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Chemical analysis and electrical conductivity of tellurium phosphate glasses doped with bismuth oxide

A. ABDEL-KADER*, A. A. HIGAZY*, M. M. ELKHOLY*,
R. M. EL-BAHNASAWY‡
**Physics Department, and ‡Chemistry Department, Faculty of Science, Menoufia University, Menoufia, Egypt*

The chemical composition and the temperature dependence of d.c. electrical conductivity are presented for TeO_2–P_2O_5 and Bi_2O_3–TeO_2–P_2O_5 glass systems. The results have shown that the network former ion has a substantial effect on the electrical conductivity of oxide glasses. Log σ and activation energy values were found to be sensitive to the addition of TeO_2 and Bi_2O_3. They showed an anomalous behaviour.

1. Introduction

Many phosphate glasses have been investigated by various authors [1–7]. In almost all cases it has been found that when these glasses have been prepared by melting the constituents in air, loss of oxygen and phosphorus occurred. In this case the composition of the final glass product may differ from the starting composition, so a complete analysis of the TeO_2–P_2O_5 and Bi_2O_3–TeO_2–P_2O_5 glasses was clearly necessary to relate their properties to gradual changes in glass composition.

Phosphate glasses containing transition metal oxides have received a great deal of attention due to the existence of the transition metal ion in more than one valence state. The conduction process [8–17] in such glasses is believed to take place by the transfer of electrons from a transition metal ion in the low valence state to the one in the high valence state: i.e. the glass former P_2O_5 does not play a major role in the electrical conduction. Also, the conduction process in V_2O_5–Bi_2O_3 glasses [18] and V_2O_5–TeO_2 glasses [11] is attributed to the valency exchange between V^{4+} and V^{5+}.

The effects of the basic glass formers P_2O_5 and B_2O_3 on the electrical conduction have been investigated by Kennedy and Machenzie [19] and Higazy *et al.* [7], who found that the network former ions have a real effect on the conduction mechanism.

The present investigation forms part of a programme to explore the information which can be obtained about the effect of the network-forming ions on the electrical conductivity of oxide glasses. The d.c. electrical conductivity of the prepared TeO_2–P_2O_5 and Bi_2O_3–TeO_2–P_2O_5 glasses were studied in an attempt to interpret the effect of the network-forming ions on the conduction process.

2. Experimental procedure

2.1. Preparation of glasses

The binary TeO_2–P_2O_5 glasses were prepared by melting the appropriate mixture of Analar phosphorus pentoxide, P_2O_5, and Analar tellurium oxide, TeO_2, using open alumina crucibles heated in an electric furnace open to the atmosphere. The mixture was heated first at 250 °C for 1 h and then transferred to a second furnace held at 800 °C for 45 min. The glass melts were stirred occasionally with an alumina rod, to ensure homogeneous melts. Each melt was cast into two mild steel moulds to form glass rods of 3 cm long and 1 cm diameter. Then the glasses were annealed at 300 °C for 1 h. After this time, the furnace was switched off and glasses were allowed to cool to room temperature. The ternary Bi_2O_3–TeO_2–P_2O_5 glasses were prepared using the same procedure described in the binary TeO_2–P_2O_5 glasses, except that the melting temperature was held at 900 °C for 1 h. All glasses were examined by X-ray diffraction and no diffraction lines were observed confirming the glass formation.

2.2. Chemical analysis

2.2.1. Determination of phosphorus and bismuth contents

The concentration of phosphorus and bismuth in the present glass systems was determined by the gravimetric chemical technique. The phosphates were determined as ammonium magnesium phosphate hexahydrate ($MgNH_4PO_46H_2O$) and the bismuth was determined as bismuth oxyiodide (BiOI). The procedure followed was given by Vogel [20].

2.2.2. Determination of tellurium content

The following procedure was employed to determine the Te content in the present glass systems: the solution contains $\leqslant 0.2$ g Te in 50 cm^3 3M hydrochloric acid was heated to boiling point. Then 15 cm^3 15% aqueous hydrazinium chloride and 25 cm^3 saturated solution of sulphur dioxide were added. This mixture was heated to boiling point and maintained for 5 min; a precipitate was formed. The precipitate was collected in a weighed porcelain filter crucible, then washed with hot water and ethanol and dried at 105 °C. The crucible was cooled to room temperature in an evaluated desiccator containing silica gel and then weighed as Te.

2.2.3. The d.c. electrical conductivity measurements

For the measurements of d.c. electrical conductivity, electrodes were formed by brush painting silver paste. The d.c. electrical conductivity was measured as a function of temperature, using a spring-loaded sample holder in a wire-wound cylindrical furnace. In this study, the current was measured by means of a Keithley electrometer model 616, with a smoothing adjustable power supply (0–1 kV). A fixed voltage of 300 V was applied. The temperature of the specimen was measured using a chromel–alumel thermocouple.

3. Results and discussion

Our chemical analysis data for the TeO_2–P_2O_5 and Bi_2O_3–TeO_2–P_2O_5 glass systems has shown that a substantial loss of P_2O_5 occurred during the melting processes (see Tables I and II). The data of Table I have established that the range of glass formation for the TeO_2–P_2O_5 glass system produced by melting TeO_2 with P_2O_5 is continuous from pure P_2O_5 up to 100 mol % TeO_2 (starting composition) with no region of stable immiscibility existing.

The variation of the glass density with TeO_2 content (mol %) is shown in Fig. 1. From an examination of this figure, it may be observed that the TeO_2–P_2O_5 glass system can apparently be divided into three compositional regions on the basis that there is a change in the compositional gradient (see Fig. 1); i.e. over the first composition range (0–64 mol %) the gradient increases by a factor of 0.02/mol % TeO_2. In the second range (64–80 mol %) the compositional gradient increases by a factor of 0.047/mol % TeO_2 and in the third region (80–98.4 mol %) the factor is 0.078/mol % TeO_2.

Fig. 2 shows a plot of density against Bi_2O_3 content for Bi_2O_3–TeO_2–P_2O_5 glasses. This figure shows an increase with increasing Bi_2O_3 content (mol %), which is probably attributable to a change in the compaction of the glass structure, i.e. the compact structure of Bi_2O_3–TeO_2–P_2O_5 glasses increases with increasing Bi_2O_3 content.

The variation of d.c. electrical conductivity, $\log \sigma$, with the reciprocal of the absolute temperature, T^{-1}, for the glass system TeO_2–P_2O_5 is shown in Figs 3 and 4. The plot of d.c. electrical conductivity, $\log \sigma$, against T^{-1} for Bi_2O_3–TeO_2–P_2O_5 glasses is shown in Figs 5 and 6. From an inspection of these figures it is noted that the electrical conductivity for all glasses

TABLE I Composition and density for TeO_2–P_2O_5 glasses

Sample	Starting composition (mol %)		Density	Analysed composition (mol %)	
No.	TeO_2	P_2O_5	(g cm^{-3})	TeO_2	P_2O_5
Pure P_2O_5	–	100	2.52	–	100
T_4	20	80	3.13	28.18	71.82
T_6	30	70	3.30	36.15	63.85
T_8	40	60	3.50	45.72	54.28
T_{10}	50	50	3.74	52.42	40.58
T_{12}	60	40	3.89	64.28	35.72
T_{14}	70	30	4.34	69.51	26.49
T_{16}	80	20	4.47	76.49	23.51
T_{18}	90	10	4.83	81.09	18.91
T_{20}	100	–	5.23	98.40	–

TABLE II Composition and density for the glass of 50 TeO_2–50P_2O_5 mol % with the addition of Bi_2O_3

Sample	Starting Bi_2O_3	Density	Analysed composition (mol %)		
no.	(g/100 g glass)	(g cm^{-3})	Bi_2O_3	TeO_2	P_2O_5
T_{10}	0	3.74		59.42	40.58
$(TB)_1$	2	3.24	5.80	54.89	39.31
$(TB)_2$	5	3.71	14.15	50.14	35.71
$(TB)_3$	10	3.89	25.11	44.07	30.82
$(TB)_4$	15	3.92	26.50	43.45	30.05
$(TB)_5$	20	3.99	30.77	40.62	28.61
$(TB)_6$	30	4.11	46.11	31.19	22.70
$(TB)_7$	40	4.19	57.20	25.11	17.69

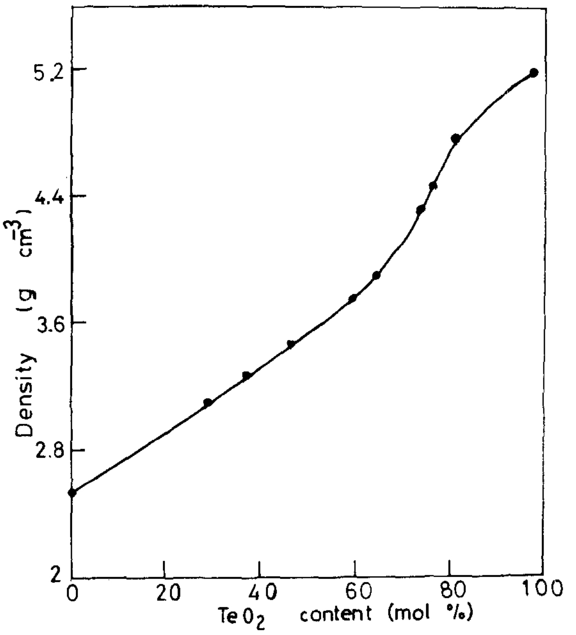

Figure 1 Variation of density with TeO_2 content (mol %) (chemically analysed composition) for TeO_2–P_2O_5.

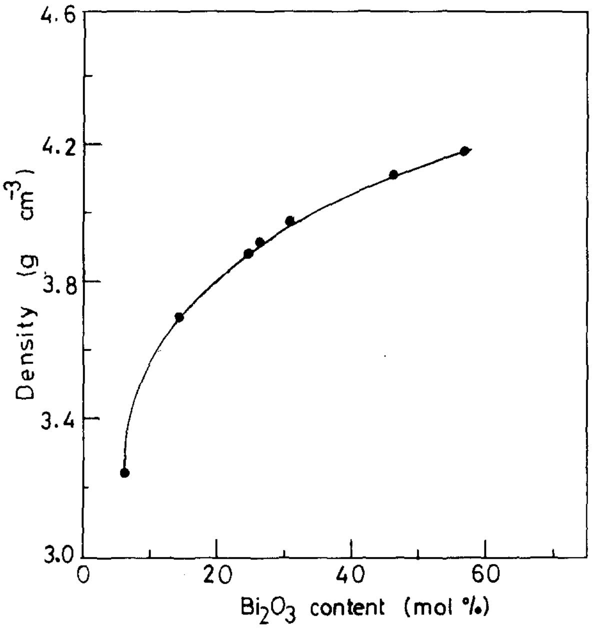

Figure 2 Variation of density with Bi_2O_3 content (mol %) (chemically analysed composition for Bi_2O_3–TeO_2–P_2O_5 glasses.

shows that the log σ versus T^{-1} plots give a good straight line, in the temperature range 476–606 K, which reflects the semiconducting behaviour of the specimens under study. This can be taken as evidence that the activation energy for this glass system in this temperature range is independent of temperature.

As mentioned above, the aim of the present work was to examine the effect of the network former on the electrical properties of semiconducting oxide glasses. Thus the present glass systems TeO_2–P_2O_5 and Bi_2O_3–TeO_2–P_2O_5 glasses were prepared from the basic oxide glass formers Bi_2O_3, TeO_2 and P_2O_5. In the case of phosphate glasses containing oxides of Na, Ca, Zn, Mg, Ti, Co, Ni, Mo, V, Fe, . . . , etc., i.e. the oxides of the network modifier cations, the electrical

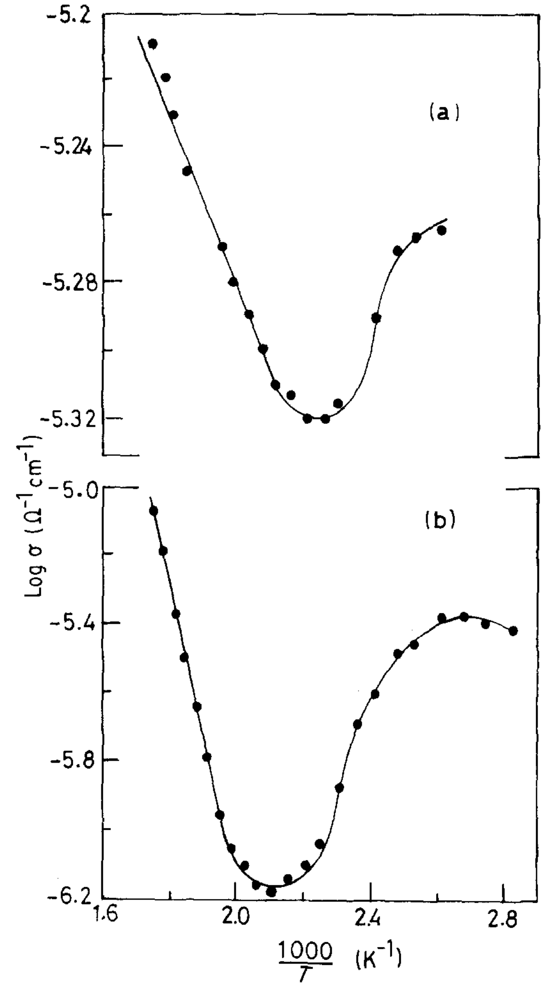

Figure 3 D.c. electrical conductivity of TeO_2–P_2O_5 as a function of inverse temperature, $1/T(K^{-1})$. (a) 45.72 mol % and (b) 59.42 mol % TeO_2.

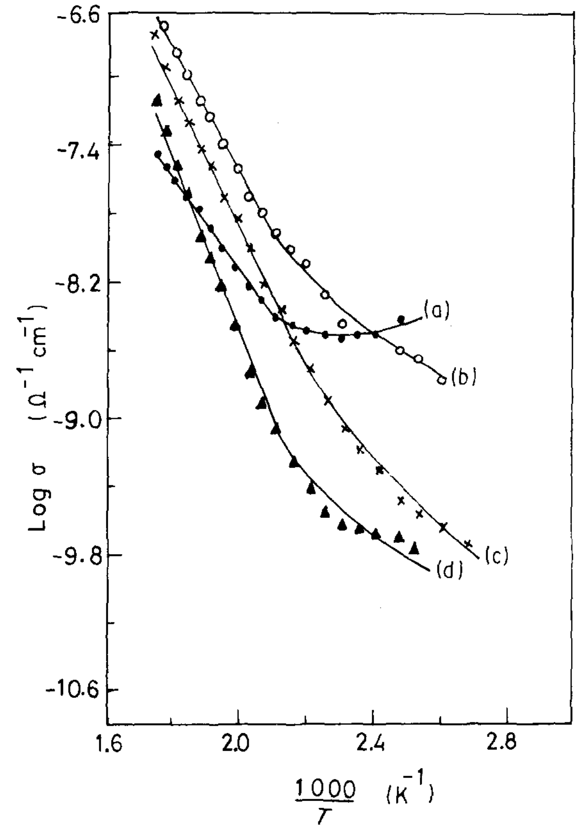

Figure 4 D.c. electrical conductivity as a function of inverse temperature, $1/T(K^{-1})$ (a) 64.28 mol %, (b) 73.51 mol % (c) 76.49 mol % and (d) 81.09 mol % TeO_2 content.

conduction in these glasses is related to the concentration of these oxides [21]. Also for the binary glass systems V_2O_5–Bi_2O_3 [18], V_2O_5–TeO_2 [11], the electrical conduction of these glasses is attributed to the concentration and the valence exchange between V^{4+} and V^{5+}. For the above glass systems, it has been reported that the glass formers P_2O_5, TeO_2 and Bi_2O_3 do not play a major role in the electrical

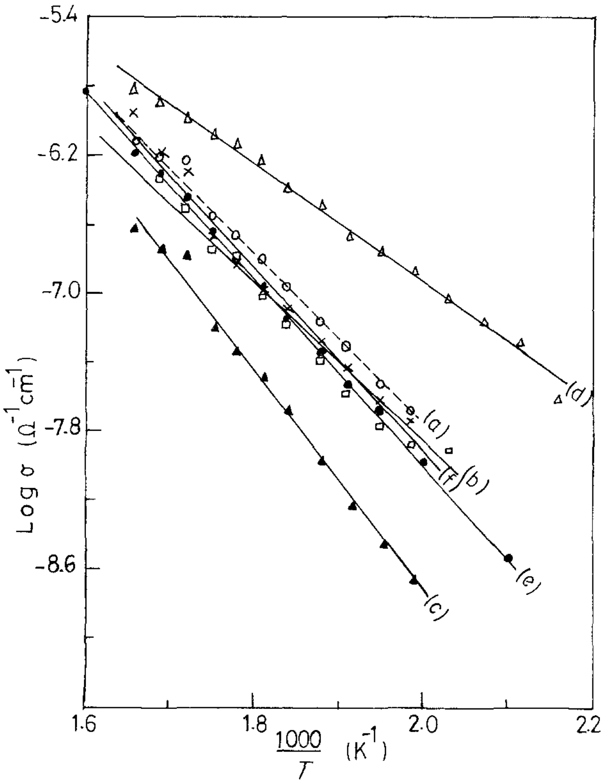

Figure 5 D.c. electrical conductivity of Bi_2O_3–TeO_2–P_2O_5 glasses as a function of inverse temperature, $1/T(K^{-1})$. (a) 14.15 mol %, (b) 25.11 mol %, (c) 26.50 mol %, (d) 30.77 mol %, (e) 46.11 mol %, (f) 57.20 mol % Bi_2O_3.

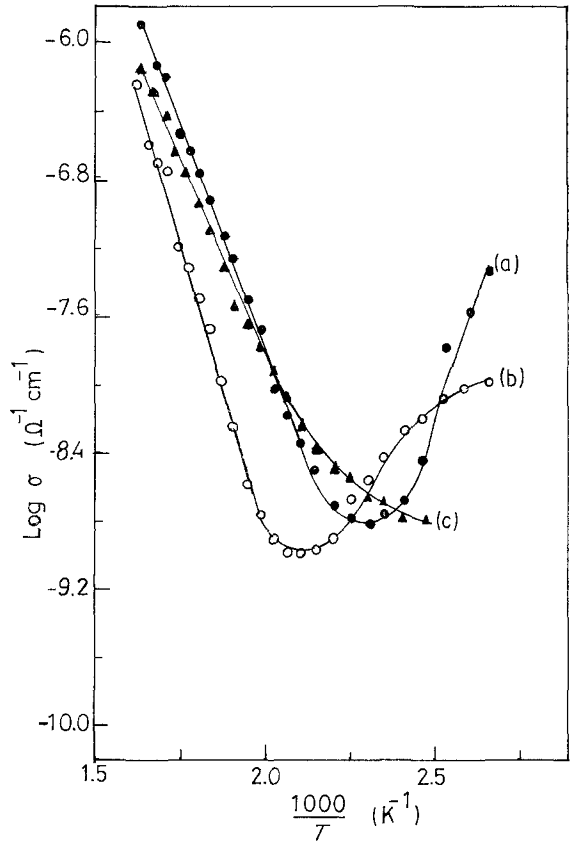

Figure 6 D.c. electrical conductivity of Bi_2O_3–TeO_2–P_2O_5 glasses as a function of inverse temperature, $1/T(K^{-1})$. (a) 14.15 mol %, (b) 26.50 mol % and (c) 57.20 mol % Bi_2O_3.

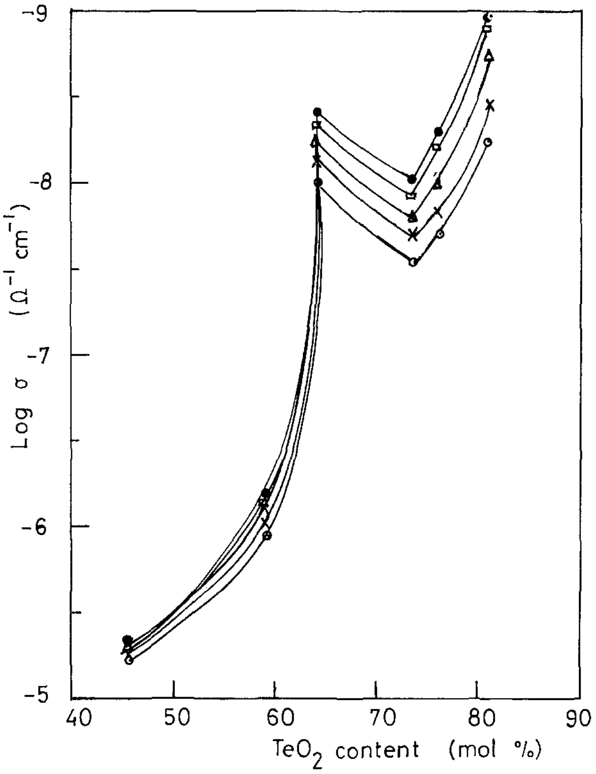

Figure 7 The variation of log σ with TeO_2 content (mol %) at five different temperatures for TeO_2–P_2O_5 glasses. (●) 474 K, (□) 483 K, (△) 493 K, (×) 532 K, (○) 543 K.

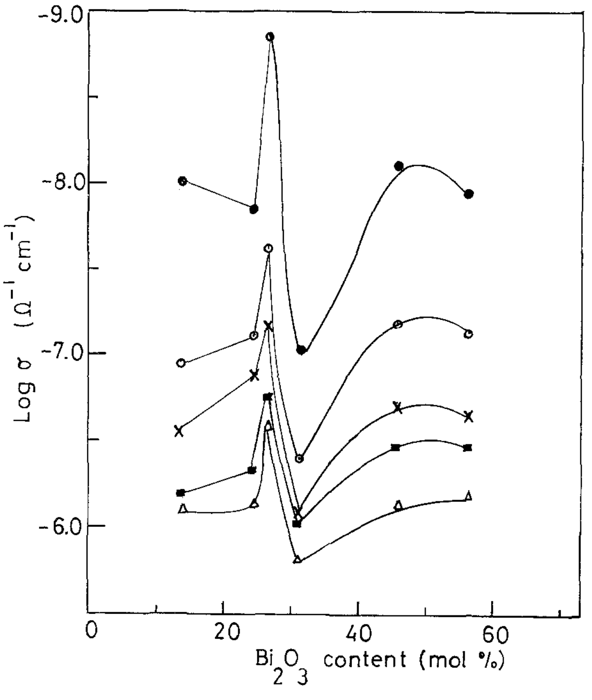

Figure 8 The variation of log σ with (Bi_2O_3 content (mol %) at six different temperatures for Bi_2O_3–TeO_2–P_2O_5 glasses. (●) 493 K, (○) 543 K, (×) 573 K, (■) 583 K, (△) 603 K.

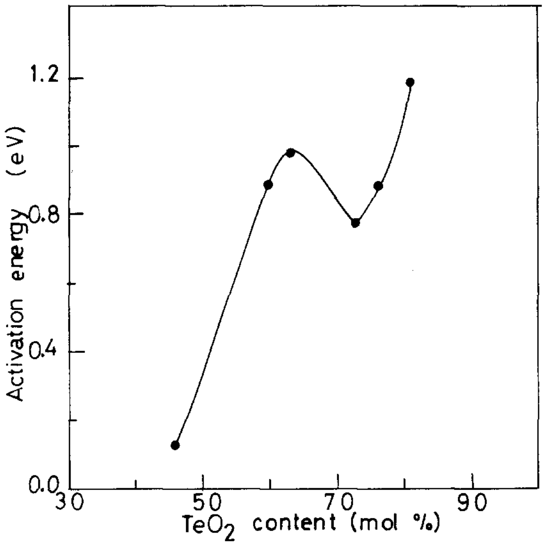

Figure 9 Variation of the activation energy with TeO_2 content (mol %) for TeO_2–P_2O_5 glasses.

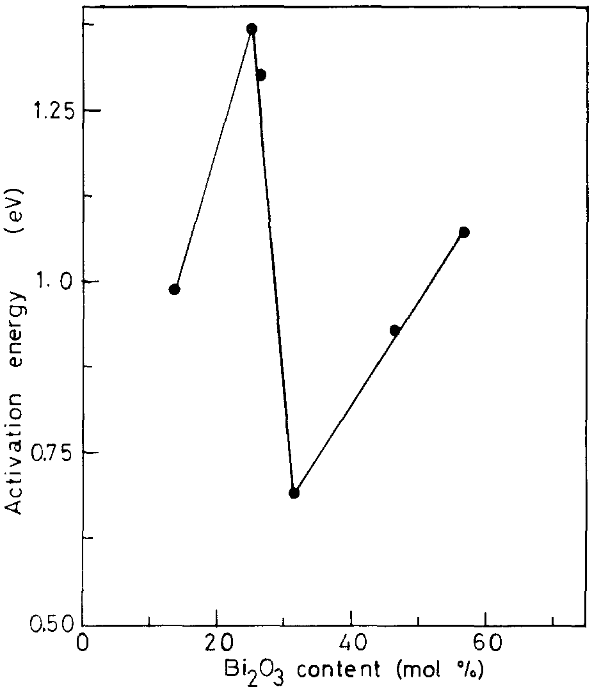

Figure 10 The variation of activation energy with Bi_2O_3 content (mol %) for Bi_2O_3–TeO_2–P_2O_5 glasses.

conduction. From the conductivity measurements of the present glass systems, which were prepared from Bi_2O_3, TeO_2 and P_2O_5 glass-former oxides, the electrical conduction may be attributed to the Bi, Te, and P, i.e. the network-former ions have a real effect on the electrical conduction of our glasses.

Fig. 7 shows the variation of log σ with TeO_2 (mol %) content at five different temperatures for the TeO_2–P_2O_5 glass system. It is clear from Fig. 7 that the compositional dependence of log σ could be divided into three-composition regions. The addition of TeO_2 in the compositional region 45.72–64.28 mol % TeO_2 leads to an increase in the values of log σ. Beyond 64.28 mol % , there is a critical compositional region of 64.28–73.51 mol % in which the values of log σ decrease, as the TeO_2 content increases from 73.51–81.09 mol % the log σ value increased rapidly. For ternary Bi_2O_3–TeO_2–P_2O_5 glass system, the compositional dependence of log σ showed three composition regions (see Fig. 8).

In the present investigation the conduction activation energy, *E*, was calculated from the slope of the log σ against T^{-1} plot using a least squares fit method. The variation of the activation energy, *E*, with TeO_2 content (mol %) for TeO_2–P_2O_5 glasses showed three composition regions, (see Fig. 9) the boundaries of which are in agreement with the three compositional behaviour regions observed in the compositional dependence of the density for the same glass system (see Fig. 1).

Fig. 10 shows the variation of the activation energy, *E*, with Bi_2O_3 (mol %) content for Bi_2O_3–TeO_2–P_2O_5 glasses. The values of *E* are seen to display an increase with increasing Bi_2O_3 content from 14.15–25.11 mol % (*E* varies from 0.99–1.37 eV). As we increase the Bi_2O_3 content from 25.11–30.77 mol %, the *E* values decreased rapidly from 1.37–0.69 eV. When Bi_2O_3 oxide increases beyond 30.77 mol % the values of *E* increase again.

The compositional behaviour regions observed in the present work (Figs 7–10) may be attributed to a structural change in the glass network. At the present time we need further investigation to explain this behaviour.

References

1. M. MUNAKATA, *J. Ceram. Assoc. Jpn* **67** (1959) 344.
2. M. MUNAKATA, *Solid State Electron.* **1** (1960) 159.
3. Bh. V. JANAKIRAMA-RAO, *J. Amer. Ceram. Soc.* **49** (1966) 605.
4. F. R. LANDSBERGER and P. J. BRAY, *J. Chem. Phys.* **53** (1970) 2757.
5. H. HARPER and P. W. McMILLAN, *Phys. Chem. Glasses* **15** (6) (1974) 148.
6. A. A. HIGAZY, and B. BRIDGE, *ibid.* **26** (3) (1985) 82.
7. A. A. HIGAZY, M. A. EWAIDA, A HUSSEIN and R. M. EL-BAHNASAWY, *Ind. J. Phys.* **63A** (2) (1989) 124.
8 C. F. DRAKE, I. F. SCANLAN and A. ENGEL, *Phys. Status Solidi* **32** (1969) 193.
9. G. W. ANDERSON and W. D. COMPTON, *J. Chem. Phys.* **52** (1970) 6166.
10 L. L. HENCH, *J. Non-Cryst. Solids* **2** (1970) 250.
11. M. SAYER and A. MANSINGH, *Phys. Rev. B* **6** (1972) 4621.
12. J. G. VAUGHAU, C. H. PERRY and D. L. KINSER, *Phys. Chem. Glasses* **18** (1977) 87.
13. C. A. HOGARTH and M. J. BASHA, *J. Phys. D. Appl. Phys.* **16** (1983) 869.
14. P. GRAY and L. C. KLEIN, *J. Non-Cryst. Solids* **68** 75 (1984).
15. A. HUSSEIN, A. A. HIGAZY and M. A. EWAIDA, *J. Mater. Sci.* **24** (1989) 457.
16. I. G. AUSTIN and N. F. MOTT, *Adv. Phys.* **18** (1969) 41.
17. L. MURAWSKI, C. H. CHANGE and T. D. MACHENZIE, *J. Non-Cryst. Solids* **32** (1979) 91.
18. ASWINI GHOSH, B. K. CHAUDHURI, *J. Mater. Sci.* **22** (1987) 2369.
19. T. N. KENNEDY and J. D. MACHENZIE, *Phys. Chem. Glasses* **8** (1967) 169.
20. VOGEL'S, "Textbook of Quantitative Inorganic Analysis", 4th Edn (ELBS Longman, 1985) pp. 499–500.
21. M. SAYER and A. MANSINGTH, *Phys. Rev. B* **6** (1972) 4629.

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