

CuAlMnO₄ from two different combinations and their structural and electrical study

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Abstract. A compound CuAlMnO₄ has been synthesised for the first time by oxide method using 1 + and 2 + copper oxides separately. Both the compounds crystallise in tetragonal unit cell with $a = 8.205$ Å and $c = 8.342$ Å. It has been observed that there are similarities in structures but dissimilarities in their electrical behaviours. The observed tetragonal symmetry, lattice dimensions and electrical behaviour are explained on the basis of solid solution of CuAl₂O₄ and CuMn₂O₄ spinels.

Keywords. Crystal structure ; electrical resistivity ; activation energy ; binary spinels.

1. Introduction

Oxidic spinels have attracted the attention of scientists because of their highly interesting and controllable physical properties, which depend upon the method of preparations (Akashi 1966), site (Millar 1968) and valence distribution (Sinha and Joglekar 1967), etc. However, the same compound does not appear to have been synthesised from different chemicals to study the physical properties of such chemically equivalent species, since it was believed that a compound with the same chemical formula and crystal structure will behave similarly in all respects. An attempt was therefore made to prepare two compounds of CuAlMnO₄ with the same chemical formula and structure, but from different chemical combinations. The structure and electrical properties of these two compounds have been studied in detail and the similarities and differences are reported in this paper.

2. Experimental

2.1. Preparation and identification

The compound CuAlMnO₄ was prepared by standard ceramic technique (Economos 1955) in two ways by taking either CuO, Al₂O₃ and Mn₂O₃ (compound A) or by taking Cu₂O, Al₂O₃ and MnO₂ (compound B). The mixtures were heated at 850° C for 120 hr and were slowly cooled to room temperature for about 10 hr. The heat treatment was the same for both compounds. The formation was checked by powder method using filtered Fe-K_α radiation. The diffraction

patterns of these compounds do not show presence of reacting oxide or other binary oxides but are only due to a single phase. Both the compounds prepared from different reacting oxides crystallise in distorted spinel structure with $a = 8.205 \text{ \AA}$ and $c = 8.342 \text{ \AA}$.

2.2. Electrical resistivity

For the determination of DC resistivity, pellets of 1.25 cm diameter and of 0.3 cm thickness were prepared. Dimensionally identical pellets were chosen to avoid the differences in specific resistances arising due to stray capacitances and porosity, etc. In short both the compounds were studied under identical conditions. Colloidal graphite was used as a good contact material. The measurements were carried out in the temperature range 373 K to 673 K in steps of 10 K by applying a constant voltage (6 V) across the pellet. Radart 1203 L C R bridge was used to determine the resistance.

3. Results

Both the compounds have a tetragonal structure. The relative intensities of all the planes except (317) and (008) were found to be same (table 1). The small

Table 1. Crystallographic data of CuAlMnO_4 spinel.

| h | k | l | I/I_0 observed A | I/I_0 observed B | d (obs.) A | d (cal.) B |
|-----|-----|-----|--------------------------|--------------------------|-----------------|-----------------|
| 1 | 1 | 1 | 10 | 10 | 4.730 | 4.763 |
| 2 | 2 | 0 | 25 | 25 | 2.890 | 2.901 |
| 3 | 1 | 1 | 100 | 100 | 2.471 | 2.477 |
| 2 | 2 | 2 | 22 | 22 | 2.309 | 2.380 |
| 4 | 0 | 0 | 25 | 25 | 2.051 | 2.051 |
| 2 | 0 | 4 | 12 | 12 | 1.857 | 1.859 |
| 4 | 2 | 2 | 14 | 14 | 1.679 | 1.679 |
| 5 | 1 | 1 | 28 | 28 | 1.581 | 1.580 |
| 4 | 0 | 4 | 25 | 25 | 1.458 | 1.462 |
| 4 | 4 | 0 | 30 | 30 | 1.450 | 1.450 |
| 6 | 0 | 2 | 8 | 8 | 1.303 | 1.300 |
| 3 | 3 | 5 | 15 | 15 | 1.260 | 1.263 |
| 5 | 3 | 3 | 14 | 14 | 1.251 | 1.255 |
| 4 | 4 | 4 | 4 | 4 | 1.187 | 1.190 |
| 5 | 5 | 1 | 3 | 3 | 1.155 | 1.130 |
| 6 | 4 | 2 | 9 | 9 | 1.097 | 1.101 |
| 3 | 1 | 7 | 10 | 25 | 1.077 | 1.083 |
| 7 | 3 | 1 | 30 | 30 | 1.069 | 1.069 |
| 0 | 0 | 8 | 4 | 8 | 1.034 | 1.043 |
| 8 | 0 | 0 | 10 | 10 | 1.027 | 1.026 |

Average lattice dimensions

$$a = 8.205 \text{ \AA}$$

$$c = 8.342 \text{ \AA}$$

difference is due to the internal arrangement of ions. The resistivity for A (figure 1) is of the order of 10^2 ohm-cm, at 373 K and 10^1 ohm-cm at 673 K. The activation energy (ΔE) in the temperature range 373 K–488 K. was 0.216 eV and 0.264 eV above 488 K. An upshoot is observed at the rise in the activation energy by 0.05 eV.

On the other hand the plot for compound B is rather complex and can be subdivided into five different parts (figure 1) of which *bc* and *ef* parts are almost parallel to *qr* and *pq* of the compound A. This indicates that at least for these two portions the activation energies are of the same order in both the compounds.

4. Discussion

Ternary spinel may be viewed as a solid solution of binary spinels, which may help in understanding the behaviour of such spinel. Substituted copper manganites have given rise to much discussion because of the several possible valence distributions possible (Sinha and Joglekar 1967; Kulkarni and Mande 1974). This is more serious than the problem of site distribution since Cu and Mn can exist in more than one oxidation states and can occupy different sites in varied proportions. In the present case the problem of valence distribution is not serious

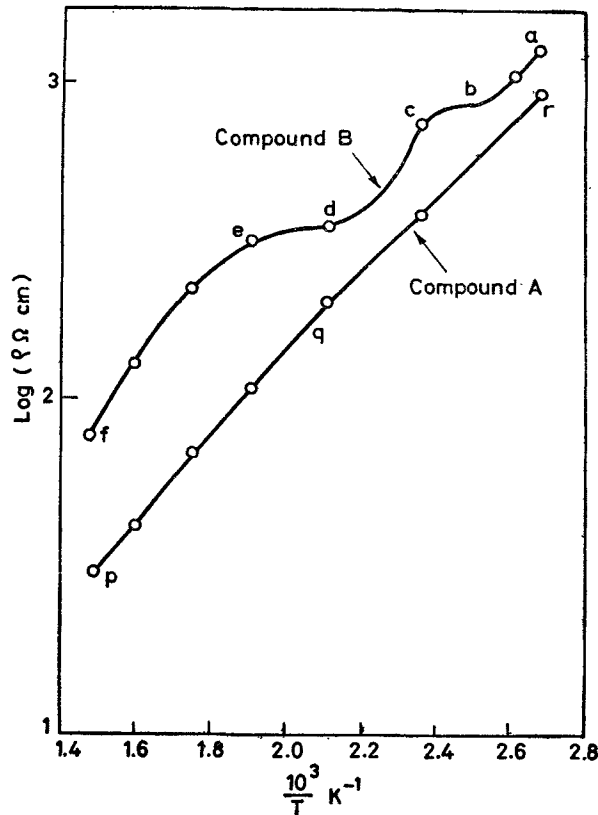
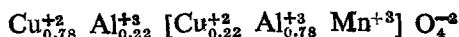


Figure 1. $\log \rho$ versus $10^3/T$ for CuAlMnO_4 compounds.

since the configuration containing Mn^{+4} and Cu^{+1} is not favoured energetically. Also, the observed symmetry shows the presence of distortive ions Cu^{+2} and Mn^{+3} . The distortions due to Cu^{+2} and Mn^{+3} are opposite and unbalanced, giving $c > a$. The unit cell dimensions of $CuAlMnO_4$ are intermediate to those of $CuAl_2O_4$ (Stones 1966) and $CuMn_2O_4$ (Kulkarni and Mande 1974). Therefore structurally these three compounds are similar and the former may be viewed as a solid solution of the last two spinels in equal proportions. Table 1 shows that the relative intensities for the planes (317) and (008) are different in two cases indicating that these small differences may be due to slight rearrangements of cations or packing of anions.

The resistivity plots for A and B are different but point out that they are semi-conductors. A and B have equal ΔE for some temperature ranges (figure 1). The dissimilarities in ΔE may be due to ionic rearrangement or different packing of anions which in effect can alter it considerably because of variations in ionic distances. An interesting feature in this work is that though the starting materials were different the product was structurally and chemically the same except for slight differences in electrical behaviour. The observed small degree of distortion, lattice constant and activation energy may be understood from the following site and valence distribution of the compound :



by assuming it as a solid solution of two well-known binary spinels $CuAl_2O_4$ and $CuMn_2O_4$ without altering the site distribution (Delorme 1958; Kulkarni and Mande 1974) in solid solution.

The idea of solid solution cannot be extended in understanding ΔE of a compound as it depends upon all the ions present in the lattice. As Al^{+3} is an inert ion it will rarely take part in conduction and hence ΔE will be mainly due to hopping of electrons amongst Cu^{+2} and Mn^{+3} ions as in $CuMn_2O_4$. Thus one expects the ΔE of the compound to be close to that of $CuMn_2O_4$. These are almost comparable and the slightly lower value of ΔE for $CuAlMnO_4$ is evidently due to small $B-B$ distance in the former than the latter. Work on other physical properties of these compounds is in progress.

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