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EFFECTS OF TEMPERATURE, TITANIUM CONTENT AND LASER IRRADIATION ON THE ELECTROSONIC PROPERTIES OF SOME RELATED SILICATE GLASSES

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ABSTRACT

In the present communication, pure and various titania-containing silicate glasses have been synthesized and identified. Extensive studies of the temperature dependence of the DC electrical conductivity, activation energy for conduction, ultrasonic attenuation, and attenuation coefficient as a function of temperature of these specimens were examined and discussed in detail. Promising results were obtained and the role of titanium and laser irradiation were clearly defined.

Finally, a correlation for the electrical $\log \sigma$, ΔE and ultrasonic (α) properties has been proposed for the first time for the electronic glass industry.

INTRODUCTION

Oxide glasses form a group of substances known by the common name of non-crystalline amorphous semiconductors.

At present, from our point of view, the following problems are of greatest interest. One of these problems relates to the kind of electronic spectrum change due to the disorder in the immediate vicinity of the edges of the permitted energy band and the role of this change in transport processes; during amorphization the band edges become diffuse. In this connection, an experimental investigation of the temperature dependence of electrical conductivities and comparison of these experimental data with optical data is of great importance.

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Closely related to the above problem is that of doping. Some results given show that admixtures which do not appreciably influence the stationary conductivity play an important role in the non-equilibrium processes changing, for example, the kinetics of photoconductivity and the shape of the thermostimulated current curves; taking into account that the addition of such elements as Ag and Cu in comparatively small quantities essentially increases the conductivity of some glasses, in particular the glasses As_2S_3 and As_2Se_3 [1–4]. Hayward [5], studying the electrical conductivities and cation mobilities of Na_2O–Al_2O_3–SiO_2 glasses, indicated that for Na : Al ≈ 1 and glasses within the Na_2O–SiO_2 immiscibility boundaries and extending into the aluminous field, the electrical behaviour is influenced by anion modifications. Tsuchiya and Horiuchi [6] studied the electrical properties of silver-containing oxide glasses in the temperature range 20–130°C. Recently, Abou Sekkina [7] investigated the effect of heat treatments and active mineralizers on the DC electrical conductivity and some related properties of some alkali alumino-silicate glasses, deducing a useful tool for a quality control in the semiconductor glass industry.

Regarding ultrasonic studies, the attenuation of sound waves in dielectrics and semiconductors has been discussed in Akhiezer's theory [8]. Two of this theory's commonly used modifications were presented by Mason and Bateman [9,10] and Woodruff and Ehrenreich [11] for the region $\omega\tau > 1$, where ω is the angular frequency of the sound waves and τ is the relaxation time. The temperature dependence of the ultrasonic attenuation in single crystals of bismuth–germanium oxide has been previously studied [12,13].

As far as the authors are aware, no reference has been found in the literature concerning the effect of temperature, titania doping, and laser irradiation on the electrical and ultrasonic properties of alkali silicate glasses. The purpose of the present investigation is to solve this problem and, if possible, to correlate electrical properties with ultrasonic behaviour for the materials under investigation.

EXPERIMENTAL

Material synthesis

A batch of each glass composition (see Table 1) weighing 50 g was prepared from chemically pure materials. Silica was introduced as pulverized Dutch sand of the highest grade available. Potash was added as A.R. anhydrous potassium carbonate. Titanium oxide as TiO_2 (titania) was used. The batches were melted in Pt–2% Rh crucibles in an electrically-heated SiC furnace at about 1400°C. The melting was continued for 4 h with several rotations of the melt to achieve a good homogeneity. The melt was then poured onto a preheated (500°C) stainless-steel marver in the form of discs

of about 0.6 cm thickness and 1.6 cm diameter. The discs were immediately subjected to careful annealing in a controlled muffle furnace at the appropriate temperature.

DC electrical conductivity measurements

The DC electrical conductivity was measured using the two-probe method under vacuum. The circuit used was very similar to that previously described [14] with slight modifications. Measurements were made at room and elevated temperatures up to ~ 480 K and the readings were taken at 15 min after each temperature equilibration.

Ultrasonic attenuation and ultrasonic attenuation coefficient measurements

For these measurements an ultrasonic generator (PHYWE, W. Germany, model 11744.93) was used. The generator's outputs are sine-shaped ultrasonic waves and pulses with 3-μs duration and 1-kHz frequency. The amplitude of the ultrasonic sine wave generated was evaluated at a frequency of 800 kHz by a double-beam cathode ray oscilloscope. Pure vegetable oil was used as the bonding medium between the transducer and the receiver. The amplitude of the longitudinal wave is determined as a function of temperature. The A/A_0 ratio is then obtained, where A_0 and A are the amplitudes of the ultrasonic wave in the absence and presence of sample, respectively. Hence, the attenuation–temperature relationship of the longitudinal waves is studied in the temperature range 298–328 K.

The test samples are in the form of discs (0.6 cm thick; 1.6 cm diameter).

Laser irradiation

The test glass samples were exposed to 320 laser pulses (chosen to attain high response) using a homemade nitrogen laser [15] at room temperature (25°C). A representative sample showing the highest response to acoustic attenuation was examined as a function of temperature.

TABLE 1

The various glass compositions synthesized

Glass No.	Glass composition (wt%)		
	K_2O	SiO_2	TiO_2
I	25	50	25
II	20	50	30
III	15	50	35
IV	10	50	40
V	5	50	45

RESULTS AND DISCUSSION

Hence, the measurement of electrical conductivity was undertaken over a selected, relatively low temperature range in order to avoid excessive heat treatments on glass compositions. Moreover, relatively high proportions of TiO_2 were used for better induced semiconductivity to the test silicate glasses. Figure 1 represents the variation of electrical conductivity as a function of temperature ($\log \sigma$ vs. $1000/T$ K^{-1}) for the various TiO_2 alkali–silicate glasses. Since there is a positive temperature coefficient of electrical conductivity ($d\sigma/dT$) for each straight line, the materials investigated therefore possess semiconducting behaviour in both cases. The temperature range investigated was chosen in order to avoid any further heat treatment (excessive heating) and corresponds to electronic conductivity.

The conductivity varies exponentially with temperature according to the well-known relationship [16]

$$\sigma = \sigma_0 \, e^{-\Delta E/KT}$$

The relatively slight response of σ with temperature variation involves ΔE values which can be interpreted by a simple single-band model in most cases. Values of ΔE were calculated (Table 2) and assumed to correspond to the activation energies of defect mobilities.

From Figs. 1 and 2, and Table 1, it can be easily seen that the electrical resistivity and its attendant activation energy for conduction, and the energy gap, gradually fall with the rise in titania content of up to 40 wt%. This behaviour could be ascribed to the transformation of titanium tetrahedra ($-TiO_4-$) to titanium octahedra ($-TiO_6$) [17] at increasing TiO_2%. The latter would have higher coordination numbers and thus run continuously through the whole glass network. Alternatively, this may offer an easier path for current flow through the specimens. The net result is the attainment of

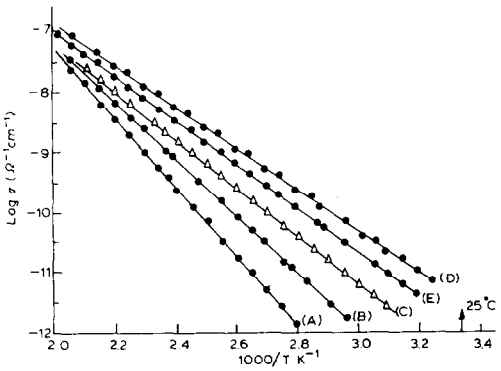

Fig. 1. Illustration of the variation of electrical conductivity, $\log \sigma$ (Ω^{-1} cm^{-1}), as a function of the reciprocal of the absolute temperature, $1000/T$ (K^{-1}), for various titania-containing silicate glasses: (A) 25; (B) 30; (C) 35; (D) 40; (E) 45% TiO_2.

higher electrical conductivity and lower activation energy for conduction, which gradually progresses as a function of TiO_2 content up to 40 wt% (see Table 2, and Figs. 1 and 2). Beyond 40 wt% TiO_2 the trend is reversed. Thus, 40 wt% TiO_2 could be considered as representing a saturation state. The reason for the increased electrical resistivity and its attendant activation energy for conduction for 45% TiO_2 content may be attributed to the partial nucleation of the silicate glasses as induced by the slight excess of titania. This may offer a barrier energy for current flow and thus decrease the electrical conductivity obtained and increase its attendant activation energy for conduction.

The attenuation coefficient (α) is simply given [18] by the following relation

$$A = A_0 \, e^{-\alpha x}$$

where x is the sample thickness.

TABLE 2

Values of the room temperature electrical conductivity ($\log \sigma_{25}$), activation energy (ΔE), energy gap ($2\Delta E$) obtained for various titania alkali–silicate glasses

Glass No. [a]	TiO_2 (wt%)	$\log \sigma_{25}$ (by extrapolation; $\Omega^{-1}\,cm^{-1}$)	Activation energy (eV)	Energy gap (eV)
I	25	−15.00	1.10	2.20
II	30	−13.700	0.95	1.90
III	35	−12.500	0.80	1.60
IV	40	−11.500	0.70	1.40
V	45	−12.00	0.75	1.50

[a] See Table 1.

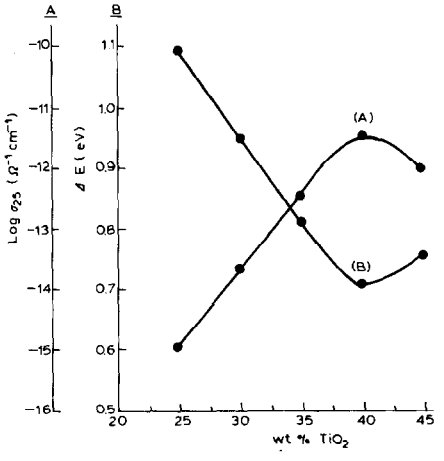

Fig. 2. Schematic representation of the variation of: (A) the room-temperature electrical conductivity ($\log \sigma_{25}$); and (B) activation energy for conduction, ΔE (eV), as a function of titania content.

Several measurements were carried out in this investigation. These measurements depend on the values of A/A_0 obtained from the oscilloscope. Thus, Fig. 3A shows the temperature dependence of $(1 - A/A_0)$. In accordance with Folds [19,20], a frequency of 800 kHz was chosen for suitable losses to attain detectable readings and reliable data. At lower frequencies, the diffraction effects are larger and may therefore be responsible for the observed attenuation. From Fig. 3A, curves (a), nearly straight-line relationships display the attenuation behaviour of the longitudinal ultrasonic wave amplitude as a function of temperature rise. Thus, the observed increase of wave attenuation on curves (a), and ultrasonic attenuation coefficient, α (Fig. 3A, curves b), as a function of temperature rise, are most probably correlated to the decrease of viscosity, decreased density and melting point of the sample, and the interaction between acoustic waves and both of the

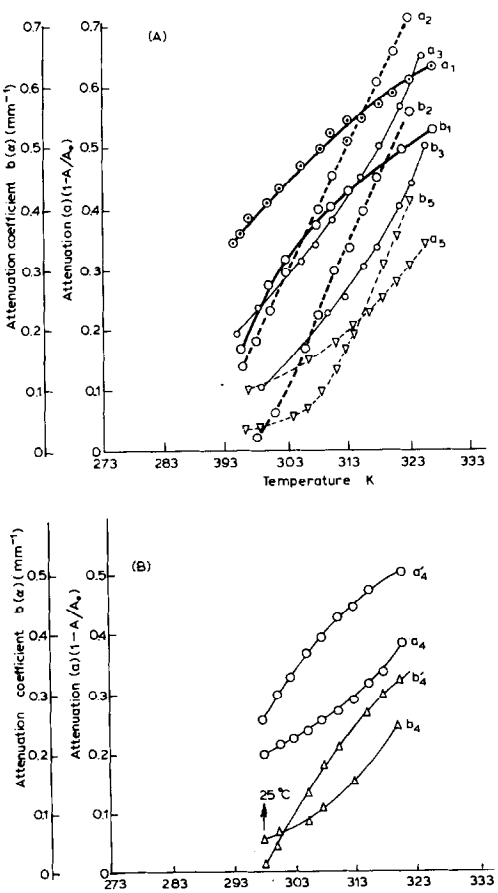

Fig. 3. Diagrammatical representation of the temperature dependence of ultrasonic attenuation (a) and attenuation coefficient (b) of silicate glasses containing 25–45 wt% TiO_2. (A) 25 wt% TiO_2 (a_1, b_1), 30 wt% TiO_2 (a_2, b_2), 35 wt% TiO_2 (a_3, b_3), 45 wt% TiO_2 (a_5, b_5); (B) 40 wt% TiO_2 (a_4, b_4), after laser irradiation (a', b'_4).

charge carriers and thermal phonons in the polycrystalline solids investigated [21]. There are four different physical mechanisms through which acoustic phonons interact with charge carriers, which have been discussed in a review by Spector [21]. These mechanisms are: (1) electromagnetic coupling; (2) magnetoelastic coupling; (3) deformation potential coupling; and (4) piezoelectric coupling. Alternatively, a considerable variation in the values of ultrasonic attenuation and attenuation coefficients obtained (see Fig. 3), takes place as a function of TiO_2 content. This requires that the ultrasonic attenuation and ultrasonic attenuation coefficient are inversely proportional to the titania content of the glasses investigated. Thus, in conformity with the values deduced from conductivity data presented here, this could be explained on the basis of the ratio of titanium octahedra to tetrahedra formed, and/or different geometries [22], at increasing titania content.

For the effect of laser irradiation, Fig. 3B curves (a', b'), both ultrasonic attenuation and the ultrasonic attenuation coefficient are considerably increased after laser irradiation (320 pulses). This could probably be correlated with the decreased density of the medium as a result of the interaction of the nitrogen laser pulses with glass constituents.

Figure 4 shows the variation of the room-temperature (25°C) electrical conductivity, $\log \sigma_{25}$ (curve A), and the activation energy for semiconductions, ΔE (eV, curve B), as a function of the room-temperature ultrasonic

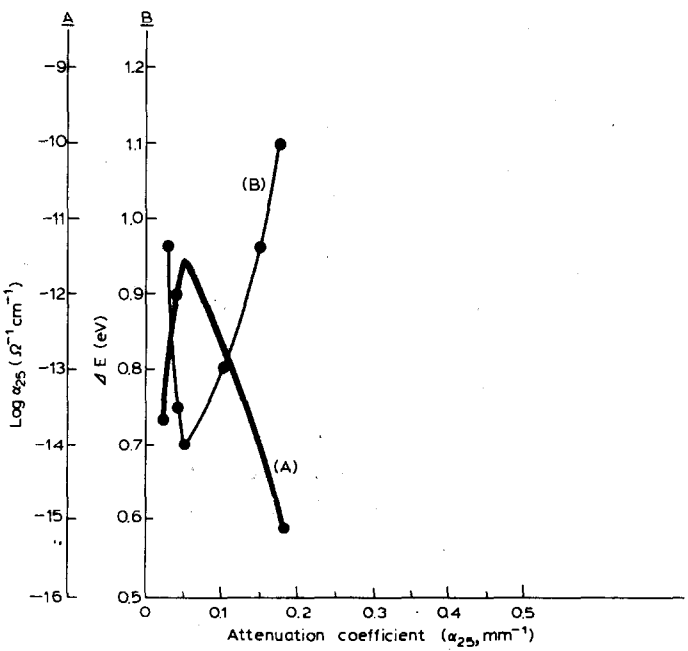

Fig. 4. Correlation of the variation of room-temperature electrical conductivity (A) and activation energy for conduction (B) as a function of the ultrasonic attenuation coefficient, α.

attenuation coefficient, α, for different titania-containing glasses. From both Figs. 3 and 4 it can easily be seen that the room temperature electrical conductivity ($\log \sigma_{25}$) becomes higher, whereas both the activation energy for conduction and the attenuation coefficient become lower, as a function of titania content in the glasses investigated. This may be correlated with changes in the relative proportion of the titanium tetrahedra and octahedra present and/or the interaction of titania with the glass composition and the ultrasonic longitudinal wave attenuation.

GENERAL DISCUSSION AND CONCLUSION

For the titanium-substituted alkali–silicate glasses investigated, the electrosonic (electrical and ultrasonic) characteristics evaluated have a common general trend, namely, the electrical resistivity, activation energy for conduction, energy gap, ultrasonic attenuation, and ultrasonic attenuation coefficient are considerably decreased as a function of titania content. Furthermore, laser irradiation (320 pulses) was found to increase the ultrasonic parameters. This could be plausibly correlated with the formation of decomposition centres and a decreased density of the medium as a result of laser irradiation damage. The latter in turn may affect the relative proportion of titanium tetrahedra to octahedra. Consequently, the conductivity data were found helpful in explaining this behaviour as being due to the increased semiconductivity of various glass samples as a function of titania content. Thus, titania additions interact with glass compositions creating donor centres in the sense that it may act as a modifier for these semiconducting glasses. According to the theory of ultrasonic attenuation in piezoelectric semiconductors developed by Hutson and White [23], ultrasonic attenuation may result from the interaction of mobile charge carriers with the longitudinal electric fields of piezoelectric origin.

Using mathematical analysis, the curve representing a correlation between the electrical conductivity ($\log \sigma$) and the ultrasonic attenuation coefficient (Fig. 4, curve A) was found to fit Abou Sekkina's relation of the form

$$-\log \sigma = a\alpha^2 + b\alpha + c$$

where, a, b and c are -1440, 196 and -17.7, respectively.

Finally, a correlation amongst the electrical and ultrasonic properties was proposed and established for titania glasses investigated for the first time.

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