{0.05}\text{Al}_{0.02}\text{Fe}_{0.93})^A$	$[\text{Co}_{0.95}\text{Cr}_{0.1}\text{Al}_{0.08}\text{Fe}_{0.87}]^B$
0.2	$(\text{Co}_{0.08}\text{Al}_{0.04}\text{Fe}_{0.88})^A$	$[\text{Co}_{0.92}\text{Cr}_{0.2}\text{Al}_{0.16}\text{Fe}_{0.72}]^B$
0.3	$(\text{Co}_{0.10}\text{Al}_{0.06}\text{Fe}_{0.84})^A$	$[\text{Co}_{0.90}\text{Cr}_{0.3}\text{Al}_{0.24}\text{Fe}_{0.56}]^B$
0.4	$(\text{Co}_{0.12}\text{Al}_{0.08}\text{Fe}_{0.80})^A$	$[\text{Co}_{0.88}\text{Cr}_{0.4}\text{Al}_{0.32}\text{Fe}_{0.40}]^B$
0.5	$(\text{Co}_{0.15}\text{Al}_{0.1}\text{Fe}_{0.75})^A$	$[\text{Co}_{0.85}\text{Cr}_{0.5}\text{Al}_{0.40}\text{Fe}_{0.25}]^B$

can be seen that both Al^{3+} and Cr^{3+} ions predominately occupy the octahedral sites, which is consistent with their preference for large octahedral site energy. With increasing Al^{3+} and Cr^{3+} content, the fraction of Al^{3+} and Cr^{3+} ions in octahedral sites increases, while Fe^{3+} ions in octahedral sites decreases linearly.

4. Conclusions

The distribution of cations in the $\text{CoAl}_x\text{Cr}_x\text{Fe}_{2-2x}\text{O}_4$ system has been studied using Bertaut method by analyzing the locations of ions in the ideal spinel. This study revealed that, with the addition of Al^{3+} and Cr^{3+} , the Al^{3+} and Cr^{3+} ions predominately occupied the octahedral sites, which are correlated to their preference for large octahedral site energy. Correspondingly, the fraction of Fe^{3+} ions in octahedral sites decreases linearly.

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