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THE ELECTRICAL AND OPTICAL PROPERTIES OF SODIUM GERMANATE GLASSES

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Résumé.— On a mesuré la conductivité électrique d'une série d'échantillons du système $\text{Na}_2\text{O} - \text{GeO}_2$ depuis l'ambiante jusqu'à 350°C . Les résultats sont interprétés en termes de gaps électriques qui décroissent linéairement avec la teneur en Na_2O des verres. Les seuils d'absorption ont été mesurés et analysés en termes de transitions indirectes à travers un gap optique qui croît également linéairement avec Na_2O . Cependant, on a trouvé que le gap optique est environ le double du gap électrique correspondant.

Abstract.— The electrical conductivities of a series of specimens in the system $\text{Na}_2\text{O}-\text{GeO}_2$ were measured at temperatures ranging from room temperature to 350°C .

These results are interpreted in terms of electrical gaps, which decrease linearly with the Na_2O content of the glasses.

Their absorption edges are measured and analysed in terms of forbidden non-direct transitions across an optical energy gap which is also found to increase linearly with the Na_2O content of the glasses. However, the optical gap was found roughly to be twice the corresponding electrical gap.

1. Introduction.— The conductivity of glasses and amorphous films has been the subject of an extremely wide range of experimental and theoretical studies (1-4). It is clear even with materials devoid of long range order and with band tailing beyond the normal conduction and valence bands a forbidden gap exists and may be estimated from measurements of electrical conductivity as a function of temperature as well as from optical absorption measured as a function of photon energy.

In the present work the results of conductivity measurements with varying Na_2O content in the system $\text{Na}_2\text{O} - \text{GeO}_2$ are reported. As the Na_2O content is increased the value of activation energy and hence the electrical gap decreases accordingly.

The optical absorption in the specimens was carefully measured. An analysis of the absorption near the absorption edge is presented and discussed in terms of a Davis and Mott. (5) model of the energy levels in amorphous materials. The optical energy gap also decreases linearly with the increase in Na_2O content.

2. Experimental.— The raw materials used for the preparation of the glasses were reagent grade Na_2CO_3 (as a source for Na_2O) and GeO_2 , both of purity 99.99 % and were supplied by Fisher Scientific Company. The glass batch (compositions are given in table-1) was melted in platinum crucible using an electric furnace at temperatures from 1200°C to 1250°C for three hours depending upon the composition. The molten glass was casted on a stainless steel surface in the form of circular pallets of diameter 1 cm. For each composition more than two specimens were casted which varied in thickness from 2 mm to 5 mm.

The glass samples were polished using diamond-paste down to minimum grit size of $0.1\mu\text{m}$. Due to hygroscopic nature of germanium dioxide glass, acetone was used

in the process of polishing. Gold was evaporated onto the faces of the specimen to form a guarded electrode system which consisted of a main electrode of 5 mm in diameter, a ring shaped guard electrode and an electrode opposite. The temperature of the sample was monitored using a chromel-alumel thermocouple attached to the sample.

For each composition (table 1) the absorbance of two specimens of different thicknesses was measured at normal incidence using a Perkin Elmer 202 UV/visible spectrometer. Fig.2 is an example of the absorbance curves for the composition E₅ and samples thickness 3.30 mm and 2.09 mm.

Table - 1

Melt No.	Chemical Composition, electrical and optical energy gaps			
	GeO ₂ con- tent (wt%)	Na ₂ CO ₃ con- tent (wt%)	Activation Energy E (eV)	Optical gap E ₀ (eV)
E ₀	100	0	1.00	-
E ₁	90	10	0.92	3.64
E ₂	85	15	0.86	3.57
E ₃	80	20	0.80	3.48
E ₄	75	25	0.74	3.41
E ₅	70	30	0.67	3.33

3. Results And Discussion

3.1. Time dependence of direct currents.- The time dependence of current at an applied voltage of 30V was studied for the specimens of different compositions. The polarization effects were observed and the resistivity of the specimens increased with time. This suggests that the ionic currents are dominant. Dominant ionic currents in Na₂O - GeO₂ glasses has also been reported by Evstropov et al. (6).

3.2. d.c. conductivity.- Fig.1 shows the plot of logarithmic conductivity against the reciprocal of absolute temperature for a series of glass specimens. In many types of ionically conducting oxide glasses, it is well known that these plots are linear in conformity with the following equation:

$$\sigma = \sigma_0 \exp\left(-\frac{\Delta E}{KT}\right) \quad \dots \dots \dots (1)$$

where σ is the conductivity σ_0 is a constant for a given glass, K is the Boltzman constant, T is absolute temperature and ΔE is the activation energy for conduction. All the graphs shown here contain straight lines, which are numbered in ascending order as the sodium ion concentration in the specimens increases.

Table 1 lists the derived values of the activation energy and relates them to composition and to the measured values of optical energy gap E₀.

A plot of activation energy against GeO₂ concentration is shown in Fig.4. It is clear that increasing the Na₂O content causes a decrease in the activation energy for ion transport. At high sodium concentrations, it is easier for the transport of

Fig.1: Semilog plots of conductivity versus reciprocal temperature for Na₂O-GeO₂ glasses.

mobile ions to take place at given temperature and electric field strength, and hence the increase is equivalent conductance.

3.3. Optical absorption.— Fig.2 shows measurement of absorbance (A) against wavelength for two specimens with same composition E_5 (table 1) and thickness $x_1=3.30$ mm and $x_2=2.09$ mm. The absorption coefficient $\alpha(\lambda)$ which is a function of wavelength λ was calculated from the following relation:

$$\alpha(\lambda) = \frac{A_1(\lambda) - A_2(\lambda)}{x_1 - x_2} \quad \dots \dots \dots (1)$$

$\alpha(\lambda)$ was calculated for wavelengths at intervals of 5 nm from Fig.2. This data was then analysed by the well established theory for the absorption in amorphous materials given by Davis & Mott (5). According to the theory K- conservation rule breaks down in amorphous materials and K is not a good quantum number. Further, if the matrix element for momentum vector for optical transitions is taken constant (this assumption is valid in the present case as the energy range concerned is small) then the absorption can be represented by

$$(\alpha E)^{\frac{1}{2}} = C(E - E_0) \quad \dots \quad (2)$$

where E is the photon energy and E_0 is the optical band gap, and C is a constant.

Figure 3 shows plots of $(\alpha E)^{\frac{1}{2}}$ against E for the different compositions of the glasses listed in table 1. The plots suggest that the absorption follows equation (2). E_0 , the band gap for all the compositions studied was obtained by extrapolating the lines to cut E- axis (figure 3). For an example, in the case of composition E_5 , E_0 was found to be

3.33 eV and the corresponding wavelength is 372.4 nm. This value of λ is indicated by an arrow in fig.2. Alternately, the absorption edge may be defined as the photon energy at which the absorption starts increasing from the zero value. This is equivalent to saying that the absorption edge is the wavelength at which the curves A_1 and A_2 (Fig.2) start deviating from their constant value. This value lies very close to the value determined from the equation (2) and shown by an arrow in Fig.2. A similar agreement was reached in all the five compositions.

Fig.2: Absorbance as a function of wavelength for two samples of same composition E_5 (table 1). Plot A_1 is for sample thickness 3.3 mm and A_2 for 2.09 mm.

Fig.3: Plots of $(\alpha E)^{\frac{1}{2}}$ against E for different compositions (table 1).

It may be mentioned that in the present work specimens of two thicknesses were studied in order to eliminate refractive index term in the formula for absorbance. Otherwise separate measurement for the refractive index was needed.

In Fig.4 E_o is plotted against specimen composition. It is clear that E_o decreases linearly as the Na_2O content is increased. E_o for 100% GeO_2 is estimated to be 3.69 eV in its amorphous state and at room temperature.

4. Conclusion.-The electrical conductivities and optical absorption measurements in the system $\text{Na}_2\text{O} - \text{GeO}_2$ glasses

were carefully made. The values for electrical energy gaps were obtained from conductivity data. The optical energy gaps were determined accurately from the measured absorbance in the specimens of different thicknesses.

It was found that the electrical and the optical energy gap decrease linearly with increasing content of Na_2O in the glasses. The conductivity increases with increasing Na_2O content in the glasses.

Fig.4: Dependence of activation energy and optical band gap on glass composition.

The optical absorption in the glasses is analysed in terms of non-direct transitions as formulated by Davis and Mott.

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