

Structural, magnetic and electrical study of MgCoMnO_4

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Abstract. A new compound MgCoMnO_4 has been synthesised by the oxide method. It crystallizes in a tetragonal spinel structure with $a = 8.30 \text{ \AA}$ and $c = 8.46 \text{ \AA}$. The observed crystal symmetry is associated with the existence of Mn^{+3} on the B sites. The compound is n type semi-conductor with activation energy $\Delta E = 0.33 \text{ eV}$. The electrical properties show that it can be regarded as a properly substituted MgMn_2O_4 by Co^{+3} ions. It is paramagnetic with $C_M = 5.75$ and $\theta_a = -160^\circ\text{K}$. All these results show the ionic configuration of the compound as $\text{Mg}^{+2} [\text{Co}^{+3} \text{Mn}^{+3}] \text{O}_{4\frac{1}{2}}$.

Keywords. Spinel ; electrical conductivity ; Curie molar constant.

1. Introduction

Spinel containing transition metal (TM) ions exhibit remarkable electrical and magnetic properties which are governed by the valence state and the site distribution of the cations. When two or more types of TM ions are present in the spinel, complications arise due to several possible oxidation states and site preferences. However, the bulk distortion of the lattice can indicate the presence of certain TM ions, such as, $d^4(\text{Mn}^{+3})$ or $d^9(\text{Cu}^{+2})$. The c/a ratio is suggestive of such distortive ions since their presence at the tetrahedral (A) or the octahedral (B) sites reduce or increase it.

A survey of literature on ZnMnMeO_4 , where $\text{Me} = \text{Cr}, \text{Mn}, \text{Fe}$ and Co , shows that all the compounds except the last one are tetragonal spinels. ZnMnCoO_4 is however, shown to have a cubic structure (Bongers 1957 ; Kulkarni 1970). On the other hand, while CuMnCoO_4 is expected to be cubic like CuMnMeO_4 where $\text{Me} = \text{Cr}, \text{Mn}$ and Fe , [Kulkarni and Mande (1970)] have shown it to be tetragonal. These structural contrasts in cobalt containing spinels have been associated with (Kulkarni 1970) the presence of Co^{+2} and Mn^{+4} ions in the lattice. We, therefore, thought it worthwhile to study MgCoMnO_4 because magnesium, like zinc, exists only in the divalent state and has preference for the A sites. An exhaustive survey of the literature on spinel indicates that this compound has not been studied.

2. Experimental

2.1 Preparation and identification

The compound MgCoMnO_4 was prepared by the oxide method (Economos 1955) by intimately mixing under acetone Co_2O_3 , Mn_2O_3 and MgO of AR grade in proper molar proportions. The mixture was pressed into pellets of 1.0 cm diameter under 5000 p.s.i. using 5% polyvinyl acetate as a binder. The pellets were first slowly heated up to 300°C for about 3 hr to evaporate the binder and finally fired in air at 900°C for 90 hr in an electric furnace. They were, then, furnace-cooled at the rate of 100°C/hr . The x-ray diffraction pattern was taken on Phillips diffractometer using filtered $\text{MoK}\alpha$ radiation. The formation of the compound was taken to be complete as the peaks due to reacting oxides were found to be absent in the diffractogram, thus indicating the existence of a single phase.

2.2 Magnetic susceptibility

The susceptibility measurements were carried out in the temperature range 80°K (liquid nitrogen) to room temperature using Faraday's method. The design of cryostat was similar to that described by Figgis and Nyholm (1959) with a few modifications. $\text{HgCo}(\text{CNS})_4$ was used as a calibrant. The diamagnetic contribution due to the tube and wire assembly was taken into account as only a few milligrams of the compound was used.

2.3 Electrical resistivity

In order to determine the DC resistivity a thin layer of colloidal graphite was applied on the clean and flat parallel faces of the pellets, to provide good electrical contact. DC resistance of the pellet was determined in the temperature range 373°K to 873°K in steps of 20°K by applying a steady potential difference of 2 V across the sample and measuring the current with a microammeter. The potential difference across the sample was measured with a VTVM having 11 meg-ohm input resistance. The type of charge carrier was found out by the hot probe method.

3. Results

The d values for various planes and their relative intensities measured from the heights of the peaks in the diffractogram are given in table 1. The compound is found to have a tetragonal structure with $a = 8.30 \text{ \AA}$ and $c = 8.46 \text{ \AA}$.

The variation $\log \rho$ against $1/T$ is linear showing that the well-known exponential law $\rho = \rho_0 \exp(\Delta E/KT)$ is obeyed in the temperature range covered. The activation energy ΔE as calculated from the graph is 0.33 eV. The resistivity is of the order of $6 \times 10^4 \text{ ohm-cm}$ at room temperature and $2 \times 10^1 \text{ ohm-cm}$ at 873°K . The hot probe test indicates that the compound is n type semiconductor.

Table 1. Results of x-ray diffraction study of MgCoMnO₄

<i>d</i> in Å (observed)	<i>d</i> in Å (calculated)	<i>I</i> / <i>I</i> ₀ (observed)	Plane (h k l)
4.83	4.82	10	1 1 1
2.93	2.93	35	2 2 0
2.51	2.51	100	3 1 1
2.12	2.12	15	0 0 4
2.05	2.07	20	4 0 0
1.70	1.70	8	4 2 2
1.60	1.60	26	5 1 1
1.47	1.48	38	4 0 4
1.46	1.47	24	4 4 0

Tetragonal : $a = 8.30 \text{ \AA}$ $c = 8.46 \text{ \AA}$

The variation of $1/\chi_M$ against T is also linear indicating that the compound is paramagnetic in the temperature range investigated and obeys Curie-Weiss law

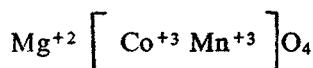
$\chi_M = C_M / (T - \theta)$. The reciprocal molar susceptibilities $\left(\frac{1}{\chi_M}\right)$ at room temperature and 80°K are found to be 110.10×10^1 mole/emu and 44.04×10^1 mole/emu. The observed Curie molar constant (C_M) is 5.75 and the asymptotic Curie temperature is found to be -160°K .

4. Discussion

The possible valence structures for MgCoMnO₄ are the following:

(i) Mg⁺²Co⁺³Mn⁺³O₄ or (ii) Mg⁺²Co⁺²Mn⁺⁴O₄.

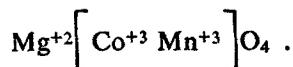
It is well-known that Mn⁺³ (d^4) produces a prolate distortion of the oxygen octahedra about the *B* sites. The compound MgCoMnO₄ is expected to have the same cubic structure like ZnCoMnO₄ since both zinc and magnesium exist only in the divalent state and have preference for the *A* sites. However, the observed crystallographic results show that it is tetragonal with $c > a$. The observed symmetry can only be explained to be due to the presence of Mn⁺³, the JT ions on the *B* sites. Hence the valence structure (ii) may be ruled out. The site distribution of cations was decided from the knowledge of site preference energies for Mg⁺² (5.0 k cal/g. at wt. — *A* sites) and Mn⁺³ (3.1k cal/g. at. wt. — *B* sites) (Miller 1959). It is therefore reasonable to assume that Mg⁺² ions are at the *A* sites and Mn⁺³ ions on the *B* sites. The situation does not change even if Co⁺³ ions are present in the structure because, like Mn⁺³, they also have a strong preference for the *B* sites. The ionic structure for the compound can, therefore, be written as



Our magnetic susceptibility data also confirms the first valence structure. The theoretical C_M (spin only) values for the above two valence structures are 6.0 and 3.74 respectively. The observed C_M value (5.75) is more close to the

theoretical C_M value for ($\text{Co}^{+3} + \text{Mn}^{+3}$) combination but much higher than the theoretical value of C_M for the ($\text{Co}^{+2} + \text{Mn}^{+4}$) combination. Thus the combination ($\text{Co}^{+3} + \text{Mn}^{+3}$) is found to be more stable than ($\text{Co}^{+2} + \text{Mn}^{+4}$) combination. In spinels, the large negative values of θ_a are indicative of stronger B - B interactions as in ZnMn_2O_4 (Aiyama 1966), MgMn_2O_4 (Muramori and Miyahara 1960), CoMn_2O_4 (Boucher *et al* 1968). In these compounds the B sites are occupied by Mn^{+3} ions indicating that the $\text{Mn}_B^{+3} - \text{Mn}_B^{+3}$ interactions are strong. On the other hand, in ZnCo_2O_4 , where A sites are occupied by the non-magnetic ions Zn^{+2} like MgCo_2O_4 and B sites are occupied by Co^{+3} ions, the small negative value of θ_a (-50°K) (Cossee 1956) shows that the B - B interactions among $\text{Co}^{+3} - \text{Co}^{+3}$ ions are weaker. Similarly the small negative value of θ_a in Co_3O_4 (Roth 1964) is also suggestive of weaker $\text{Co}_B^{+3} - \text{Co}_B^{+3}$ interactions. In MgCoMnO_4 , the A sites are occupied by the non-magnetic ions (Mg^{+2}) and hence A - A interactions are absent. The value of θ_a (-160°K), suggests that the $\text{Co}_B^{+3} - \text{Mn}_B^{+3}$ interaction is weaker than $\text{Mn}_B^{+3} - \text{Mn}_B^{+3}$ interaction but stronger than $\text{Co}_B^{+3} - \text{Co}_B^{+3}$ interaction.

The observed ionic configuration suggests that this compound can be regarded as (i) a solid solution of MgMn_2O_4 and MgCo_2O_4 or (ii) MgCo_2O_4 substituted by Mn^{+3} ions or (iii) a Co^{+3} substituted MgMn_2O_4 . In the absence of a detailed investigation of the electrical behaviour of MgCo_2O_4 , it is rather difficult to apply the first and second idea in the present case. However, it is possible to explain the electrical behaviour of this compound by regarding it as MgMn_2O_4 in which some of Mn^{+3} ions have been substituted by Co^{+3} ions. The activation energy of this compound is 0.33 eV, with electrons as carriers. This is the same as the activation energy of MgMn_2O_4 (0.33 eV) which is also n type (Kshirsagar and Sabane 1971). It is well-known that a slight substitution may alter the ΔE in spinels considerably (Jonker 1959). But in the present case, the substitution of Mn^{+3} by Co^{+3} ions on the B sites has not altered the activation energy. The room temperature resistivity of MgMnCoO_4 is also close to that of MgMn_2O_4 ($\sim 10^5$ ohm-cm) (Kshirsagar and Sabane 1971). This idea also explains well the lower value of axial ratio c/a for MgCoMnO_4 (1.02) than for MgMn_2O_4 (1.15) (Navrotsky and Kleppa 1968) as Co^{+3} ion is non distortive and replacement of Mn^{+3} by Co^{+3} has reduced concentration of Mn^{+3} the J-T ion, on the B sites. Thus the structural, magnetic and electrical studies lead to the ionic structure as



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