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A Study of Structural Properties of $CuMn_2O_4$ Synthesized by Solid State Method

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Abstract
$CuMn_2O_4$ was synthesized by Solid State method. MnO_2 and CuO were used as precursors. The temperature of synthesis was 850°C. X-ray diffraction analysis (XRD) revealed that the $CuMn_2O_4$ was synthesized. XRD results showed that the prepared compound was polycrystalline and had cubic structure. The lattice constant was a=8.359 °. The volume of unit cell was V=584.14 A^{o3}. The space group of symmetry was determined from JCPDS data and it was Fd3m. The results show that there are a compressive strain at 750°C and 950°C and tensile strain at 850°C. It was revealed from differential thermal analysis that the physical water was removed at 134.30°C. The thermal characteristic of prepared compound showed that the formation of it starts after (700)°C. DTA data revealed that the 850°C was the optimum degree of synthesis of $CuMn_2O_4$ which agree with XRD results. the compound decomposes at 950°C.
Keywords: copper manganite (CuMO), mixed oxides, solid state reaction, spinel.

1. Introduction

Many compounds of the AB_2X_4 family, in particular oxides (X = O), crystallize at ambient conditions in the spinel structure. Spinel is the magnesium aluminum oxide member of this large group of materials. It has the formula $MgAl_2O_4$ and gives its name to the family of compounds that share the same structural arrangement. Consequently, here we will name as spinel to any material of general formulation AB_2X_4 which crystallizes in the cubic (isometric) crystal system with space $Fd\bar{3}m$. In this structure, shown in Fig.1.1, the X anions are located at (u,u,u). They are arranged in a cubic closepacked lattice. In addition, the cations A and B occupy in the lattice respectively tetrahedral (1/8, 1/8, 1/8) sites, and octahedral (1/2, 1/2, 1/2) sites

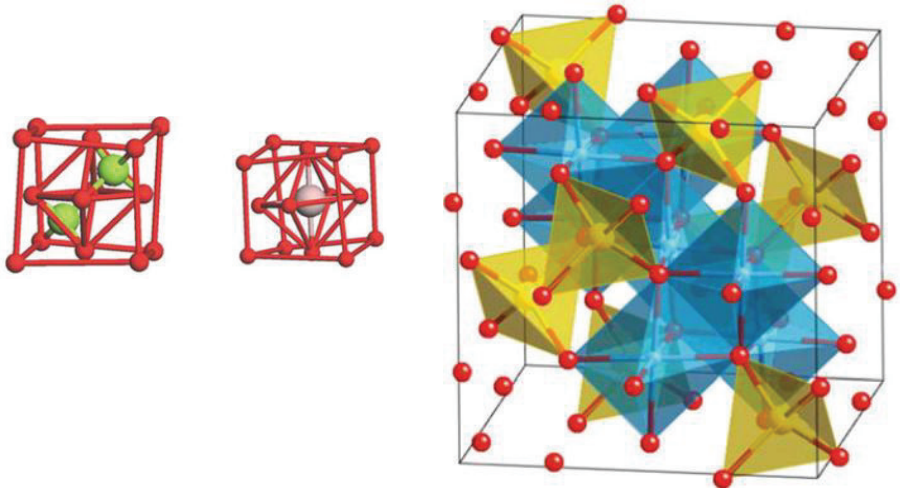


Fig.1.1 Schematic view of the spinel structure with octahedral (blue) and tetrahedral units (yellow) Oxygen atoms are represented in red.

Transition metal manganite possessing spinel structure with formula of MMn_2O_4 (M=Cu, Ni, Zn, Ca or others) can be described as cubic, closely-packed arrangement of oxygen atoms, and M^{+2} and Mn^{+3} ions can occupy either tetrahedral (A) or octahedral (B) sites [1]. The unit cell contains 32 anions forming 64 tetrahedral interstices and 32 octahedral interstices; of these 8 tetrahedral and 16 octahedral sites are occupied by cations. These are called (A) and (B) sites respectively. The unit cell of an ideal Spinel $CuMn_2O_4$ is shown in Fig.1.

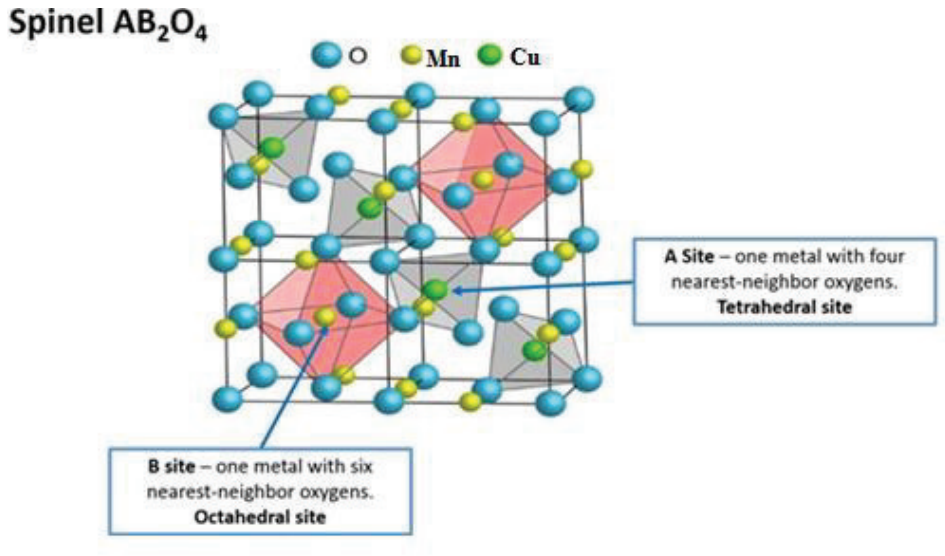


Fig (1) The unit cell of an ideal spinel structure

Such material have widespread use and attracted the attention of some investigators as good catalysts for some industrial reactions for example $CuMn_2O_4$ [1].

In the present study, $CuMn_2O_4$ was synthesized by Solid State method. Structural properties were studied using X-ray diffraction. The thermal characteristic of prepared compound was done by DTA data.

2. Experimental details

Starting and Chemicals and sample preparation

Manganese Oxide MnO_2 (M/s Avonchem Uk 99.9 %), Copper Oxide CuO (M/s Sigma Aldrich. Ltd. 99.99%), Acetone (eurolab above 99.8%) were used as precursors. Solid State method was used to prepare the samples.

The spinel materials can be prepared by many methods such as solid-state reaction of metal oxides at high temperatures[2]. In the wet chemical process, the powders are synthesized in liquid systems by means of co-precipitation[3]. Citrate-nitrate gel combustion [4], sol-gel [5], sol-spray processes, polymeric gel, and hydrothermal processes [6].

Compounds used in this study were obtained by high-temperature solid state reaction taking a stoichiometric rate of CuO:MnO_2. The specimens were grounded in agate mortar by adding the acetone as a useful material for obtaining homogenous mixture. Then using the compressor that the samples were pressed into table forms, and placed in a porcelain crucible and heated at 850℃ for 3 hours in air. After that the samples were removed and reground for 5 minutes and heated again in the same temperature for 3 hours. By this method, manganite particles with a narrow size distribution may be obtained with high purity [7]. The phase purity were characterized by x-ray powder diffraction using Diffractometer Philips-PW-1840 (CuK_α) and wavelength $\lambda = 1.5406\ °A$.

The weights of the raw materials used in account out of the molar weights of raw materials according to the following equation:

$$CuO + MnO_2 \rightarrow CuMn_2O_4$$

During heating above 500℃ oxidation number of manganese turned from (+4) to (+3) and MnO_2 to Mn_2O_3 [8].

$$MnO_2 \xrightarrow{500℃} Mn_2O_3$$

Table (1) shows the weights of the raw materials used and calculated in accordance with the previous equation, and weights required were calculated on the basis that the composite output desired amount equal to 10gr.

Table (1)

Cu:Mn	1:1	
name oxide	MnO_2	***CuO***
oxide mass(gr)	5.276421	**4.848849**

3. Results and discussion

3.1. Structural Properties

X-ray Diffraction (XRD) is one of the primary techniques used to characterize materials[9]. XRD can provide

information about crystalline structure in a sample even when the crystallite size is too small for single crystal X-ray diffraction, purity of the substance, transition to different phases, lattice constants and presence of foreign atoms in crystal lattice**.** The XRD patterns of the samples were taken using X-Ray Powder Diffractometer (Philips-PW-1840) using radiation source (λ=1.5406A^o)**.** XRD patterns of the sample at different baking temperatures are shown as follow.

Fig 1. shows the XRD pattern of CuMO, which prepared by a solid state method and annealed at 700°C for 6 hours

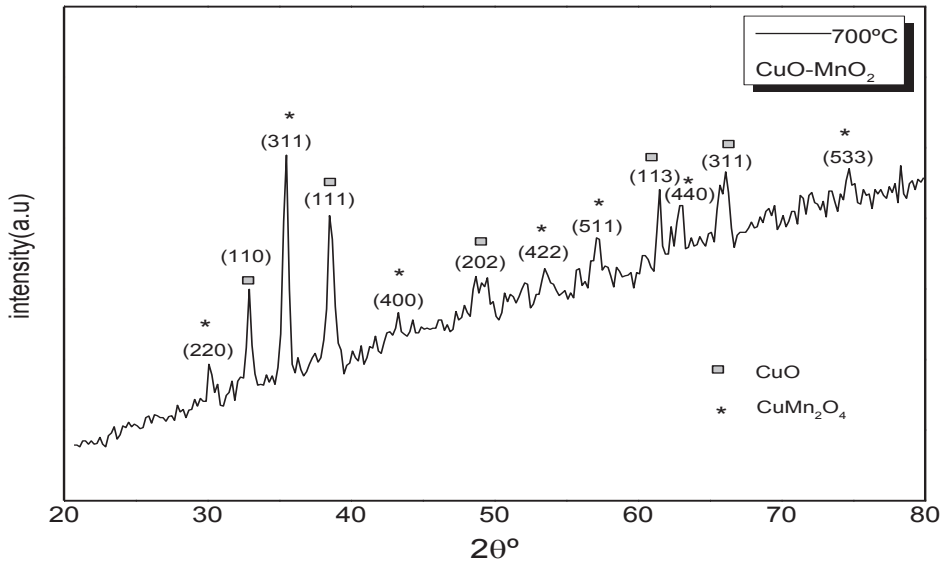


Fig 1. x-ray diffraction of the incomplete output in wholesale MnO_2-CuO scheme (T = 700°C)

As seen in this figure, there are some peaks belong to the desired compound was manufactured in addition to residue peaks (low intensities) of raw materials which are oxides. These peaks decrease with follow-up synthesis process and the desired compound peaks look more until the synthesis of a single phase was done.

Fig 2. shows the XRD pattern of Copper Manganite compound annealed at 850°C for 6 hours.

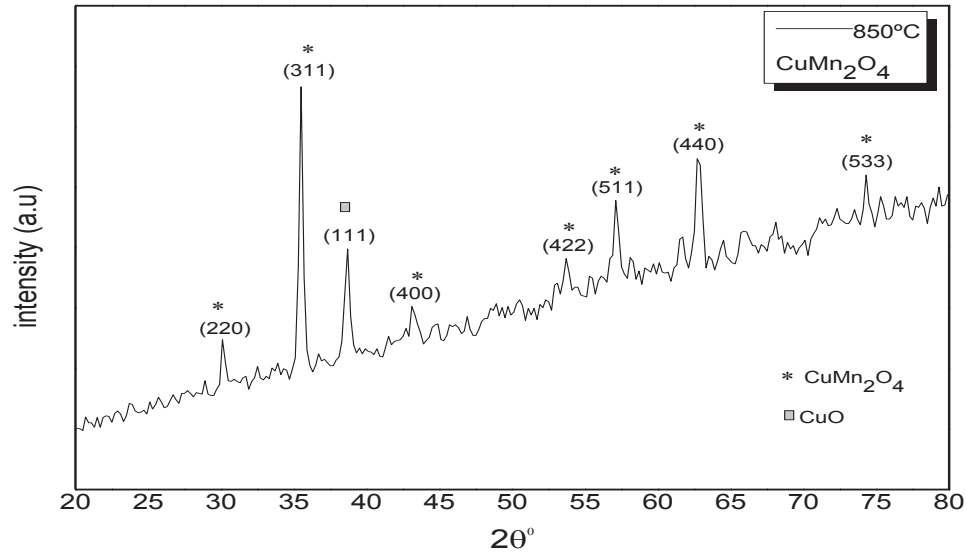


Fig 2. x-ray diffraction pattern of $CuMn_2O_4$ annealed at T = 850°C.

All the diffraction peaks are indexed and are compared with the standard JCPDS data (JCPDS No.34-1400 card). The $CuMn_2O_4$ compound is polycrystalline with cubic structure.

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

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

Table (2) shows diffraction angle , inter planar distance and Muller indexes that calculated from XRD pattern .

Table (2) diffraction angle, inter planar distance and Muller indexes

2Θ°	Θ°	I%	$d_{exp}(A°)$	$d_{card}(A°)$	hkl
30.140	15.07	19.6	2.963	2.944	220
35.510	17.755	100	2.526	2.510	311
43.300	21.65	7.7	2.088	2.084	400
53.815	26.9075	7.2	1.702	1.700	422
57.250	28.625	17.3	1.608	1.603	511
62.880	31.44	24	1.477	1.473	440
74.34	37.17	7.5	1.275	1.27	533
a=8.359 $A°$					

The basic cell size was calculated according to cubic pattern by the following equation:

$$V = a^3$$

the experimental density ρ_t of the resulting material in a manner flask density (picknometer)[10] was measured. Depending on the material's density, the number of formulas in a single crystalline cell Z was calculated according to the following equation:

$$\rho = \frac{MZ}{N_a V}$$

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

$$Z = \frac{N_a . V . \rho}{M} = 8.008 \approx 8$$

Following the method of rounding it was found out that Z = 8[2], and therefore the general formula for the content of the basic cell can write as follows: $Cu_8Mn_{16}O_{32}$

The obtained results are presented in Table (3).

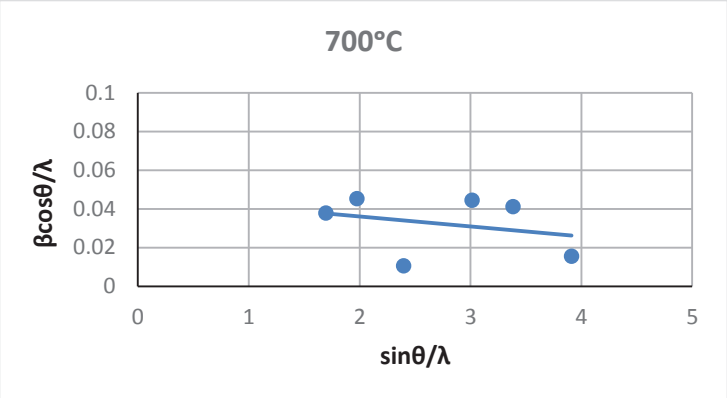
Table (3) lattice constant, basic cell size, Z and density

lattice constant a (A°)	basic cell size v $(A°)^3$	experimental density ρ_t (gr/cm^3)	Z	Theoretical Density ρ_E (gr/cm^3)
8.359	584.14	5.399	8	5.24

The grain size and strain were calculated using Scherrer's equation [11][9]:

$$\beta . \frac{cos\theta}{\lambda} = \frac{k}{L} + 4\varepsilon . \frac{sin\theta}{\lambda}$$

Fig 3. shows the variation of $\beta \cos\theta / \lambda$ versus $\sin\theta / \lambda$.



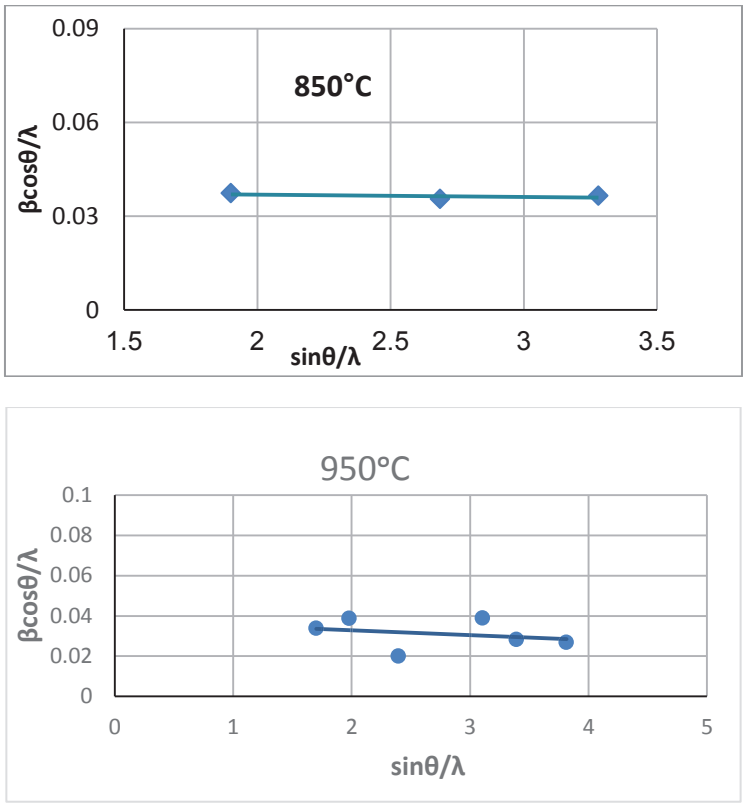


Fig 3. The variation of $\beta\cos\theta/\lambda$ versus $\sin\theta/\lambda$.

The obtained grain size and strain are noted in table 4.

Table (4): grain size, and Strain

T(°C)	(*L*)) nm (grain size	Strain (ε)
700	20.00	0.0013-
850	85.321	0.0019
950	24.668	-0.0006

It is necessary to point that the heating up of the compound Manganite to a higher degree of 950°C leads to the disintegration of the raw materials as shown in Fig. 3.

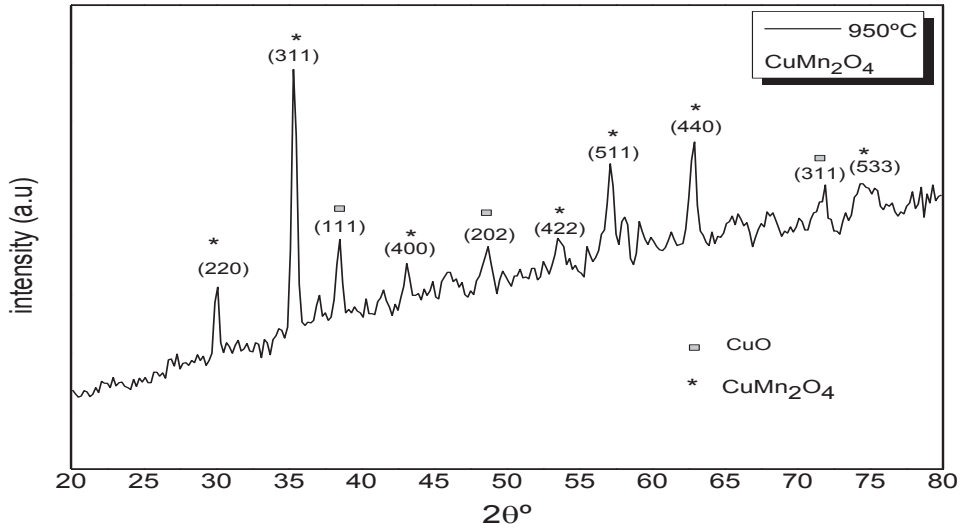


Fig3. x-ray diffraction of the compound resulting $CuMn_2O_4$ scheme (T = 950°C)

3.2 Thermal analysis

The study of the thermal behavior of the resulting compound and thermal stability of synthesized manganite were done by DTA data. **Fig**.**4** shows the DTA curve $CuMn_2O_4$ before annealing. It was revealed that the diagram includes many absorption peaks (Endothermal effects) and Exothermal peaks[12].

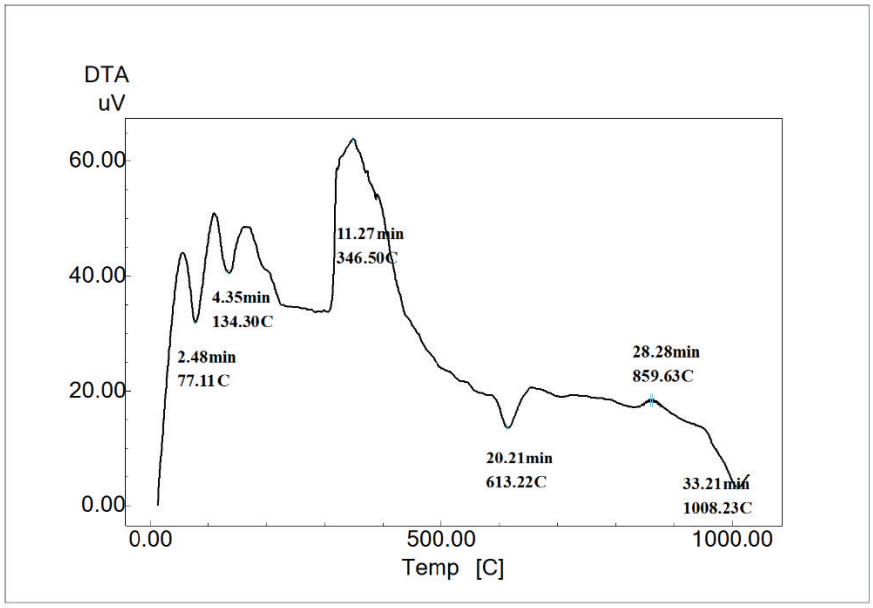


Fig 4. DTA curve of the $CuMn_2O_4$ compound before annealing.

The effect endothermic at degrees 134.30°C and 77.11°C indicating a loss of acetone and water molecules that are absorbed from the surrounding medium experience. The effect exothermic at degree 346.50°C indicating crystal transition of CuO [13]and the thermal effect at the degree 613.22°C shows the composite $CuMn_2O_4$ turned into noncrystallized phase (amorphous). At 859.63°C, $CuMn_2O_4$ was formed and decompose at 1008.66°C to precursors.

Fig.**5** shows the DTA curve $CuMn_2O_4$ after annealing.

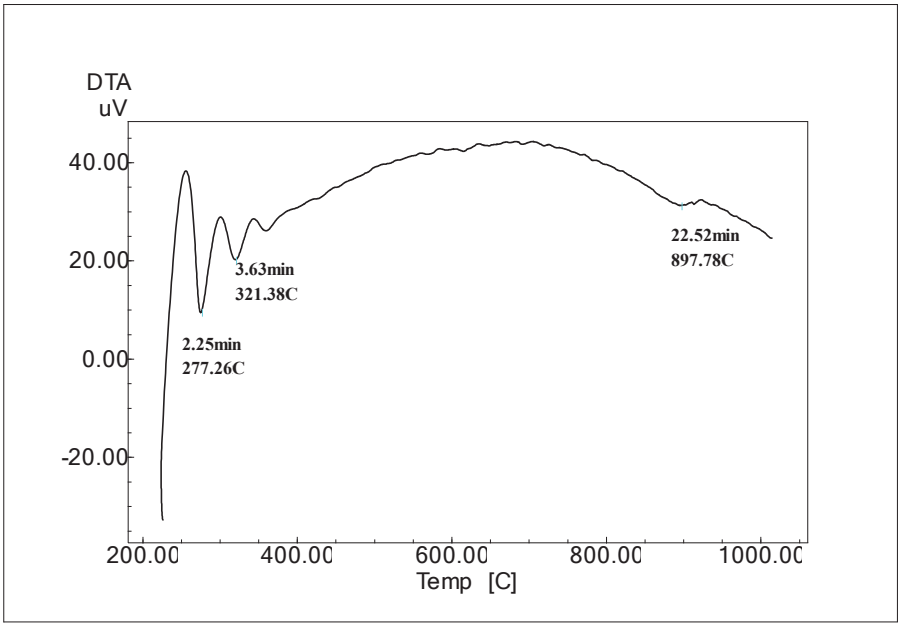


Fig 5. DTA curve of the compound $CuMn_2O_4$ after annealing.

It was noted from fig.4 that the effect endothermic at degree 277.2°C and 321.38°C indicating crystal transition of $CuMn_2O_4$ which agree with XRD results. After that the curve indicate to thermal stability of $CuMn_2O_4$ up to 897.78°C.

4. Conclusions

Spinel $CuMn_2O_4$ was synthesized successfully via Solid state-method . The physiochemical characterization of $CuMn_2O_4$ revealed that a formation of the compound was at 850℃. It had cubic structure and crystalline size of $CuMn_2O_4$ was about 85nm. $CuMn_2O_4$ was stability in wide thermal range so, it is a potential semiconducting material which can be used as a semiconductor in thermoelectric devices.

5. References

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