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Electrical conductivity of zinc–barium phosphate glasses

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A series of binary and ternary zinc–barium phosphate glasses was prepared, their densities were measured and their electrical properties were studied. A linear dependence of density with BaO content was observed in barium phosphate glasses while a breaking point in the linearity of the density curves occurs at about 40% ZnO concentration for the zinc–barium phosphate glasses. The d.c. conductivity measurements show that the activation energy is increased when P_2O_5 is replaced by BaO or ZnO, respectively. In the ternary glasses the activation energy appears to be relatively unaffected when BaO is replaced by ZnO, but at approximately 40%ZnO, there is a rise in the value of activation energy. Such a pronounced change in density and activation energy could be due to the change in the coordination of ZnO in this region. The linear log σ–$1/T$ curves and also the value of σ_0 suggest that the conduction mechanism in these glasses is similar to those in many other oxide glasses that have been investigated.

1. Introduction

Phosphate glasses containing a significant content of transition metal ions are regarded as semiconductors, and their electrical properties have been studied fairly extensively [1]. The physical properties of phosphate glasses containing zinc have received little previous attention. The semiconducting properties of transition metal oxide glasses are mainly due to the existence of the transition metal ion in two different valency states within the glass. In the case of ZnO, the deviation from stoichiometry causing electronic conductivity, is an excess of zinc (n-type semiconductor), where the electronic conduction occurs after thermal excitation of electrons from a zinc atom adjacent to a vacant oxygen lattice point converting a normal lattice ion into Zn^{2+}. Thin films of ZnO also display the properties of an n-type semiconductor [2, 3]. Non-crystalline films of zinc oxide have been formed by reactively sputtering zinc metal on to a low-temperature substrate [4]. The non-crystalline films crystallize when heated to 75 to 100 °C. An increase in the electrical conductivity and also a change in the optical absorption corresponding to an increase in the band gap from 3.2 to 5.4 eV, following the change from a crystalline to a non-crystalline state, has been observed. The increase in the electrical conductivity with crystallization was interpreted in terms of a reduced carrier concentration and reduced mobility in the previous non-crystalline state.

2. Experimental procedure

The glasses were prepared from reagent grade P_2O_5, ZnO and BaO. They were melted in alumina crucibles at 1000 °C in an electrically heated furnace in an atmosphere of air for 3 h. After stirring the glass melts from time to time, they were cast on a clean metal surface and subsequently coin-shaped samples of thickness of about 3 mm were made. The glasses were annealed at 400 °C and were then ground and polished. After thorough cleaning of the specimens, gold electrode layers were deposited by vacuum evaporation giving a guard ring circuit arrangement. The ohmic behaviour of all contacts was checked using conventional methods. The current was measured by a Keithley 610C electrometer. All conductivity measurements were performed under a vacuum of about 10^{-5} torr (1 torr = 133.322 Pa). The densities of the glasses were determined by weighing them in air and in ethyl methyl ketone as immersion liquid.

3. Results

3.1. Density measurement

Table I shows the batch composition, and also the densities of the glasses studied. Fig. 1 shows the density of the binary system P_2O_5–BaO indicating that it increases linearly with increase in BaO content of the glasses. This linear dependence suggests that in this range of composition, the glasses were formed without

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TABLE I Composition and density of glasses studied

Glass no.	P_2O_5 content (mol %)	BaO content (mol %)	ZnO content (mol %)	Relative density
5010Z	50	40	10	3.67_8
5020Z	50	30	20	3.46_1
5030Z	50	20	30	3.30_0
5040Z	50	10	40	3.14_5
7010Z	70	20	10	3.19_1
8010Z	80	10	10	3.07_6
9010Z	90	0	10	2.83_7
8020B	80	20	0	3.09_4
7030B	70	30	0	2.20_6
6040B	60	40	0	3.47_0
5545B	55	45	0	3.60_9
5050B	50	50	0	3.65_5
8020Z	80	0	20	2.82_4
7030Z	70	0	30	2.82_6
5545Z	55	0	45	2.80_5
5248Z	52	0	48	3.01_2
5050Z	50	0	50	3.12_2

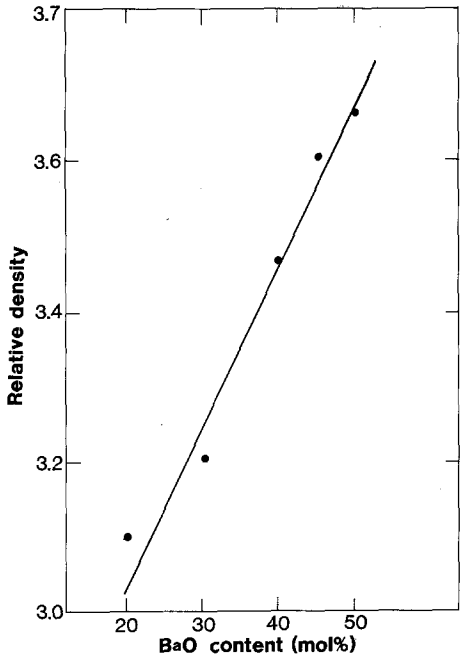

Figure 1 Density of barium phosphate glasses as a function of barium oxide content.

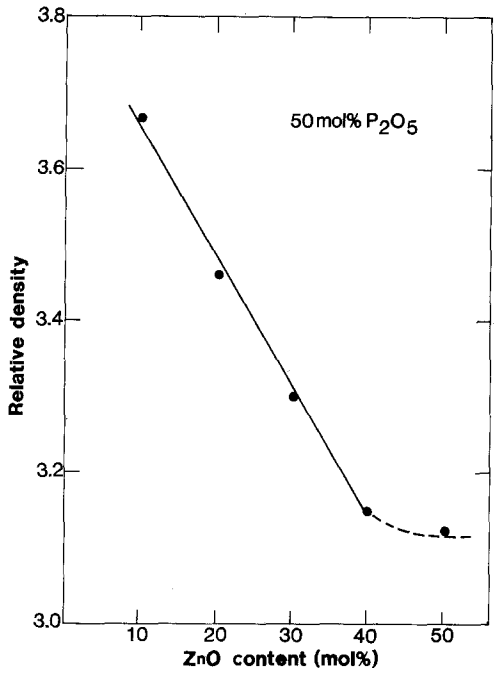

Figure 2 Density of zinc–barium phosphate glasses as a function of zinc oxide content.

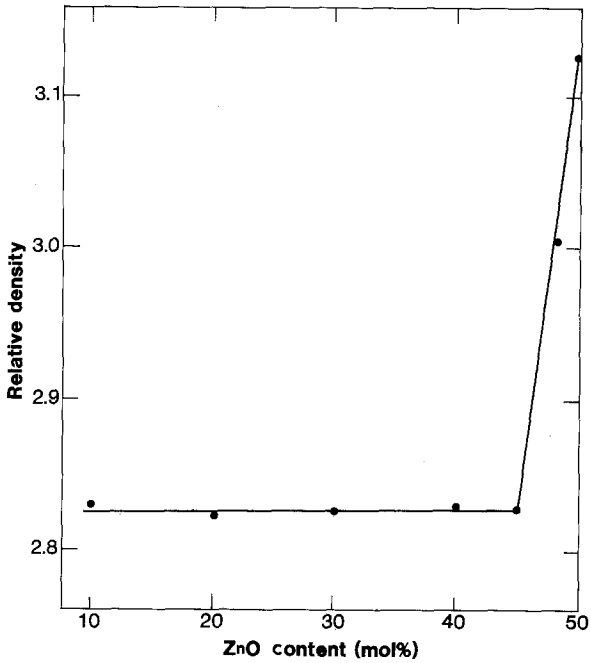

Figure 3 Density of binary zinc phosphate glasses as a function of zinc oxide content.

significant structural changes. Figs 2 and 3 show the densities of binary and ternary zinc phosphate glasses as a function of composition. A breaking point in the linearity of the density curves occurs at about 40% ZnO concentration in these glasses. Such behaviour for ZnO has also been reported earlier for zinc phosphate [5, 6] and zinc silicate glasses [7–9]. The change in the density of these glasses could be due to the change in coordination of ZnO in this region. In zinc phosphate glasses the Zn^{2+} ions are four-fold coordinated and act as network formers in the composition range from pure P_2O_5 to the metaphosphate composition. With further addition of ZnO, the Zn^{2+} act as modifiers with six-fold coordination and the Zn^{2+} ions enter voids in the structure. Thus the change in the density can be regarded as evidence for changes in the behaviour of zinc oxide in the glass.

3.2. Electrical conductivity measurement

The d.c. conductivity, σ, of the glasses was measured over the temperature range 20 to 350 °C. A typical plot of $\log\sigma$ against $1/T$ is shown in Fig. 4. As can be seen, the curve is a good straight line over a considerable range of temperature, but there is a departure from linearity at about room temperature. The activation energies were calculated from the slopes of the straight lines of $\log\sigma$–$1/T$ plots. The values of σ_0, obtained by extrapolation of the $\log\sigma$–$1/T$ plots to $1/T = 0$, were of the order of 10^2 to $10^3\,\Omega^{-1}\,cm^{-1}$. In the binary systems there is an increase in the activation energy, and thus in the electrical activation energy, W, when P_2O_5 is replaced by either BaO or ZnO. Fig. 5 shows

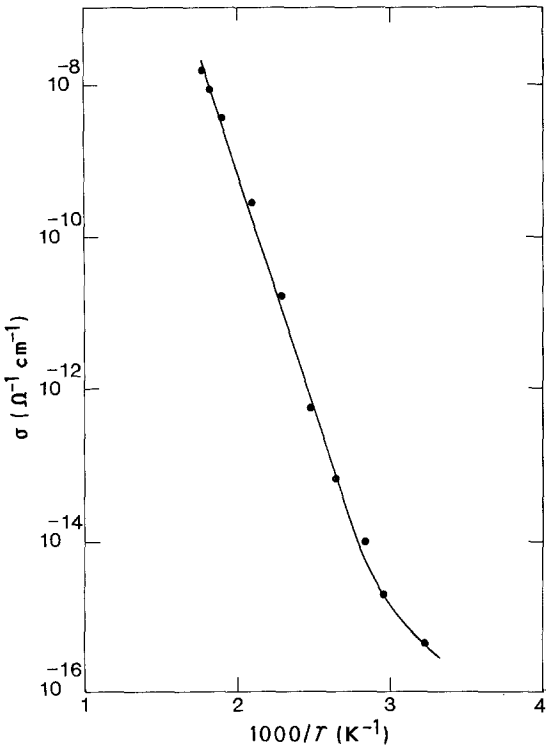

Figure 4 Typical electrical conductivity of a zinc–barium phosphate glass as a function of $1/T$. (Glass no. 5040Z with gold electrodes.)

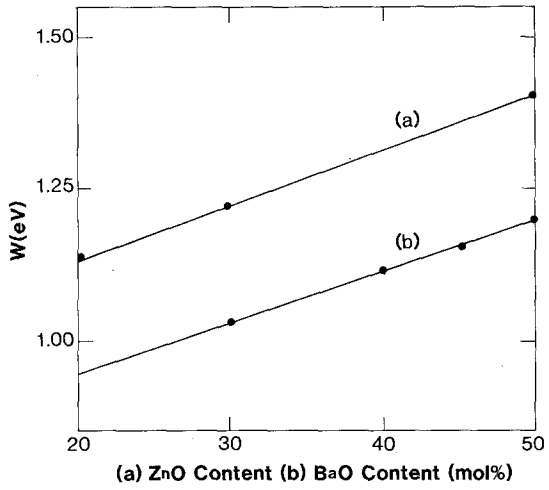

Figure 5 Activation energy as a function of ZnO or BaO content for binary phosphate glasses, (a) ZnO–P_2O_5, (b) BaO–P_2O_5.

the variation of W with the concentration of metal oxide in the glass. There is an increase in the electrical activation energy in the ternary system containing 10% ZnO, with increasing P_2O_5 content as shown in Fig. 6. In glasses with 50% P_2O_5 and 50% (BaO + ZnO), the activation energy appears to be relatively unaffected by replacing BaO by ZnO up to 40% ZnO, but somewhere between 40% and 50% there is a rise in the activation energy, as seen in Fig. 7. Such a pronounced change was also observed in the density measurements and may well be due to the change in the co-ordination of ZnO in this region.

In order to study the effect of different electrode materials, copper and silver were used and results were similar to those obtained using gold electrodes. This could be taken as evidence that the conduction in

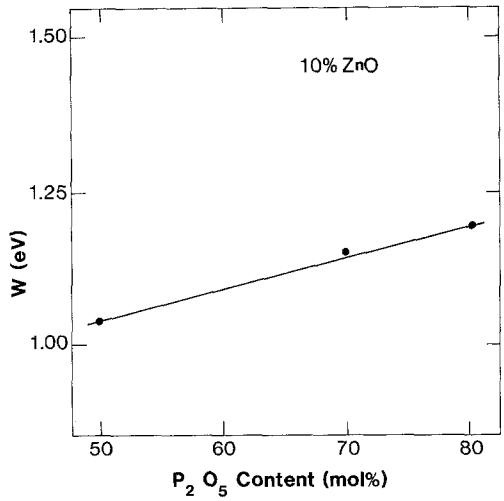

Figure 6 Activation energy of zinc-barium-phosphate glasses as a function of P_2O_5 content.

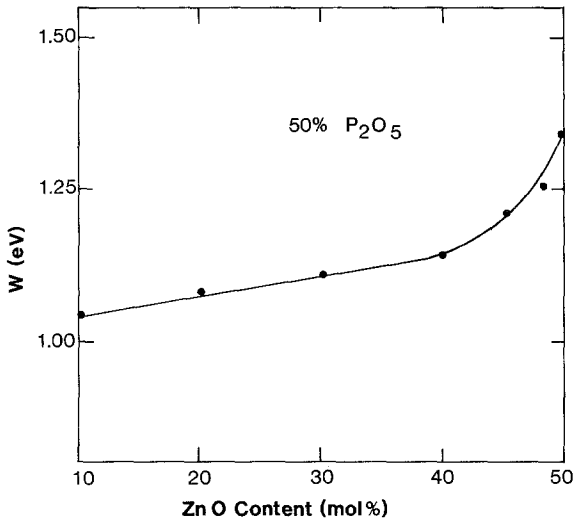

Figure 7 Activation energy as a function of ZnO content for a series of zinc-barium-phosphate glasses.

these glasses is due to a bulk effect and is not significantly dependent on any surface phenomena. The time dependence of resistance was measured and no change in resistance was observed, indicating that there is no polarization in our glasses and thus the conductivity would be electronic rather than ionic.

4. Discussion

It was first shown by Stuke [10] that the electrical conductivity of many semiconducting glasses obeys the relationship

$$\sigma = \sigma_0 \exp(-W/kT) \quad (1)$$

where W is the electrical activation energy, T is the absolute temperature, and σ_0 is a constant related to the effective density of states. According to Mott and Davis [11], for the group of materials having a value of σ_0 between 10^2 and $10^4\ \Omega^{-1}\ cm^{-1}$ conduction is due to carriers excited into extended states. For the group of materials having a value of σ_0 of the order of $10\ \Omega^{-1}\ cm^{-1}$ they suggest that the conduction is due

to carriers excited into localized states at the band edges. Values much less than this for σ_0 could correspond to conduction due to carriers hopping between localized states near the Fermi energy. From conductivity data we may conclude that for the binary glass systems P_2O_5–ZnO and P_2O_5–BaO no change in transport mechanism appears over the whole temperature range except near room temperature and it is found that the activation energy increases with increasing concentration of metal oxide. The conductivity of the ternary glass system P_2O_5–ZnO–BaO appears to be slightly dependent on ZnO concentration up to 40% ZnO. For greater amounts of ZnO the activation energy increases considerably and this could be due to the change in coordination of ZnO in the glass. The linear and uniform $\log \sigma$–$1/T$ dependence at high temperatures (above room temperature) of the glasses studied and also the value of σ_0, indicate that the conduction processes in our samples are similar to those in many other oxide glass systems that have been studied.

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