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Semiconducting properties of barium vanadate glasses doped with barium chloride

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Semiconducting barium vanadate glasses doped with $BaCl_2$ from 0 to 15 mol% were studied. Electrical d.c. conductivity σ measurements and an electron spin resonance investigation in the X-band were made. The concentration dependence of d.c. conductivity exhibits a minimum at 7 mol% $BaCl_2$. The activation energy increases with increasing $BaCl_2$ content up to 7% and decreases at higher concentrations of $BaCl_2$. The temperature dependence of the d.c. conductivity shows the effect of $BaCl_2$ as an oxidizing agent which controls the electrical conductivity, as a result of modification of the reduced vanadium valence ratio and a change in concentration of the paramagnetic ions. The plots of $\log \sigma$ versus $1000/T$ are linear for all the $BaCl_2$-doped glasses. The data of the d.c. investigations were analyzed in terms of small polaron theory, and this confirms the applicability of the polaronic hopping model of electrical transport. The influence of $BaCl_2$ content on density indicates that in this ternary system the additivity role is not obeyed. The minimum occurs at the same concentration of 7 mol% $BaCl_2$ as noted for the electrical conductivity.

1. Introduction

The term semiconductor glass refers to a class of glass having electrical conductivity greater than $10^{-9}\ \Omega^{-1}\,\mathrm{cm}^{-1}$ at room temperature. It is generally recognized that glasses containing transition metals such as V, Fe, Co and Mn which can be accommodated in more than one valency state exhibit semiconductivity and that conduction in such glasses is due to a hopping process, which in this case involves the transfer of an electron or a hole between ions of the same transition metal in different valence states.

Of the transition metal oxides which cause semiconductivity in a glass, V_2O_5 is unique by being itself a glass-former. Thus, glasses containing V_2O_5 are of great interest for studying the correlation between electrical properties and glass network structure. The present work extends the study by considering a fixed proportion of vanadium in a system of glasses of the general formula $65V_2O_5-(35-x)BaO-xBaCl_2$, i.e. glasses of constant vanadium content in which $BaCl_2$ is progressively substituted for BaO.

A number of glasses were made, so that the trends in properties (d.c. electrical conductivity, electron spin resonance (ESR), density, thermal activation energy, optical band gap) could be studied as a function of chlorine content. The results of this study are consistent with those of Hogarth and Popov [1] and also suggest that chlorine ions are weakly bonded into the glass network above 7% $BaCl_2$.

2. Experimental procedure and results

2.1. Glass preparation

Glasses of composition given by the general formula $65V_2O_5-(35-x)BaO-xBaCl_2$ where $x = 0, 3, 5, 7, 10, 12.5$ and 15 were prepared. An attempt was made to melt a glass containing 20 mol% $BaCl_2$ but this resulted in crystallization during cooling. Examination by X-ray diffraction revealed that the crystalline phase was $BaCl_2$. Glasses were melted in 30 g batches in silica crucibles at 750 °C for 10 min. The glasses, which were very fluid, were then cast on to stainless steel plates which were preheated to 400 °C. Each plate was immediately transferred to a preheated furnace, held for 2 h and then allowed to cool to room temperature. Annealing temperatures were based on prior knowledge of the glass transformation temperature. During melting a significant loss of chlorine occurred and it was in order to minimize this loss that a short melting time was used. Measurements of weight loss on melting were made by weighing the crucible before melting and by weighing the crucible and sample after melting. The results are shown in Table I which indicates that essentially no loss occurred for glasses containing < 10 mol% $BaCl_2$, whereas a gradually increasing weight loss was observed for glasses containing more $BaCl_2$. It was assumed that chlorine volatil-

TABLE I The effect of melting on composition of glasses

Batch composition (mol%)			
V_2O_5	BaO	$BaCl_2$	Weight loss (%)
65	35	0	0
65	32	3	0
65	30	5	0.10
65	28	7	0.15
65	25	10	0.20
65	22.5	12.5	0.15
65	20	15	0.30

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ized from the glass. Certainly the glass containing 15 mol% $BaCl_2$ was observed to emit vapours during melting and contained many very fine bubbles after casting. The weight loss discussed above indicates that the glasses assumed to have the highest chlorine content probably contain less chlorine than that indicated by the batch composition. Since the trends observed in this study do not depend upon the exact composition, it was decided in the first instance to plot all data on the basis of the original batch composition.

2.2. Electrical conductivity measurements

The electrical circuit used for d.c. conductivity was composed of a Keithley 610 C electrometer capable of measuring an electric current down to 10^{-14} A, a high-voltage d.c. power supply and a specially designed specimen holder with heating unit and thermocouple. A similar circuit was used by Khan *et al.* [2]. Gold electrodes including guard rings (to eliminate surface leakage current) were deposited on to 2 mm thick polished glass samples by vacuum evaporation. All the measurements were made under a vacuum of about 10^{-5} torr to avoid atmospheric effects. A constant voltage was supplied to the test specimens and the circulating currents were measured. The sample temperature was monitored using a Chromel–Alumel thermocouple attached to the sample. The temperature dependence of conductivity is illustrated in Fig. 1, where $\log \sigma$ is plotted against the reciprocal of absolute temperature, and the straight-line relationship appears to hold fairly well. The effect of chlorine replacing some of the oxygen in the glass may be seen in Fig. 2. The addition of $BaCl_2$ to the glass showed that up to 7% $BaCl_2$ the conductivity decreases slowly, but for greater than 7% the conductivity rose again. Similar results were obtained by Hogarth and Popov [1] on the P_2O_5–CuO–$CuCl_2$ glass system.

2.3. Activation energy

The activation energy W was calculated from the slope of the curve in Fig. 1 from the relation

$$W = 0.198 \frac{\Delta(\log \sigma)}{\Delta(1/T)} \quad \text{eV}$$

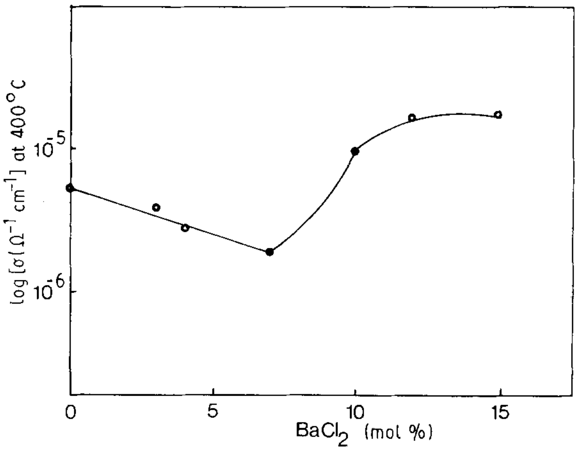

Figure 1 The logarithm of conductivity versus glass composition for 65% V_2O_5–(35 – X)BaO–$X$$BaCl_2$ at 400 K. The sample was annealed at 200 °C for 2 h.

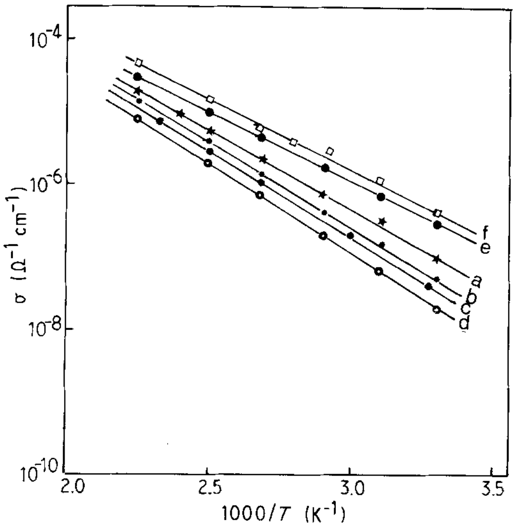

Figure 2 Electrical conductivity as a function of reciprocal temperature, showing the dependence on the concentration of chlorine in the glasses. $BaCl_2$ content (mol%): (a) 0, (b) 3, (c) 5, (d) 7, (e) 10, (f) 15.

assuming that the semiconducting glasses obey the exponential law $\sigma = \sigma_0 e^{-W/kT}$ where σ is the electrical conductivity, σ_0 is the pre-exponential factor, W is the conductivity activation energy, T is the absolute temperature and k is the Boltzmann constant. It is seen that the activation energy W increases as the conductivity decreases (Fig. 3). Similar results have been observed by others [3–5].

2.4. Optical measurements

Thin blown films of glass samples of V_2O_5–BaO–$BaCl_2$ were prepared using the method described by Hogarth and others [1]. The optical absorption coefficients of these glasses were measured at room temperature in the wavelength range λ of 200–700 nm using a Perkin–Elmer Model 137UV spectrometer. The general formula for the optical absorption coefficient $\alpha(\omega)$ is given by

$$\alpha(\omega) = \frac{1}{L} \ln\left(\frac{I_0}{I_t}\right)$$

where I_0 and I_t are the intensities of incident and transmitted light, respectively, and L is the thickness of the sample.

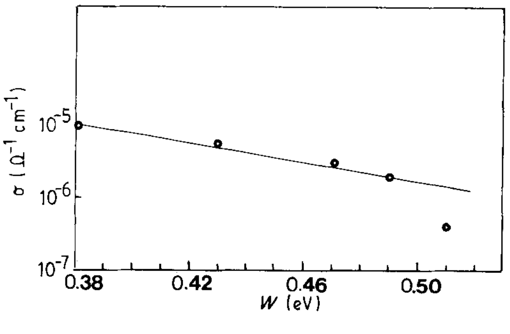

Figure 3 The relationship between the room-temperature electrical conductivity and the activation energy.

The absorption spectrum as a function of λ in the visible range shows that, in contrast to crystalline V_2O_5, there is no sharp absorption edge (which is a characteristic of the glassy state) and it also illustrates the variation of absorption edge as the percentage of $BaCl_2$ is increased. The optical data obtained from the spectra as described by Davis and Mott [6] are plotted in Fig. 4 as the quantity $(\alpha\hbar\omega)^{1/2}$ against the photon energy $\hbar\omega$ and the values of E_{opt} are determined by extrapolating the linear parts of the curves to $(\alpha\hbar\omega)^{1/2} = 0$. The graphs show straight lines with some deviations at lower photon energies, which according to Redfield and Afromowitz [7] were due to the imperfections in the materials. The linear variation of $(\alpha\hbar\omega)^{1/2}$ with $\hbar\omega$ is taken as evidence of non-direct interband transitions. Table II shows that the values of E_{opt} increase continuously up to 7% $BaCl_2$ and thereafter decrease. This is due to the change of the structure of glass as the chloride ions replace the non-bridging oxygen ions. The values of E_{opt} lie in the range of 2.04–2.23 eV as indicated in Table II. At low concentrations of $BaCl_2$, the chloride ions act as bridging ions and provide connectivity for the vitreous network and consequently increase the values of E_{opt}, but for higher percentages of $BaCl_2$ (>7%) it is possible that the chloride ions are loosened and act as non-bridging ions, resulting in a reduction of E_{opt}.

2.5. Density measurement

Fig. 5 illustrates the influence of $BaCl_2$ on the density. As chlorine replaces oxygen, the density of the glass goes through a minimum, indicating that the simple additivity rule is not obeyed. The minimum density occurs at the same critical concentration of 7% $BaCl_2$ as the other parameters, and from this observation we suggest that this variation is probably due to the formation of a glass structure of different packing arrangement with differing vanadium reduced valency ratio. Density measurement was used to calculate the quantities molar volume V_m, the average vanadium ion separation R, the number of sites N and the small polaron radius r_p. Assumptions were made that the transition-metal ions are uniformly distributed and that all have the opportunity to take part equally in the conduction. The total vanadium concentration was calculated by the equation

$$N = \frac{\rho_G(w)N_0}{\text{A.W.}} \times 100$$

where N is the total transition-metal ion concentration, ρ_G is the density of glass, w is the weight percentage of vanadium, N_0 is Avogadro's number and A.W. is the atomic weight of vanadium.

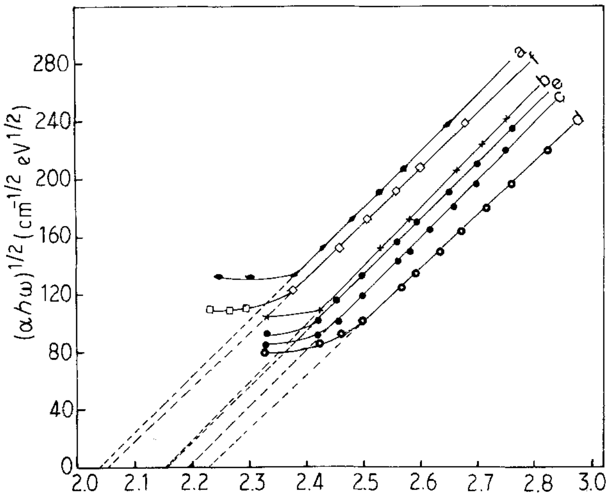

Figure 4 $(\alpha\hbar\omega)^{1/2}$ plotted against $\hbar\omega$ as function of content of $BaCl_2$ for samples of the same thickness, 6.5 μm. $BaCl_2$ content (mol%): (a) 0, (b) 3, (c) 5, (d) 7, (e) 10, (f) 15.

TABLE II The effect of composition on E_{opt} and activation energy (W)

	BaCl₂ content (%)						
	0	3	5	7	10	12.5	15
E_{opt} (eV)	2.04	2.16	2.18	2.23	2.16	–	2.05
W (eV)	0.43	0.47	0.51	0.49	0.38	0.38	0.39

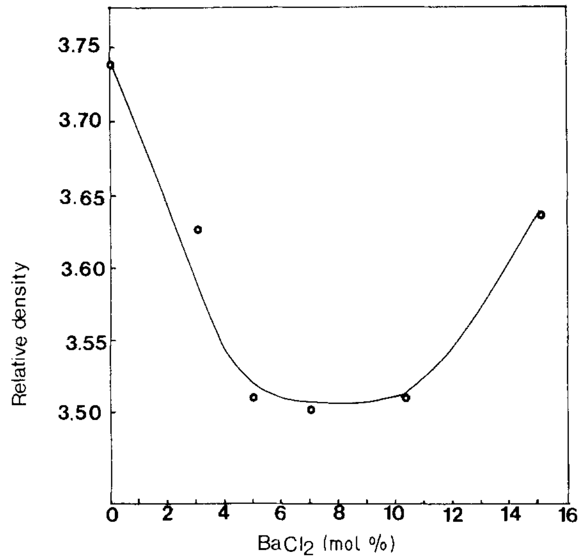

Figure 5 Relative density as function of $BaCl_2$ content for samples annealed at 200 °C for 2 h.

The average V–V spacing, R, was calculated using the total ion concentration:

$$R = \left(\frac{1}{N}\right)^{1/3}$$

Many investigators have calculated the small polaron radius, r_p, from the relation

$$r_p = \left(\frac{\pi}{6N}\right)^{1/3}$$

i.e. r_p decreases as the number of sites increases. The derived parameters calculated from the above equation are recorded in Table III. Experiments show that the values of r_p are not far from 0.15 nm, as expected from the theory of small polarons.

2.6. Electron spin resonance

ESR has been used to examine the localization of unpaired electrons, which is typical in transition metal

TABLE III Derived parameters calculated from density measurements

V_2O_5 (%)	BaO (%)	$BaCl_2$ (%)	Relative density	TM ion content (%)	Number of sites (10^{22} cm^{-3})	Site spacing, R (nm)	Small polaron radius, r_p (nm)
65	35	0	3.74	38.1	1.68	0.390	0.157
65	32	3	3.63	38.1	1.63	0.394	0.158
65	30	5	3.51	38.1	1.58	0.398	0.160
65	28	7	3.50	38.1	1.57	0.399	0.161
65	25	10	3.51	38.1	1.58	0.398	0.160
65	22.5	12.5	–	38.1	–	–	–
65	20	15	3.64	38.1	1.64	0.393	0.158

compounds and is important in connection with the investigation of the electrical conductivity mechanisms of semiconducting oxide glasses which require a knowledge of the valence states of the transition-metal ions that are present in the glass. All ions and molecules which have unpaired electrons are paramagnetic and have magnetic moments. The transitions are induced through a coupling of the magnetic dipole moment of the resonating electrons to the magnetic component of the external microwave radiation. The classical resonance condition for a free electron in a magnetic field H_0 is given by

$$h\nu = g\beta H_0 = 2.0023\beta H_0$$

where h is Planck's constant, ν is the frequency of the microwave radiation applied perpendicular to H_0, β is the Bohr magneton and g is the spectroscopic splitting factor. Landsberger and Bray were the first to use the technique for determining the $[V4^+]/[V5^+]$ ratio in P_2O_5–V_2O_5 glasses. In the present work, we have established that the introduction of $BaCl_2$ into glasses with a fixed content of V_2O_5 leads to a systematic variation in the $[V^{4+}]/[V^{5+}]$ ratio.

2.6.1. *ESR experiment and techniques*

Approximately 0.25 g samples of coarsely powdered glass were contained in 3 mm internal diameter Pyrex tubes, inserted into the ESR cavity operating at X-band frequency using a Varian E3 ESR spectrometer. All instrument settings (modulation amplitude, time constant and magnetic field) were kept constant for all samples. ESR spectra of the unannealed glasses of $65V_2O_5$–$(35-x)BaO$–$xBaCl_2$ were measured at both room temperature and liquid nitrogen temperature. Ammonium vanadyl, $(NH_4)_2 \cdot VO(C_2O_4)_2 \cdot 2H_2O$, was used as a standard for the spin concentration determination of $[V^{4+}]$ in the glasses. Total vanadium in the glass was determined by standard chemical procedures.

The samples were scanned for 2 min in a scan range of 1000 G. The spin concentration for each glass was estimated by the expression $B = (A_1/A_2)Y$, where A_1 and A_2 are the areas under the microwave absorption versus magnetic field strength curves for the glass and the standard sample, respectively. The value of Y, which is the number of spins for the standard sample, was found by the relation

$$Y = W_S N_0 / M_S$$

where W_S is the weight and M_S is the molecular weight of the standard.

It must be borne in mind that the spin densities are only approximately calculated by double integration of the first derivative of spectra, due to uncertainties regarding the active sample volume, which is controlled by the penetration depth of the microwave signal and the assumption made that proportionality between the ESR signal and the microwave field exists. Given these uncertainties, the amount of V^{4+} in 100 g of glass was estimated by using the equation

$$Z = 100 M_G B / N W_G$$

where M_G is the molecular weight and W_G is the weight of glass. The values of spin concentration and $[V^{4+}]$ are quoted in Table IV.

3. Discussion

3.1. ESR spectra

ESR spectra of glasses with different contents of $BaCl_2$ exhibit resolved hyperfine structure due to the interaction of a third unpaired electron with the ^{51}V nucleus. A similar observation was made by Ahmed *et al.* [8] for binary V_2O_5–BaO glass. It was found that the spectra of samples at 77 and 300 K were virtually identical; the $C = [V^{4+}]/[V_{total}]$ values were calculated to be 0.020–0.55 and the spin concentrations in the range $(1.79–3.45) \times 10^{20}$ spin cm^{-3} (Table IV) and approximately varied in the same way as other measured parameters.

Fig. 6 shows that there is a gradual decrease of spin concentration with increasing $BaCl_2$ content up to 7% but further introduction of chlorine causes a rapid increase of spin concentration. Furthermore the values of C remain constant up to 7% $BaCl_2$ but increase for further addition of chlorine.

3.2. Conclusions

The analyses of the experimental data and derived parameters reveal that beyond 7% addition of $BaCl_2$ there is a systematic change in the behaviour of the glass system. The addition of chlorine up to 7% depresses the spin concentration but beyond this value it increases, indicating structural changes. Also it is observed that conductivity and density behave in the same way, and the minimum conductivity which occurs at 7% $BaCl_2$ can be interpreted as being due to the reduction in concentration of hopping centres. The

TABLE IV Parameters of ESR spectra of glasses in the system V_2O_5–BaO–$BaCl_2$

$BaCl_2$ (mol %)	Weight of sample (g)	V_{total} (g)	Spin concentration		V^{4+} content in 100 g of glass	$C = \frac{[V^{4+}]}{[V_{total}]}$
			Spin g^{-1}	Spin cm^{-3}		
0	0.1504	38.1	9.15×10^{19}	2.06×10^{20}	0.774	0.020
3	0.1277	38.1	1.05×10^{20}	1.89×10^{20}	0.762	0.020
5	0.1210	38.1	1.10×10^{20}	1.88×10^{20}	0.749	0.019
7	0.1503	38.1	8.48×10^{19}	1.79×10^{20}	0.717	0.018
10	0.1447	38.1	1.69×10^{20}	3.15×10^{20}	1.430	0.037
12.5	0.1466	38.1	1.52×10^{20}	3.28×10^{20}	1.286	0.034
15	0.1200	38.1	1.79×10^{20}	3.45×10^{20}	2.116	0.055
Standard	0.0172	–	–	–	–	–

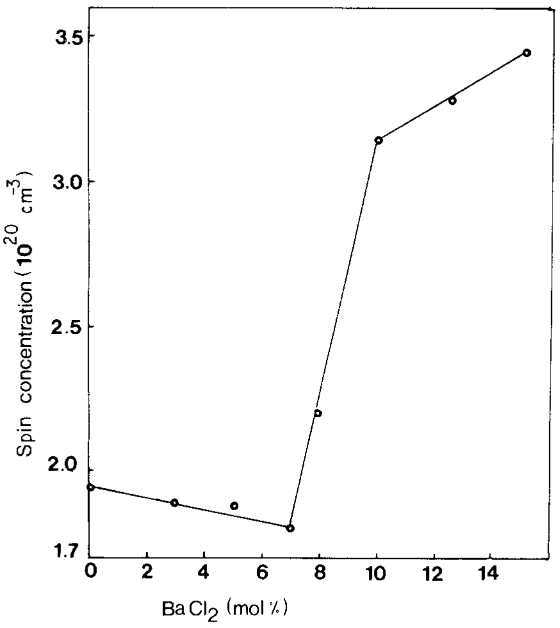

Figure 6 The dependence of the total spin concentration on $BaCl_2$ content for glasses of the V_2O_5–BaO–$BaCl_2$ system.

logarithm of conductivity versus activation energy gives a straight line which implies that the pre-exponential term α_0 is constant for all samples. The small values for C may be due to the relatively small portion of powdered glass in the test tube which has been exposed to the radiation. General suggestions may be made concerning the low and high contents of $BaCl_2$ in these glasses as follows.

At low chlorine content, the chloride ions act as bridging ions by breaking up the V–O–V bridging bonds and the new bridge bonds provide connectivity for the vitreous network. These bridging chlorine ions are difficult to free from sites, since a pair of bonds must be broken and consequently, as expected, reduce the conductivity. The conductivity decrease was also associated with an increase in activation energy, optical gap and a reduction in the spin concentration.

At a high admixture of $BaCl_2$ ($> 7\%$) it is possible that the chlorine ions act as non-bridging ions shifting the optical band edge to lower energies (i.e. reduction of E_{opt}), suggesting that the degree of disorder in these glasses has thereby increased and the chlorine ions have become more loosely bonded to the network.

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