Structural and electrical properties of the system ZnFeMnO_4 - GaCoMnO_4

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Abstract. X-ray crystallographic and electrical conductivity studies of the system ZnFeMnO_4 - GaCoMnO_4 were carried out with a view to investigating the cation distribution. The system is tetragonal in the range of $0 \leq x \leq 20$ and cubic in the range $40 \leq x \leq 100$ (where x denotes the mole percentage of GaCoMnO_4). The plot of $V^{1/3}$ vs. composition shows a break at the transition region. The value of oxygen ion parameter (u) decreases with increase in concentration of Ga^{3+} at A-site. The electrical resistivity-temperature behaviour obeys Wilson's law. Thermoelectric coefficient (α) values vary between 37 and 230 $\mu\text{V/K}$. The mobility of holes calculated from IR and conductivity data is of the order of $10^{-9}\text{cm}^2/\text{V-sec}$. X-ray intensity calculations and conductivity measurements suggest the ionic configuration of the system to be, $\text{Zn}^{2+}_{1-x}\text{Ga}^{3+}_x [\text{Fe}^{3+}_{1-x}\text{Co}^{2+}_x\text{Mn}^{3+}] \text{O}_4^{2-}$

Keywords. Crystal structure; oxygen ion parameter; electrical resistivity; activation energy; thermoelectric coefficient.

1. Introduction

Spinel (AB_2O_4) show interesting structural, electrical and magnetic properties (Blasse 1964; Goodenough 1966; Rao and Subba Rao 1970). In these compounds properties are controlled by the nature of ions, their charge and site distribution amongst eight tetrahedral and sixteen octahedral sites. Based on the literature it is observed that the ionic configuration of gallium cobalt manganite reported from magnetic measurements is $\text{Ga}^{3+}[\text{Co}^{2+}\text{Mn}^{3+}]\text{O}_4^{2-}$ (Bongers 1957) while recently x-ray spectroscopic study suggested its configuration as $\text{Ga}^{3+}[\text{Co}^{3+}\text{Mn}^{2+}]\text{O}_4^{2-}$ (Kulkarni *et al* 1974). The above results indicate ambiguity in the ionic configuration of GaCoMnO_4 . The problem of ionic configuration of this compound can be decided if one arrives at the definite oxidation state of manganese as it plays an important role in structural and electrical properties. We have attempted

to examine this problem with the help of electrical conductivity and x-ray studies in the case of the ZnFeMnO_4 - GaCoMnO_4 system.

2. Materials and methods

The end members ZnFeMnO_4 and GaCoMnO_4 were first synthesized from appropriate mixture of high purity component oxides by solid state reaction using standard ceramic technique. For the preparation of solid solutions, mixtures of end members were intimately ground in acetone. The dried mass was mixed with the binder. Then pellets were prepared by using 15,000 psi pressure and were fired at 1173K for 100 hr. X-ray analysis of the compounds was carried out on Philips diffractometer using $\text{Cu-K}\alpha$ radiation with Ni-filter. The areas under different hkl peaks were determined by counting the number of squares in the cm-graph paper and their values were given in relation to the area under the peak for 311 reflection which was taken as 100. The oxygen ion parameter (u) was calculated from 111 reflection since it is very sensitive to u parameter value. The intensity values were calculated by varying u parameter from 0.375 to 0.395 at the interval of 0.002 and the value which matches well with observed intensity is taken as u parameter.

The dc resistivity measurements were carried out using LCR Marconi bridge. The end faces of each pellet were coated with a thin layer of conducting silver paste and measurements were carried out from room temperature to 673 K using two probe technique. Thermoelectric coefficient measurements were carried out from room temperature to 437 K. The infrared spectra were recorded on Beckman IR double beam spectrophotometer from 1000 to 250 cm^{-1} using KBr pellets.

3. Results and discussion

The compound ZnFeMnO_4 is tetragonal ($a=8.28\text{\AA}$ and $c=8.78\text{\AA}$) while compound GaCoMnO_4 is cubic ($a=8.37\text{\AA}$ and $u=0.381$). The results of x-ray analysis are given in table 1 and the plot of lattice constant vs composition in figure 1. An indexed x-ray diffraction pattern of 50:50 mole percent of ZnFeMnO_4 and GaCoMnO_4 is given in table 2. It is observed from table 1 that the system is tetragonal in the range $0 \leq x \leq 20$ and cubic in the range $40 \leq x \leq 100$ (where x denotes the mole percentage of GaCoMnO_4). The plot of $V^{1/3}$ vs composition showed a break in volume where there is a change in the crystal structure (figure 1). Such a break has also been reported in Zn-Ge-Co-Mn oxide spinel system (Wickham and Croft 1958). The sudden change in the volume at the critical composition can be attributed to the change in the elastic energy of the crystal (Goodenough and Loeb 1955). It is observed from table 1 that u parameter decreases with increase in concentration of Ga^{3+} ions at A-site. This may be due to replacement of Zn^{2+} by Ga^{3+} which is 20% smaller in radius (Shannon and Prewitt 1970). In order to accommodate Ga^{3+} in place of Zn^{2+} ions at A-site, there is contraction in tetrahedra consisting oxygen ions which ultimately reflects in decrease in u parameter but preserving cubic symmetry, where $x \geq 40$.

Figure 1. Plot of lattice constant vs composition for the system $\text{ZnFeMnO}_4\text{—GaCoMnO}_4$.

Table 1. Lattice constant, c/a ratio, oxygen ion parameter, room temperature resistivity, activation energy and thermoelectric coefficient values for the system $\text{ZnFeMnO}_4\text{—GaCoMnO}_4$.

ZnFeMnO_4 : GaCoMnO_4	a Å	c Å	c/a	u	$\rho_{\text{RT}}(\text{ohm-cm})$	$\Delta E(\text{eV})$	$\alpha \left(\frac{\mu\text{V}}{\text{K}} \right)$
100 : 0	8.28	8.78	1.062	—	5.4×10^5	0.48	230
80 : 20	8.27	8.65	1.046	—	5.0×10^5	0.50	80
60 : 40	8.37	8.37	1.000	0.385	4.1×10^5	0.51	50
50 : 50	8.38	8.38	1.000	0.384	3.4×10^5	0.49	45
40 : 60	8.36	8.36	1.000	0.383	3.3×10^5	0.50	41
20 : 80	8.36	8.36	1.000	0.382	2.7×10^5	0.49	38
0 : 100	8.37	8.37	1.000	0.381	2.5×10^5	0.48	37

Table 2. An indexed x-ray diffraction pattern of $\text{Zn}_{0.5}^{2+} \text{Ga}_{0.5}^{3+} \left[\text{Fe}_{0.5}^{3+} \text{Co}_{0.5}^{2+} \text{Mn}^{3+} \right] \text{O}_4^{2-}$.

I (observed)	I (calculated)	$1/d^2$ (observed)	$1/d^2$ (calculated)	hkl
4.7	4.6	0.0428	0.0427	111
33.8	36.2	0.1138	0.1139	220
100	100	0.1566	0.1566	311
8.3	7.2	0.1710	0.1708	222
12.1	13.1	0.2276	0.2278	400
10.9	13.1	0.3414	0.3417	422
26.5	24.4	0.3836	0.3895	511
39.9	43.6	0.4543	0.4560	440

Structure = cubic

Lattice constant $a = 8.38 \pm 0.02 \text{ Å}$, $u = 0.384$

X-ray intensity calculations of the system were carried out to investigate the cation distribution. The structure factors for the planes 220, 400 and 422 have been calculated since these planes are very sensitive to distribution of cations.

The diffraction intensities of various reflections have been estimated from peak areas and compared with calculated values for following models in which (i) Zn^{2+} and Ga^{3+} (ii) Zn^{2+} and Fe^{3+} (iii) Zn^{2+} , Fe^{3+} and Ga^{3+} (iv) Zn^{2+} , Co^{3+} and Ga^{3+} and (v) Zn^{2+} , Ga^{3+} and Mn^{2+} are present at A-site using the formula

$$I_{hkl} = |F^2|_{hkl} \cdot P \cdot Lp, \quad (1)$$

where F = structure factor, P = multiplicity factor and Lp = Lorentz polarisation factor. The atomic scattering power of various ions were taken from literature (International tables 1964). The intensity ratios I_{220}/I_{400} and I_{422}/I_{400} were calculated for the various models and were compared with the observed intensity ratios. By comparing the intensity ratios of different models suggested above, the following two configurations were found to be in good agreement :

- (i) $\text{Zn}^{2+}_{1-x} \text{Ga}^{3+}_x [\text{Fe}^{3+}_{1-x} \text{Co}^{2+}_x \text{Mn}^{3+}] \text{O}_4^{2-}$ and
- (ii) $\text{Zn}^{2+}_{1-x} \text{Ga}^{3+}_x [\text{Fe}^{3+}_{1-x} \text{Co}^{3+}_x \text{Mn}^{3+}_{1-x} \text{Mn}^{2+}_x] \text{O}_4^{2-}$.

In the first configuration, manganese is present in only one oxidation state while in the second it is present in two different oxidation states. Since room temperature resistivity ($\rho_{\text{RT}} = 10^5 \text{ ohm-cm}$) and activation energy values ($\Delta E \simeq 0.5 \text{ eV}$) are fairly high throughout the system indicating the presence of manganese in only one oxidation state. We have observed similar results in the system $\text{Zn} [\text{Fe}_{1-x} \text{Mn}_x \text{Cr}] \text{O}_4$ (Jain and Darshane 1980). Similarly it has been reported that electrical conductivity in transitional metal oxides is high if the material contains the cations of same element but their valency differing by unity situated at the similar site in the crystal e.g. $\text{Fe}^{3+} [\text{Fe}^{2+} \text{Fe}^{3+}] \text{O}_4^{2-}$, $\rho_{\text{RT}} \simeq 10^{-2} \text{ ohm-cm}$ (Verwey *et al* 1951). Similarly in the case of copper manganite (Jogalekar and Sinha 1967) the electrical resistivity and activation energy values are low because of the presence of manganese in two different oxidation states

In all the compositions of the system, plots of $\log \rho$ vs $10^3/T$ (figure 2) were linear indicating the semiconducting nature of the compounds. Wilson's law $\rho = \rho_0 \exp (\Delta E/kT)$ is obeyed in all the compositions. The activation energies were calculated from the linear plots. The electrical conductivity σ is given by the relationship

$$\sigma = p e \mu, \quad (2)$$

where p = number of holes per unit volume, e = electronic charge and μ = mobility of holes. Using the above equation the value of mobility comes out to be $10^{-8} \text{ cm}^2/\text{V-sec}$. The mobility of charge carriers can also be calculated using the equation (Heikes and Johnston 1957)

$$\mu = \frac{ed^2\nu \exp (-\Delta E/kT)}{kT},$$

where the notations have their usual meaning. In the above equation the value of ν was calculated from the strong IR band observed at 600 cm^{-1} ($\nu = 1.8 \times 10^{13} \text{ Hz}$). The value calculated from the above equation is of the order of $10^{-9} \text{ cm}^2/\text{V-sec}$. We have also observed such a low mobility in the system $\text{Zn} [\text{Ga}_{2-x} \text{Mn}_x] \text{O}_4$ (Jain and Darshane 1980).

Figure 2. Plot of $\log \rho$ vs $10^3/T$.

The plots of thermo e.m.f. against temperature were linear for all the compounds of the system and the values of α varied between $+37$ and $+230$ $\mu\text{V/K}$ indicating p -type semiconductivity. In the present system if iron is present in $3+$ oxidation state (Darshane and Jain 1981; Deshpande *et al* 1979) then the other possible combination at B -site is of Mn^{4+} and Co^+ . This combination can be ruled out since it is energetically unstable.

From the results of electrical conductivity we suggest the following model for the system deduced from x-ray intensity calculations

The above configuration indicates the presence of manganese in $3+$ oxidation state in gallium cobalt manganite.

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