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Synthesis and Characterisation of Structural and Electrical Properties of CuMn2O4 Spinel Compound

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ABSTRACT

CuMn2O4 was synthesized by the solid-state method. MnO2 and CuO were used as precursors. The optimum temperature of synthesis was 850°C. XRD results showed that the prepared compound had a cubic structure with Fd3 m space group. The lattice constant and unit cell volume were a=8.359Å and V=584.14A°3 respectively. The grain size was calculated by the Debye-Scherrer method and was 33.49 nm for CuMn2O4 annealed at 850°C. The experimental density was calculated and compared to the theoretical density. The results were ρt= 5.399 gr/cm^3 and ρE = 5.24 gr/cm^3. The electrical properties of the compound showed that it behaves like a semiconductor, and the activation energy of the compound was 0.1535 eV.

KEYWORDS

Activation energy, copper manganite (CuMO), mixed oxide, solid-state reaction, spinel

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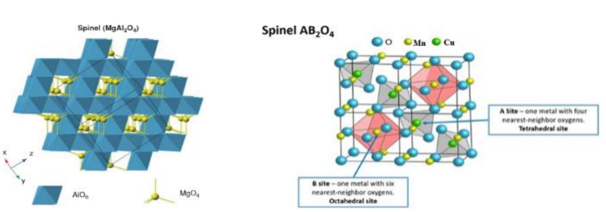
1. Introduction

Spinels are a member of a large group of materials. They are mixed oxides with the general formula AB_2X_4, where X = O, A and B are cations with oxidation states 2 and 3, respectively. The parent spinel is $MgAl_2O_4$. Oxide ions form a ccp structure. Mg^{+2} and Al^{+3} cations are located in tetrahedral and octahedral sites, respectively. Many oxides and sulphides have the spinel structure that gives its name to the family of compounds that share the same structural arrangement. Consequently, we will use the word spinel to refer to any material of general formula AB_2X_4, which crystallizes in a cubic crystal system with space group $Fd\bar{3}m$. In this structure, shown in Figure 1(a) the X anions (oxide anions) are arranged in a cubic close packed structure, whereas the cations A and B occupy tetrahedral (1/8, 1/8, 1/8) and octahedral (1/2, 1/2, 1/2) sites, respectively.

Figure 1: (a) Schematic view of the spinel structure with octahedral (blue) and tetrahedral units (yellow). (b) The unit cell of spinel structure of $CuMn_2O_4$ (West, 2014)



The unit cell of $CuMn_2O_4$ spinel is shown in Figure 1(b). It is a transition metal manganite with the formula MMn_2O_4 (M=Cu, Ni, Zn, Ca or others), and can be described as a cubic close packed structure (Errandonea *et al.*, 2010). The unit cell contains 32 anions forming 64 tetrahedral sites and 32 octahedral sites. Eight tetrahedral and 16 octahedral sites are occupied by cations.

These materials have attracted much attention due to their wide uses in many applications. The spinel $CuMn_2O_4$ has been studied since it has unique electrical, magnetic, thermoelectric and catalyst properties. $CuMn_2O_4$ compound can be applied as an oxidation catalyst for removing air pollutants, such as monoxide and nitrous oxide from exhaust gas, and for destroying volatile organic compounds (VOCs) (Deraz and Abd-Elkader, 2013; Trapp *et al.*, 2017; Sobhani-Nasab *et al.*, 2020).

The spinel materials can be prepared by many methods, such as solid-state method (Waskowska *et al.*, 2001), co-precipitation (George and Sugunan, 2008), citrate-nitrate gel combustion (Barros *et al.*, 2001), sol-gel (Habibi and Fakhri, 2016; Enhessari *et al.*, 2016; Zhang *et al.*, 2020) and hydrothermal processes (Durrani *et al.*, 2012). Out of these methods, the solid-state method was selected because it is the simplest and most common way of preparing solids. High temperatures are generally required, typically between 500 and 2000°C, and thermally unstable MnO_2 returns to Mn_2O_3 at temperatures above 500℃. As a result, this method was selected. During heating above 500℃, the oxidation number of manganese turned from +4 to +3 and MnO_2 to Mn_2O_3 (Berbenni *et al.*, 2006; Shaheen and Selim, 1998).

In this study, $CuMn_2O_4$ was synthesized by the solid-state method. The structural properties were studied using X-ray diffraction and the electrical properties were also studied.

2. Materials and Methods

2.1. Starting Chemicals and Sample Preparation

The $CuMn_2O_4$ high purity (99.99%) powder was prepared by the solid-state method. The two oxides, CuO (99.99%, M/s Sigma Aldrich. Ltd) and MnO_2 (99.99%, M/s Avonchem UK), were used as a precursor. Suitable amounts of these powders in the cation ratio Cu:Mn=1:1 were weighed, then mixed and ground in a pestle mortar. After this, Acetone was added for 15 minutes to form a homogeneous mixture. The grinding process was repeated three times for each sample. The resulting mixture was then dried by heating it to 100℃ for a period of time to remove moisture. The powder was then pressed (5000 Kg/cm^2) into pellets 1cm in diameter and 2mm in thickness, to bring the interacting particles closer together and to increase the possibility of interaction between the particles (West, 2014). The weights of the starting materials that were used to form the $CuMn_2O_4$ system were calculated by the following equation:

$$CuO + Mn_2O_3 \xrightarrow{>500℃} CuMn_2O_4 \quad (1)$$

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Then, the pellets were placed in a porcelain crucible and heated at 850 ℃ for 6 hours in air. Table 1 shows the weights of the raw materials used and calculated in accordance with the previous equation. Weights required were calculated on the basis that the desired amount equal to 10gr.

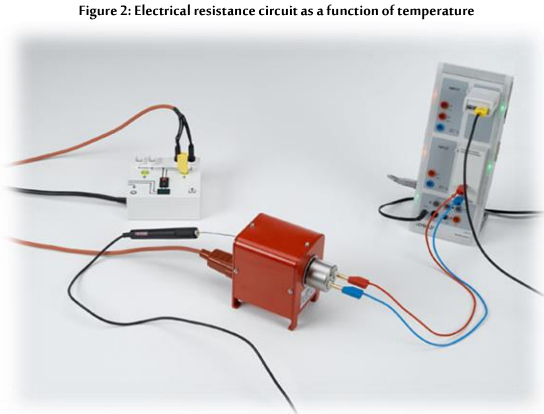
Table 1: Weights, supplier's names, and the purity of raw materials used to synthesize $CuMn_2O_4$

Cu:Mn	1:1	
name oxide	MnO_2	CuO
oxide mass (gr)	5.276421	4.848849
supplier's name	M/s Avonchem UK	M/s Sigma Aldrich. Ltd.
purity	99.99%	99.99%

2.2. Experimental Techniques

- X-ray Diffraction (XRD): The crystal structure of the final products were characterised using X-ray powder diffraction (XRD, Philips-PW-1840 with Cu-Kα radiation source λ=1.5406A°). X-ray diffraction (XRD) is one of the primary techniques used to characterise materials (Smart and Moore, 2006). XRD can provide some information about crystalline structure in a sample even when the crystallite size is too small for single crystal X-ray diffraction, including the purity of the substance, phase transitions, lattice constants and presence of foreign atoms in crystal lattice.
- Electrical Resistance Circuit: The samples were heated in the air at a temperature range of 295–667 °K to study their electrical behaviour, using the electrical circuit shown in figure 2. The sample was prepared for electrical measurements by pressing it into pellets 1cm in diameter and 2mm in thickness. Then Ag metal electrodes were deposited on its surface.

Figure 2: Electrical resistance circuit as a function of temperature

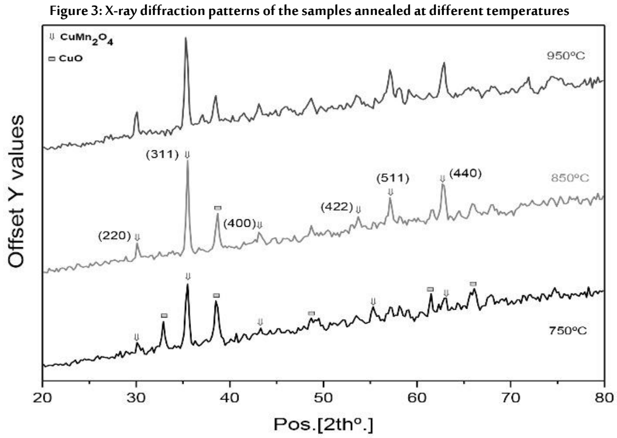


3. Results and Discussion

3.1. Compositional and Structural Characterisations

XRD patterns of the sample at different annealing temperatures were carried out. Figure 3 shows the XRD patterns of $CuMn_2O_4$, which were annealed at 750°C, 850°C, and 950°C for 6 hours.

Figure 3: X-ray diffraction patterns of the samples annealed at different temperatures



All the diffraction peaks are indexed and are compared with the standard JCPDS data (JCPDS No.34-1400 card).

It was found from Figure 3, for the sample annealed at 850°C, that all the diffraction peaks were attributed to the $CuMn_2O_4$ compound, and one peak was related to copper oxide. This indicates that the optimum temperature synthesis of $CuMn_2O_4$ compound is 850°C. The $CuMn_2O_4$ compound is polycrystalline with a cubic structure.

For the cubic system, the d-spacing is related to the lattice parameters by the following equation:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \qquad (2)$$

Table 2 shows diffraction angles, inter planar distances and Miller indexes that were calculated from XRD pattern.

Table 2: Diffraction angles, inter planar distances and Muller indexes

2θ°	θ°	I%	$d_{exp}(A°)$	$d_{card}(A°)$	hk
220	2.944	2.963	19.6	15.07	30.140
311	2.510	2.526	100	17.755	35.510
400	2.084	2.088	7.7	21.65	43.300
422	1.700	1.702	7.2	26.9075	53.815
511	1.603	1.608	17.3	28.625	57.250
440	1.473	1.477	24	31.44	62.880
a=8.359 $A°$					

The basic unit cell volume was calculated using the relation: $V = a^3$. The flask density method (picknometer) was used to measure the experimental density ρ_t of the prepared material (Agnew *et al.*, 2003). Depending on the material's density, the number of formulae in a single crystalline cell Z was calculated by the following equation:

$$\rho = \frac{MZ}{N_a V} \qquad (3)$$

where M is the molecular weight of the material, N the avogadro number and V the basic unit cell volume $(cm)^3$. Thus it was found that:

$$Z = \frac{N_a . V . \rho}{M} = 8.008$$

By using rounding, it was found that Z = 8 (Waskowska *et al.*, 2001), and therefore the general formula for the content of the basic unit cell can be written as follows: $Cu_8Mn_{16}O_{32}$. The obtained results were presented in Table 3.

Table 3: Lattice constant, basic cell size, Z and density.

a (A°) lattice constant	V $(A°)^3$ basic cell size	ρ_t (gr/cm^3) exp. density	Z	ρ_E (gr/cm^3) Th. density
8.359	584.14	5.399	8	5.24

The grain size was calculated using Scherrer's equation (Speakman, 2014; Smart and Moore, 2006):

$$D = \frac{0.9\lambda}{\beta . \cos\theta} \qquad (4)$$

where D is the grain size, λ is the wavelength of X-ray, θ is the Bragg's diffraction angle and β is the full width at half maximum of the peak in radians.

The obtained grain sizes are shown in Table 4.

Table 4: Grain sizes of the samples annealed at different temperatures

T(℃)	grain size (L)(nm)
700	44.56
850	33.49
950	30.94

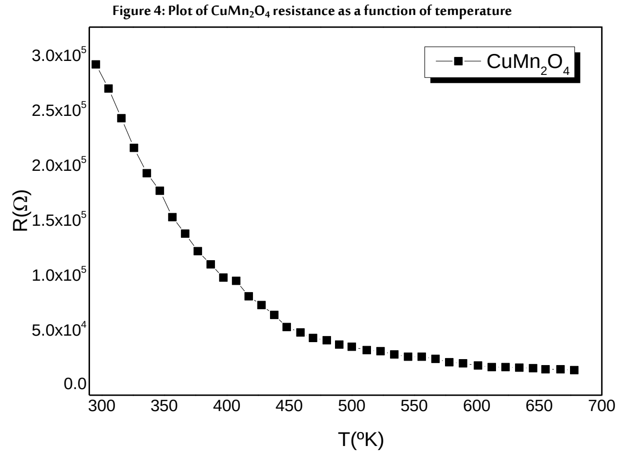
It is necessary to point out that the heating of the manganite compound to 950°C leads to the appearance of some peaks that are related to raw materials, such as $2\theta = 48.7, 71.9$ (Afriani *et al.*, 2018). As a result, we can say that the optimum temperature of $CuMn_2O_4$ synthesis is 850°C.

3.2. Electrical Properties

The electrical resistance variations of the prepared compound were studied as a function of temperature within the range of 295–667

$°K$. The electrical resistance values decreased with increasing temperature, indicating semiconducting behaviour. Figure 4 shows the exponentially decreasing of $CuMn_2O_4$ resistance.

Figure 4: Plot of $CuMn_2O_4$ resistance as a function of temperature

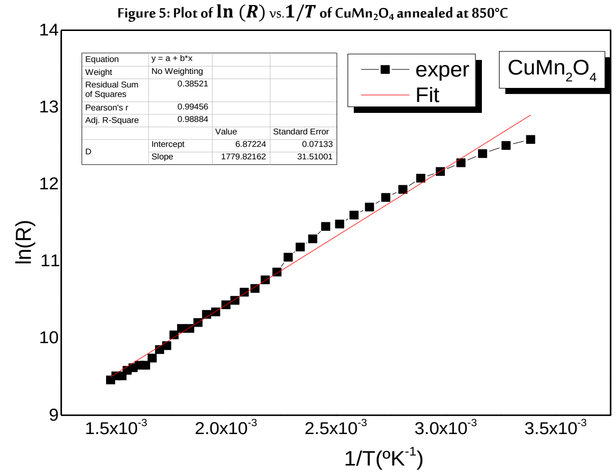


To extract the activation energy, the data were analyzed by using the relation (Das *et al.*, 2017; Ubale *et al.*, 2014; Deshpande *et al.*, 2018):

$$\mathrm{R} = R_0 \exp\left(\frac{E_a}{k_B T}\right) \quad (5)$$

where E_a is the activation energy, T is the absolute temperature and k_B is the Boltzmann constant. Figure 5 shows variation of $\ln(R)$ as a function of $1/T$ for $CuMn_2O_4$ compound.

Figure 5: Plot of $\ln(R)$ vs. $1/T$ of $CuMn_2O_4$ annealed at 850°C



The value of activation energy, E_a, was calculated from the slope of $\ln(R)$ versus $1/T$ plot. The calculated value of activation energy was:

$$\boldsymbol{E_a} = 0.1535 \text{ eV} \quad (6)$$

The activation energy value is in agreement with that identified by (Chen and Hsu, 2018).

4. Conclusions

Spinel $CuMn_2O_4$ was synthesized successfully by the solid-state method. The structural characterisation of $CuMn_2O_4$ revealed that the optimum temperature of $CuMn_2O_4$ synthesis was 850°C. It had a cubic structure. The crystalline size of $CuMn_2O_4$ annealed at 850°C was about 33nm. The electrical properties of the compound showed that it behaves like a semiconductor, so $CuMn_2O_4$ can be used as a semiconductor in thermoelectric devices. The activation energy of $CuMn_2O_4$ was calculated.

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