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ELECTRICAL CONDUCTIVITY OF BINARY LANTHANUM CUPRATES

Jayant Kher, Manisha Khaladkar, Nandini Iyer

Assistant Professor in Chemistry, Department of Applied Science, College Of Engineering Pune, Pune, Maharashtra, India[1,2,3]

Abstract: Thermal decomposition of binary mixtures of La (II) oxide and Cu (II) oxalate in the proportion of 1:1 and 1:3.5 was carried out. The end products after heating of the pure Cu (II) oxalate and the binary mixtures were tested for electrical conductivity from room temperature to 1173K.The conductivity was plotted as variation of resistance 'e' as a function of reciprocal of absolute temperature. All the pellets showed semiconduction with negative temperature coefficient (NTC) of resistance. The calcination products were characterized by XRD and other techniques.

Keywords: CuO, XRD, Cu (II) oxalate, La (II) oxide, NTC, resistivity.

I. INTRODUCTION

Electrical properties of copper oxide in recent times formed the basis of a large number of experimental investigations owing to the great technical significance of Cu_2O and it is easy to prepare copper oxide samples. La_2O_3 oxide has p-type semiconducting properties. When a binary oxide of Lanthanum (III) is made with CuO in various proportions the conductivity of mixture shows different behavior as compared to pure CuO and La_2O_3. The resistivity measurements showed that the binary mixture has Negative temperature coefficient of variation in resistance.

II. EXPERIMENTATION

The experimental procedure for these studies is divided as follows.
1. Preparation of Cu(II) Oxalate.
Cu(II)Oxalate was prepared by adding the solution of pure $K_2C_2O_4$ (Potassium Oxalate- A.R grade) drop by drop to a solution of pure Copper Nitrate(A R. grade)
2. Preparation of binary mixtures of La(II)Oxide and Cu(II) Oxalate. Binary mixtures of La(II)Oxide and Cu(II) Oxalate were prepared according to their mole proportion (1:1and1:3.5) by mechanical mixing.
3. Pure Cu(II) Oxalate was heated up to 950^o C to decompose it to CuO.
4. Binary mixtures were heated up to 950^OC
5. The end products of heating were characterized by XRD (Rikagu Miniflex).
6. The end products after heating of the pure Cu (II) oxalate and the binary mixtures were tested for electrical conduction from room temperature to 900^oC.The results are plotted as variation of resistance 'e' as a function of reciprocal of absolute temperature.

Following table indicates the abbreviations used in the experiment

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TABLE I Abbreviations Used

Type of mixture	Proportion	Heat Treatment	Notation
Pure Cu(II) Oxalate	-	900°C	CuO
Mixture A	La(II)Oxide+Cu(II)Oxalate 1:1	900°C	A (TG End Product)
Mixture B	La(II)Oxide+Cu(II)Oxalate 1 :3.5	900°C	B (TG End Product)
Product A		Sintered up to 900°C	A -P
Product B		Sintered up to 900°C	B -P

III. RESULTS AND DISCUSSION

Electrical Conduction as a function of temperature for CuO, A-P and B –P pellets. Electrical conduction as a function of temperature of CuO, A-P and B-P samples were studied. Results are shown in the Fig. 2 and tabulated in Table 1 and subsequently discussed as follows. XRD of the sintered pellets is shown in (Fig.1a). XRD of the TG end product of mixture A contains La_2CuO_4 and unreacted CuO and La_2O_3 phases while the XRD of the sintered pellet A -P (Fig.1b) contains La_2CuO_4 as a predominant phase. Similarly, TG end product of mixture B contains La_2CuO_4, and CuO phases while the XRD pattern of the sintered pellet B -P contains La_2CuO_4 as major phase. Besides the crystalline phases appeared in (Fig.1c) the pellets may be containing non-crystalline phases at the contacts of grain boundaries developed during sintering.

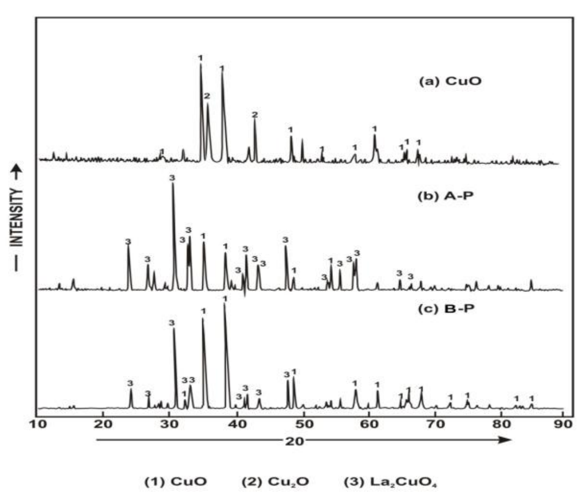

Figure 1 : XRD patterns of sintered pellets of (a) Cuo, (b) A-P and (c) B-P

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As CuO and La_2O_3 phases are parent oxides in the formation of composite phases, results obtained in the case of composite pellets are compared with those observed in the case of CuO pellet and with those reported for La_2O_3 pellet.
La_2O_3 in an insulator having band gap ~5 eV[1] and possessing strong dielectric properties[2]. The room temperature conduction of pellet of La_2O_3 observed using electrometer was found to be ~10^{-11} ohm^{-1} therefore; its contribution of conduction carriers to the carriers in composites will not be significant. Apart from this in the present laboratory the preparation of tough pellets of La_2O_3 was not possible. Hence, all the results obtained in the case of composite pellets are compared with those observed in the case of CuO pellets only.
Electrical ConductionFig.2 shows variation of electrical resistance (c) against 1/T, T being absolute temperature of pellets of CuO, A and B samples. All the pellets behave as semiconductors exhibiting negative temperature coefficient of resistance (Table 1).

A) Electrical conduction of CuO pellet: Electrical conduction of CuO pellet was studied as follows. In case of CuO pellet the initial resistance (25 kΩ) decreases gradually with the increase in temperature.
From room temperature to 330^0C with activation energy ΔE= 2.0 X 10^{-3} eV.
From 375 to 460^0C with E, 7.0 X 10^{-3} eV and thereafter, the resistance falls rapidly with ΔE= 1.4eV.
ΔE Values are calculated according to Arrhenius equation.

$$\rho = \rho_0 . \; e\Delta E/kT$$

or

$$\log \rho = \log \rho_0 + \Delta E/KT$$

or

$$2.303 \log_{10} \rho = 2.303 \log_{10} \rho_0 + \Delta E/KT$$

Where ρ = resistance at temperature T,
ρ_0 = specific resistivity, a constant term (property of material)
k = Boltzmann's constant and
E = activation energy.
And from the slope of linear relation between log c and 1/T, activation energy (ΔE) is calculated as follows.
Slope = ΔE/2.303 x k
Or ΔE = slope 2.303 x k
Earlier investigators have measured the electrical conductivity of sintered CuO pellet and found that below 650^0C the oxide is non-stoichiometric, containing excess oxygen and show p-type conduction [3,4] with activation energy of 0.15 eV. The two ΔE values are observed viz; 2.0 x 10^{-3} and 7.0x10^{-3} eV in the temperature range 30 to 460^0C (Table 1).
In their work on measurement on thermo EMF generated in CuO at elevated temperature above 65^0C Zuev *et al.* [5] have observed that the phase CuO is unstable at ~ 900^0C and local deformations are created during the formation of new phase that is the appearance of unstable stressed Cu_2O phase.
In the present work two different ΔE values are observed due to formation of Cu_2O phase on the grain boundaries of CuO phase after sintering the CuO pellet at 900^0C. Initially Cu_2O phase remains under stress which is unstable & on cooling the CuO pellet, Cu_2O phase gets stabilized on the grain boundaries along with excess oxygen.
It appears that the excess oxygen and the newly formed stressed phase Cu_2O create two energy levels in the pellet. It was not possible in this work to determine the exact nature of carriers, electrons or holes provided by these two energy levels.
In the earlier work intrinsic activation energies 1.4, 1.22 or 1.35 eV are reported [3,6] in the temperature range from ~600 to 800^0C while in the present work, ΔE 1.4 eV is observed in the temperature range from 470 to 530^0C.

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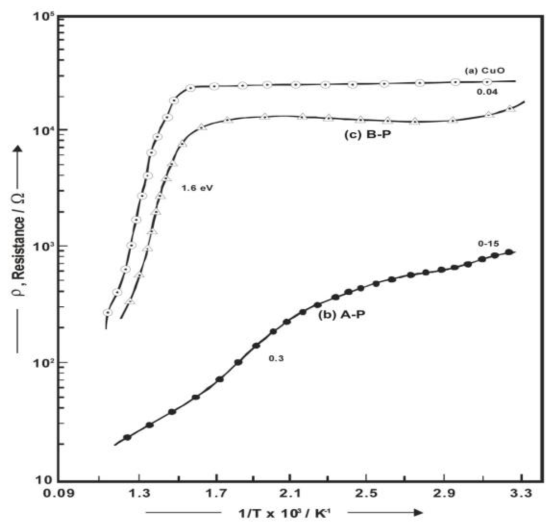

Figure 2 : Variation of resistance 'e' as a function of reciprocal of absolute temperature i.e. e vs 1/T in pellets of (a) CuO (b) A-P and (c) B-P.

B) Electrical conduction of pellet A-P: In the case of pellets of composites of CuO the variation of resistance is totally different from that observed in the case of CuO pellets.
In the case of A pellet the resistance 1.3 KΩ decreases gradually up to 282Ω in the temperature range from room temperature to 180^{0}C. It decreases up to 80^{0}C with ΔE, 0.15eV. If this process continues the resistance will further decrease up to 142Ω at 180^{0}C, on the contrary the resistance 300Ω is observed at that temperature. (Fig 2 b)
This is possible due to the following processes occurring in that temperature range.

The mobility of the conduction carrier in the same applied field decreases,
Carriers are supplied by some other phase having positive temperature coefficient of variation of resistance (Metallic behavior) and/or (iii) oxygen on the surface reacts with conduction carriers / electrons and gets chemisorbed over the surface leading to the removal of carriers. In compete pellet the three processes are probable and therefore instead of resistance 142 Ω there is a resistance of 300 Ω at 180^{0}C.

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TABLE 1

E values for Variation in the Resistance as a function of Temperature Regions for (a) CuO, (b) A-P and (c) B-P

a) CuO : Room temperature resistance 25K

	Pellet	Temperature Range / °C		
		30-330	375-460	470-530
E/eV	I	2.0×10^{-3}	7.0×10^{-3}	1.4
	II	1.97×10^{-3}	6.8×10^{-3}	1.4

b) A-P : Room temperature resistance 1.3 K

	Pellet	Temperature Range / °C			
		30-80	80-180	180-280	300-550
E/eV	I	0.142	Semiconducting non-linear	0.31	Semiconducting non-linear
	II	0.140	Semiconducting non-linear	0.29	Semiconducting non-linear

c) B-P : Room temperature resistance 16K

	Pellet	Temperature Range / °C				
		30-65	80-170	170-380	380-420	420-550
E/eV	I	3.85×10^{-2}	Metallic	Semicond-ucting non-linear	1.52	Semicond-ucting non-linear
	II	3.9×10^{-2}	Metallic	Semicond-ucting non-linear	1.55	Semicond-ucting non-linear

In the temperature range from 180 to 280^0C the resistance decreases with ΔE, 0.3 eV and thereafter up to 550^0C semi-conducting non linear variation is observed between log and 1/T. The non linear variation is also possible due to simultaneous occurrence of two, processes described above.

C) Electrical conduction of pellet B-P*:* In the case of pellet B-P, the variation of resistance shows (Fig 2c) semiconducting behavior as follows:
The semi-conducting behavior in the temperature range from 30 to 65^0C having ΔE= 0.0385 eV,
The metallic behavior from 65 to 170^0C,
Semiconducting non linear variation in log C against 1/T, in temperature range 180-380^0C,
The semiconducting behavior in the temperature range from 380 to 420^0C having ΔE= 1.52 eV and
Thereafter up to 550^0C semiconducting nonlinear variation of log C against 1/T. The ΔE values are given in Table 1.
The metallic behavior and non-linear variation of log observed in the conduction of this pellet can be explained on the basis of the processes described in the case of pellet A-P. Indeed, there exist several phases in both the pellets as observed in their XRD patterns (Fig 1). XRD patterns of pellet A-P shows lines of La_2CuO_4, Cu_2O phases and XRD pattern of pellet B-P displays lines of La_2CuO_4 and CuO phases. $CuLaO_2$ phase may be present in amorphous state in both the pellets.

IV. CONCLUSIONS

Electrical conduction of CuO changes due to conversion to Cu_2O along the grain boundaries of CuO. In the present work two different ΔE values are observed due to formation of Cu_2O phase on the grain boundaries of CuO phase after sintering the CuO pellet at 900^0C. Initially Cu_2O phase remains under stress which is unstable & on cooling the CuO pellet, Cu_2O phase gets stabilized on the grain boundaries along with excess oxygen. In case of La_2CuO_4 (samples A-P and B-P) the conduction depends on carriers. In case of mixture of Oxides after sintering the overall conduction depends upon number of phases formed and their relative proportion.

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