JOURNAL OF MATERIALS SCIENCE 25 (1990) 1913–1916

Chemical approach to the conduction mechanism in copper tellurite glasses containing lutetium oxide

M. SULEMAN MALIK, C. A. HOGARTH
Physics Department, Brunel University, Uxbridge, Middlesex, UK

Measurements of d.c. electrical conductivity were made on $65TeO_2$–$(35 - x)CuO$–xLu_2O_3 (mol %) glasses with $x = 0, 1, 2, 3, 4$. The experimental results show that when x is changed from 1 to 2 mol %, the conductivity increases due to the additional electrons obtained by the oxidation of TeO_2 as well as due to the $Cu^+ \rightarrow Cu^{2+}$ transition under the effect of interelectronic repulsion in the 4f shell of the lutetium present in the glass. When x is increased to greater than 2 mol %, the conductivity decreases because hopping is inhibited due to the formation of oxygen bridge associates or because of the strong ligand repulsive field of lutetium indicating its non-reactivity in the glassy network. The conductivity has a distinct maximum at $x = 2$.

1. Introduction

The behaviour of electrical conductivity in the transition and mixed transition metal oxide glasses has been investigated by many workers [1–4] but less work has been reported about the electrical properties of glasses containing rare earth oxides. At present there is a wide interest in studying such oxides.

Komiyama [5] has reported that the electrical conductivity decreases with the increase of the content of RE_2O_3 (rare earth oxide) in sodium silicate glasses. Buri *et al.* [6] have also reported the properties of sodium silicate glasses containing rare earth oxides and have discussed the role of rare earth ions in the glass structure [6]. Makishima *et al.* [7] have studied the properties of aluminosilicate glasses containing the oxides of the following rare earth elements, e.g. Sc_2O_3, Y_2O_3, La_2O_3, Ce_2O_3, Pr_6O_{11}, Eu_2O_3, Gd_2O_3, Tb_4O_7, Dy_2O_3, Ho_2O_3 and Yb_2O_3 and have shown that the glasses prepared by the admixture of RE_2O_3 are hard and very durable in alkaline solution, having high elastic moduli and high refractive indices. The electrical properties of glasses made from the oxides of praseodymium and phosphorus pentoxide have been studied by Magruder and Kinser [8] as a function of oxidation and reduction treatments. They have suggested that the conduction mechanism is similar to the variable valency hopping proposed by Mott [9] and the electronic conduction of the 4f series of glasses was markedly lower in magnitude than for the 3d, 4d and 5d transition metal (TM) oxide glasses. Ravishankar Harani and Hogarth have also reported [20] on the electrical properties of a range of praseodymium phosphate glasses.

Khan *et al.* [10] have shown the affects of 5 mol % of rare earth oxides e.g. CeO_2, Ce_2O_3, Eu_2O_3, Gd_2O_3, Tb_4O_7 and Yb_2O_3 on the electrical properties of vanadium phosphate glasses and demonstrated that the conductivity of these glasses is slightly higher than the corresponding compositions with the rare earth oxides. Osman [11] has also investigated the electrical behaviour of rare earth Pr_6O_{11} in copper phosphate and in copper calcium phosphate glasses and concluded that the conductivity decreases with the increase of rare earth oxide content in the glass. Lyne *et al.* [12] have studied the multiphonon relaxation of rare earth ions in oxide glasses TeO_2, GeO_2, SiO_2, P_2O_5 and B_2O_3. They have suggested that the relaxation occurs predominantly by the excitation of higher frequency vibrations associated with the stretching modes of the glass network former.

In this paper, we present the results of electrical measurements of copper tellurite glasses containing Lu_2O_3, a material whose properties have not previously been reported in the literature.

2. Experimental techniques

2.1. Glass preparation

The glasses in the system of composition $65TeO_2$–$(35 - x)CuO$–xLu_2O_3 in mol % with $x = 0, 1, 2, 3, 4$ were prepared from analar grades of TeO_2, CuO and 99.9% pure Lu_2O_3. The oxides were mixed in an alumina crucible which was placed in the furnace preheated at 300° C for 1 h to reduce the mechanical stresses and the volatilization losses. The crucible was then transferred to a melting furnace preheated at a temperature of 900 to 950° C for 2 h. During melting, the melt was stirred from time to time with an alumina rod to improve the homogeneity. At the end of the firing period, the crucible was lifted rapidly out of the furnace and the melt was quenched by pouring onto a clean stainless steel plate and cast into disc-shaped samples and these were immediately transferred and

0022–2461/90 $03.00 + .12

placed in another furnace preheated to a temperature of 300°C for 1 h to remove the surface stresses and volatile contaminants. The furnace was then switched off to cool down to room temperature and to yield stable glasses.

It was believed that the glass preparation history i.e. melting temperature, melting time, annealing time, annealing temperature, rate of cooling and melting atmosphere could affect the properties of glasses and so all these parameters were kept constant for all the glasses under investigation. The glasses were ground on both sides to make the surfaces smooth and parallel using a grinding machine (Flexibox, Model 124) and using different grades of SiC powder with Mobil liquid oil as a lubricant. Then the glasses were polished using a polishing machine with grade (6-w-42) Hyprez diamond compound paste and Hyprez fluid as a lubricant. After grinding and polishing the glasses were cleaned by acetone and dried. A three-terminal gold electrode system for providing electrical contacts was deposited on all series of glass samples using an Edwards 12″ coating unit operating at a pressure of 10^{-4} torr.

2.2. Measurements

The d.c. conductivity of the samples was measured in the temperature range 293 to 453 K. The current was measured using a Keithley 610 electrometer capable of measuring currents down to 10^{-14} A and the power supply used was a Keithley 240 A high voltage supply. The temperature of the sample was measured with a chromel–alumel thermocouple attached to the sample surface. All measurements were made under a vacuum of 10^{-5} torr to avoid atmospheric effects and were made more than once.

The d.c. conductivity of the sample at each temperature was calculated from the following relation

$$\sigma = d/RA \qquad (1)$$

where R is the resistance of the sample at each temperature measured from the slope of a linear VI plot. A is the guarded electrode area and d is the sample thickness. Also, the d.c. conductivity is a negative exponential function of inverse temperature and may be expressed by the usual equation

$$\sigma_{\text{d.c.}} = \sigma_0 \exp(-W/kT) \qquad (2)$$

where W is the activation energy.

The resistance of all the glasses was measured as a function of time to check the nature of the conduction mechanism. A fixed voltage of 100 V was applied for a period of 5 h and the resistance ($R = V/I$) was measured continuously. The variation of resistance with time at room temperature is shown in Fig. 1 and indicates that apart from the initial short term variation of resistance with time, the current is found to be constant and this can be taken as evidence that the conductivity would be due to the transport of electrons, showing the absence of a significant polarization effect in the glasses. The d.c. conductivity and the voltage–current characteristics are very sensitive to temperature. The glasses show ohmic behaviour at low fields as shown in Fig. 2.

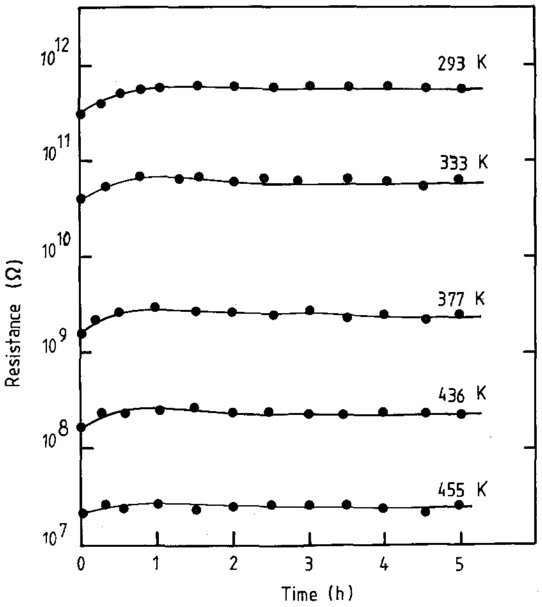

Figure 1 Variation of resistance with time for a 1 mol % Lu_2O_3 sample at different temperatures.

3. Results and discussion

Figures 3 and 4 show the variation of log σ with $1000/T$ for binary TeO_2–CuO and ternary TeO_2–CuO–Lu_2O_3 glasses, respectively. The activation energies for the glasses were calculated from the slopes of these curves. The values of d.c. conductivity and activation energy of all listed glass compositions, measured at a temperature of 444 K are given in Table I.

The conductivity against inverse temperature plots show that the conductivity increases with the increase of temperature and also show that the magnitude of conductivity becomes smallest in glasses having the highest thermal activation energy. This is consistent with the general formula proposed by Mott [9], and the variation of activation energy with Lu_2O_3 content in the present study is shown in Fig. 5. Fig. 6 shows the variation of d.c. conductivity with lutetium oxide content. The curve indicates that there is a very slight increase with the addition of 1 mol % Lu_2O_3 and the maximum in conductivity is obtained at 2 mol % Lu_2O_3 for which the corresponding activation energy

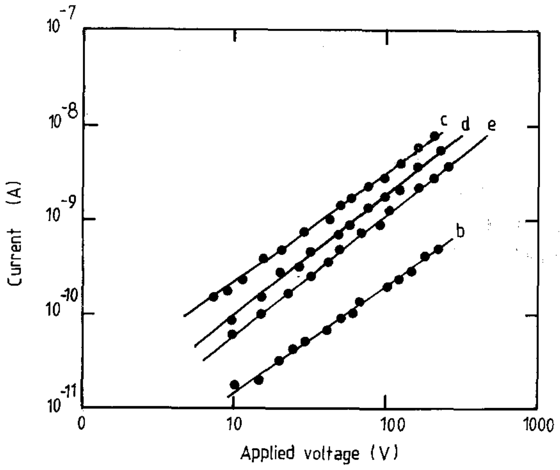

Figure 2 V–I characteristics at room temperature of four samples of TeO_2–CuO–Lu_2O_3.

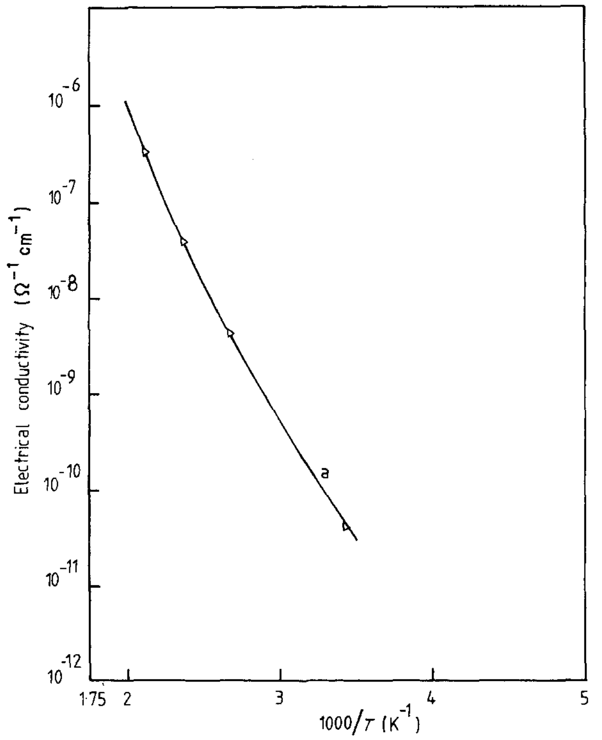

Figure 3 Conductivity as a function of inverse temperature for binary 65TeO_2-35CuO (mol %) glass sample.

is a minimum, and at more than 2 mol % Lu_2O_3 the conductivity is found to decrease gradually. Our previous investigation of copper tellurite glasses [13] reveals that copper exists in the glass as both Cu^{2+} and Cu^+ ions and the temperature independence of the Cu^{2+} content can be taken as an evidence of constant carrier concentration and an electron hopping conduction process.

In the present study it has been suggested that TeO_2 is playing a major role in enhancing the magnitude of the conductivity besides the fact that a small amount of TeO_2 is lost during heating, as reported by previous workers on other TeO_2 glassy systems [14, 15]. Thus it can be said that in the present glassy systems too, tellurium sites are participating in the conduction process to some extent. Tellurium generally exists with valency states Te^{4+} and Te^{6+} and during melting it is likely that a small proportion of TeO_2 is oxidized by the atmospheric oxygen above the melt [16]. Under these conditions additional charge transfer could occur between tellurium ions or between tellurium and copper ions.

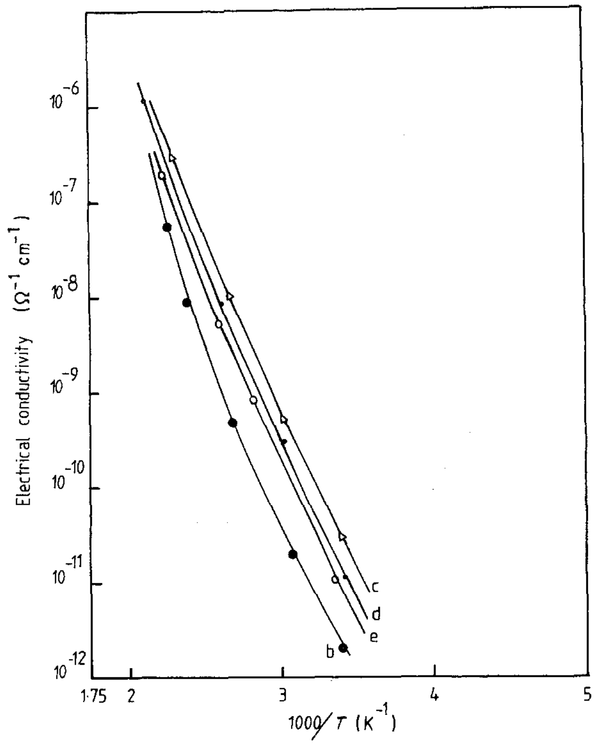

Figure 4 Conductivity as a function of inverse temperature for the four samples of TeO_2-CuO-Lu_2O_3 glasses of Fig. 2. (● 1% Lu_2O_3, △ 2% Lu_2O_3, ● 3% Lu_2O_3, ○ 4% Lu_2O_3)

TABLE I Composition and derived parameters of some copper tellurite glasses with lutetium oxide

No.	Glass number	Composition (mol %)			d.c. Conductivity at 444 K (Ω^{-1} cm^{-1})	Activation energy (eV)
		TeO_2	CuO	Lu_2O_3		
1	a	65	35	0	9.0×10^{-8}	0.69
2	b	65	34	1	9.5×10^{-8}	1.34
3	c	65	33	2	4.7×10^{-7}	0.68
4	d	65	32	3	2.9×10^{-7}	0.92
5	e	65	31	4	1.7×10^{-7}	0.93

It is significant that no charge state other than +3 (the most stable state) is known for lutetium [17] which lies at the top atomic number end of the lanthanide series and its 4f shell is completely filled so that there is no possibility for inner transitions involving 4f electrons to take place [18]. Also the ionic radius of lutetium is small (0.099 nm) [17] as compared to the other lanthanide elements and its small size indicates that its electron cloud is strongly attracted by its nucleus giving rise to high stability and structural complexity in addition to the interelectronic repulsion within the 4f shell and the weak overlapping which takes place when Lu_2O_3 is added to form a complex glass. In spite of these considerations the effect of lutetium can never be totally ignored and can well be considered significant. The contribution of Lu_2O_3 in enhancing the electronic conduction for up to 2 mol % addition can be explained on the ground that it is

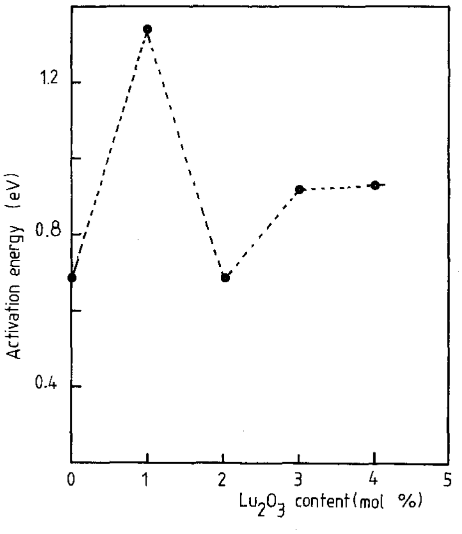

Figure 5 Activation energy as a function of Lu_2O_3 content for TeO_2-CuO-Lu_2O_3 glasses.

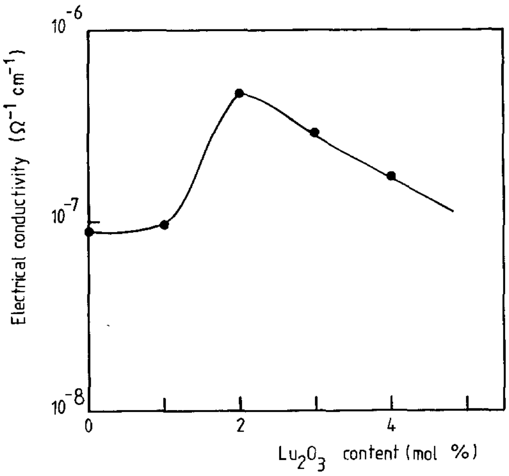

Figure 6 Conductivity plotted against Lu_2O_3 content for TeO_2–CuO–Lu_2O_3 glasses.

likely that the interelectronic repulsion and the weak overlapping of orbitals might develop a ligand repulsive field of an accelerating nature, thereby causing an increase in electron mobility which would cause an increase in the conductivity. These electrons are available as a result of the oxidation of a small portion of TeO_2 whereby the Te^{4+} ions are locally bonded as Te^{6+} ions and by the hopping phenomena taking place between the Cu^+ and Cu^{2+} centres [13].

The availability of these electrons used in the conduction mechanism can be explained by the following solid state reaction.

A small portion is oxidized as follows

$$TeO_2 \rightarrow Te^{6+} + 2O^{2-} + 2e^- \text{ (conducting electron)}$$

Some of the oxygen may be lost on conversion to oxygen molecules and will thus leave behind further free electrons in the melt which would then be retained in the glass on solidifying. Also the hopping process will be related to the following reaction.

$$Cu^+ \rightarrow Cu^{2+} + e^- \text{ (conducting electron)}$$

Furthermore the reverse of this process may also take place causing the copper ions to alter in character from Cu^+ (diamagnetic) to Cu^{2+} (paramagnetic). In this reaction the Cu^+ ion (diamagnetic) arises as a consequence of a Cu^{2+} ion (paramagnetic) accepting an electron, probably one released by the oxidation of tellurium dioxide. The Cu^+ ion can further release an electron by hopping, converting itself again into a Cu^{2+} ion. This released electron combines with one of the remaining electrons left from the oxidation of the Te^{4+} ions to Te^{6+} in TeO_2. These two electrons will be accelerated by the field caused by the interelectronic repulsion as well as by the weak overlap of orbitals in the most stable state of lutetium, and thus enhance the conduction. Beyond 2 mol % of Lu_2O_3, the conductivity decreases and the following three possible explanations can be advanced.

(1) The decrease in conductivity may be due to the diminishing number of hopping centres because of the high complexity and stability of lutetium oxide.

(2) The decrease may be due to the formation of oxygen bridge associates because of the excess charge of the rare earth oxide.

(3) The conducting electrons can be held in the complex network of Lu_2O_3 or they may rebound due to its strong repulsive field at the greater concentration of Lu_2O_3 or by the electronic cloud of higher intensity. It can thus be concluded that the addition of Lu_2O_3 at its low concentrations (up to 1 mol %) in copper tellurite glasses increases the conductivity by a small amount, up to 2 mol % of Lu_2O_3 in the glasses, it is harder for the conducting electrons to drift forward and thus the conductivity falls systematically as the Lu_2O_3 content is further increased. The above discussion shows that lutetium in copper tellurite glasses remains non-reactive chemically except in providing a ligand repulsive field due to the interelectronic repulsion effect and this argument is in close agreement with the general concept that the effects of the lanthanide are not entirely negligible [19].

References

1. G. S. LINSLEY, A. E. OWEN and F. N. HAYATEE, *J. Non-Cryst. Solids* **4** (1970) 208.
2. G. N. GREAVES, *ibid.* **11** (1973) 427.
3. L. MURAWSKI, C. H. CHUNG and J. D. MACKENZIE, *ibid.* **32** (1979) 91.
4. A. K. BANDYOPADHYAY and J. O. ISARD, *J. Phys. D.* **10** (1977) L99.
5. T. KOMIYAMA, "A study of the glass containing rare earth elements" Reports of Government Industrial Research Institute, Osaka, November 1976.
6. A. BURI, D. CAFERRA, F. BRANADA and A. MAROTTA, *Phys. Chem. Glasses* **23** (1982) 37.
7. A. MAKISHIMA, M. KOBAYASHI and T. SHIMOHIRA, *J. Amer. Ceram. Soc.* **65** (1982) c-210.
8. R. H. MAGRUDER and D. L. KINSER, *J. Non. Cryst. Solids* **45** (1981) 389.
9. N. F. MOTT, *J. Non-Cryst. Solids* **1** (1968) 1.
10. M. N. KHAN, RAVISHANKAR HARANI, M. M. AHMAD and C. A. HOGARTH, *J. Mater. Sci.* **20** (1985) 2207.
11. A. E. MOHAMMED OSMAN, PhD Thesis, Brunel University, Uxbridge, Middlesex, UK (1987).
12. G. G. LAYNE, W. H. LOWDERMILK and M. J. WEBER, *Phys. Rev.* **16** (1977) 10.
13. M. SULEMAN MALIK, C. A. HOGARTH and K. A. K. LOTT, *J. Mater. Sci. Lett.* **8** (1989) 1344.
14. R. MANCASTER and S. PARKE, *J. Non-Cryst. Solids* **24** (1977) 399.
15. V. K. DHAWAN, A. MANSINGH and M. SAYER, *ibid.* **51** (1982) 87.
16. B. W. FLYNN and A. E. OWEN, *J. Physique* Proceedings 9th International Conference on Amorphous and Liquid Semiconductors 11", edited by B. K. Chakraverty (France, 1981) p. C4-1005
17. G. F. LIPTROT, "Modern Inorganic Chemistry" 3rd edn, (Bel and Hayman, London, 1981) pp. 436, 439.
18. H. L. SMITH and A. J. COHEN, *Phys. Chem. Glasses* **4** (1963) 173.
19. B. N. FIGGIS, "Introduction to the Ligand Field" (Wiley, London, 1966) p. 327.
20. RAVISHANKAR HARANI and C. A. HOGARTH, *J. Mater. Sci. Lett.* **5** (1986) 492.

Received 9 February
and accepted 24 August 1989.