

Effect of vanadium ions on the conduction mechanism of cabal glasses

A. M. NASSAR*, M. M. EL-MOUSELY AND A. M. DARWISH

Faculty of Science, Ain-Shams University, Cairo, Egypt

(Received 6 January 1976)

The effect of small amount of V_2O_5 in the D.C. electric conduction of cabal glasses was studied, in order to identify, the nature of conduction mechanism, as well as the current carriers in such glasses. The results obtained give a strong evidence that the divalent Ca^{2+} cations are the main current carriers in glasses with low vanadium concentration. With high concentration more than 2% the superposition of the electronic conduction on the larger activation energy of ionic conduction may show slight increase in the conductivity

1. INTRODUCTION

The commonly observed high resistivity (Owen 1961, Hanyama 1962) of the glasses in the system RO, B_2O_3, Al_2O_3 have been explained by Hirayama (1962) by considering the motion of the divalent cations under the action of the applied electric field. The ease of motion of such cations is limited by the bond strength S . The possibility of the migration of the doubly charged ions, through the glass matrix has been investigated by diffusion experiments using radio-active isotopes. The results of Myuller & Pronkin (1966) give a powerful basis for the probability of migration. Also the more recent studies on diffusion made by Frischat (1966, 1969) are in consistence with such point of view. On the other hand the exceptionally high values of resistivity and activation energy of these glasses have been explained by Owen (1961) by considering that the charge carriers to be the non-bridging oxygen ions. On the other hand the electrical conductivity of high vanadate glasses (Mackenzie 1965, Dale & Stanworth 1954, Denton *et al* 1954, Myuller 1968) has been explained on the basis that the electrons are the current carriers in these glasses.

In order to identify the nature of the current carriers in the present studied glasses, it has been decided to apply the theoretical concepts of Myuller (1968) about the electrical conduction in oxide glasses. On basis of these concepts, the authors have calculated the experimental value of the modulus of conductivity $m\sigma^{ex}$ for Ca^{2+} cations in these glasses. The calculation was carried out by using the relation

$$m\sigma^{ex} = A - \log [M]$$

where A is the value of the intercept of the $\log \sigma$ vs $1/T$ plot at $1/T = 0$; and $[M]$ is the concentration of Ca^{2+} ions in mole/cc.

* Girls College, Al-Azhar University, Cairo, Egypt.

2. EXPERIMENTAL PROCEDURE

(a) *Raw materials and glass melts* :

The glass samples have been prepared in batches of 50 g Analar grade chemicals have been used. B_2O_3 was introduced as boric acid, Al_2O_3 and V_2O_5 were introduced as such, while CaO was used in the form of carbonate.

The melting was carried out in Pt 2% Rh crucibles in automatically controlled electric furnace at temperature of $1400^\circ C \pm 10^\circ C$ for four hours. After melting the molten glass was casted in iron moulds and transferred immediately to the annealing furnace at the appropriate temperature for quarter of an hour after which the furnace begins cooling with the proper rate of cooling in order to get stress and strain free samples. The base composition of the glasses prepared is CaO 38; B_2O_3 41; Al_2O_3 21.

(b) *The D.C. conductivity measurements* .

Samples of one square cm area and of 0.3 to 0.4 cm thickness with parallel sides of tolerance 15μ are used. The samples faces are coated with aqua-dage and before being dried the electrodes were applied.

The D.C. conductivity was measured using a vibrating read electrometer type VAJ 51, measuring currents up to 10^{-15} Amp. Surface conductivity has been tested by using the guard ring method. It was found that the surface conductivity represents a fraction which does not exceed 1%; thus it is negligible.

3. RESULTS AND DISCUSSION

The results obtained shown in figure 1, from which it is noticed that the relation between $\log \sigma$ and $1/T$ is a linear relation in the measuring temperature

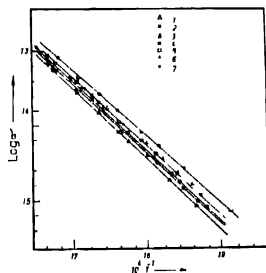


Fig. 1 Log Specific conductivity versus reciprocal of absolute temperature for 7 glasses in the system (CaO; B_2O_3 ; Al_2O_3) containing different concentrations of V_2O_5 . The numbers correspond to the numbers of glasses in table.

range (530 to 610°K). This indicates that the nature of the principle conduction mechanism in such glasses does not change with the used V_2O_5 concentrations. Table 1 shows the average values of the characteristic electric quantities by $\log \sigma_{300}$, activation energy E , and the value of A with their deviation.

Table 1

Glass No.	$\log \sigma_{300}$	$E(K\text{ cal/mole})$	$E(\text{ev})$	A	$m\sigma^{ev}\Delta m\sigma_l$	$[O] \times 10^3$	V_2O gm
1	-13.92 ± 0.06	82.852 ± 0.323	3.595	1.862 ± 0.106	3.71 - 0.6	82.12	—
2	13.85 ± 0	81.811 ± 0	3.540	1.754 ± 0	$3.608 - 0.7$	82.11	0.2
3	-13.86 ± 0.1	82.351 ± 0.415	3.569	1.891 ± 0.08	$3.642 - 0.7$	82.	0.585
4	-13.85 ± 0.05	81.874 ± 0	3.545	1.788 ± 0.048	$3.632 - 0.7$	82.95	1.0
5	-13.80 ± 0.016	81.500 ± 1.18	3.535	1.758 ± 0.226	$3.616 - 0.7$	82.53	1.5
6	-13.78 ± 0.02	82.000 ± 0.05	3.548	1.611 ± 0.1	$3.460 - 0.8$	82.45	2.0
7	-13.62 ± 0.162	79.495 ± 1.39	3.444	1.538 ± 0.429	$3.405 - 0.9$	82.38	4.0

The base glass used having the composition 38CaO/41 B₂O₃; 21 Al₂O₃ in mole.

From figures 2 and 3 it is clear that the addition of V_2O_5 in the given region of concentration, results in a very small (neghligible) decrease in the value of the activation energy E for the base glass (having $E \approx 82.85$ K.cal/mole) and a corresponding slight increase in its $\log \sigma$ (≈ -13.92).

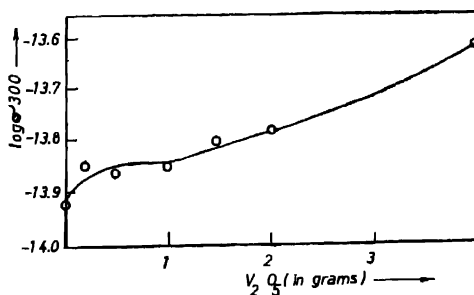


Fig 2. Relation between \log . specific conductivity (at 300°C) and V_2O_5 concentration in calal glass.

The values of the intercepts (A) given in table (1) are used to calculate the experimental modulus of conductivity $m\sigma^{ev}$ for Ca^{2+} cations. The calculated values together with its deviation $\Delta m\sigma$ from the theoretical value 4.3 ± 1 are given in table 1. It is clear that the deviation $\Delta m\sigma < 1$ for all the studied

samples, indicate the agreement of the experimental with the theoretical moduli of conductivity for Ca^{2+} cations. This may be taken as an evidence for considering Ca^{2+} as the main current carriers in all the studied samples.

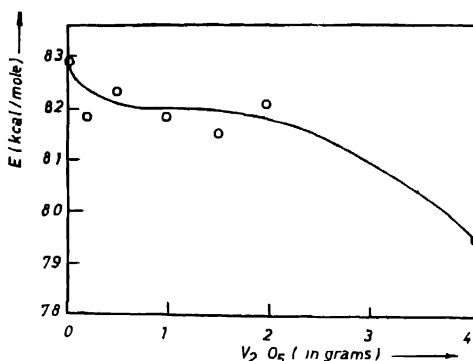


Fig. (3) Relation between the activation energy E (in kcal/mole) and the concentration of V_2O_5 , in cabal glass

The observed decrease of the activation energy and the increase of the conductivity of sample No. 7; may be attributed to either of the : for (a) The change of the conditions of binding of the Ca^{2+} cations to the oxygens of the network due to the introduction of V_2O_5 , or (b) The increase of the electronic part of conduction mechanism with the presence of vanadium ions

The change of the condition of binding of the Ca^{2+} cations affects the value of the dissociation energy of these ions from their polar sites (Myuller 1968), and consequently the activation energy E and the specific conductivity σ . This effect can be tested by the strength of oxygen backing (Schwartz *et al* 1966, Rao 1963) $[O]$, and which can be calculated using the relation

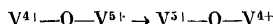
$$[O] = d_{ex} \left[\left(\frac{a}{M} \right)_{\text{CaO}} + 3 \left(\frac{a}{M} \right)_{\text{Al}_2\text{O}_3} + 3 \left(\frac{a}{M} \right)_{\text{H}_2\text{O}} + 5 \left(\frac{a}{M} \right)_{\text{V}_2\text{O}_5} \right]$$

where d_{ex} is the experimental determined glass density; a and M are the weight fractions and the molecular weight of the corresponding oxides in the glass, respectively.

The calculated values are given in table 1, from the inspection of this table we note that $[O]$ does not change and has an average value of 82.4×10^{-3} mole/cc. Therefore, it seems that the progressive addition of V_2O_5 within the given region, does not change the condition of Ca^{2+} in their polar sites in the glass structure (Rao 1963). Accordingly it may be concluded that the observed small changes

in both E and $\log \sigma_{300}$ for sample No. 7 cannot be attributed to the decrease of the dissociation energy of Ca^{2+} cations.

The increase of the electronic part of conduction due to the introduction of vanadium ions; which acts as sources for the electrons available for the conduction processes (Mackenzie 1965) according to a mechanism denoted as *the mixed valence mechanism*. In this mechanism the electron motion is a series of hopping between the two valencies V^{4+} , and V^{5+} , as represented by



It is known that the electronic conduction is largely affected (Owen 1970) by the separation a_0 between the vanadium ions. This separation was calculated using the relation

$$a_0 = \left[\frac{M}{2ad_{ez}} \right]^{1/3}.$$

For the glass No. 7 we get a value for the V—V separation $a_0 = 11 \text{ \AA}$. This value of separation may be too large to be jumped by electrons, hopping from one V ion to another during the process of conduction. But on the other hand, it has been stated by Mackenzie (1965) that the large separation between the transition metal ions in glass, in the presence of oxygen ions between two sites of hopping does not prevent the hopping mechanism. Accordingly; one may suggest that, in spite of the relatively large separation between the two V ions in our glass No. 7, there may be a definite probability for an electron to hop this distance and to affect the conduction, this was shown by Myuller (1965, 1966) to be probable in oxygen glasses.

General conclusion :

The D.C. conductivity of such glass is not affected appreciably by the existence of low concentration of vanadium. The conduction is mainly due to ionic transport of Ca^{2+} , and at high concentration of vanadium superposition of the electronic contribution is slightly observed. Lastly no evidence for conduction by non-bridging oxygen ions as previously suggested by Owen (1961). This last suggestion had been reached from another work in the same laboratory, which will be published elsewhere.

REFERENCES

- Dale A. E. & Stanworth J. E. 1954 *Research, London* 7, 38.
Denton E. P., Rawson H. & Stanworth J. E. 1954 *Nature, London* 173, 1030.
Frischat C. H. & Heurbert J. 1966 *Oel. Glastechn. Ber.*, 39, 524.
Frischat C. H. 1969 *J. Amer. Ceram. Soc.*, 52, 625.
Mackenzie J. D. 1965 *Modern aspects of the vitreous state* vol. 3, pp 126, London Butterworths.

974 A. M. Nassar, M. M. El-Mousely and A. M. Darwish

- Mueller R. L. 1965 *Structure of Glass . Electrical properties of Glass* Vol. 4, pp. 64, Edited by Mazurin, Consultant Bureau, New York.
- Mueller R. L. 1966 *Solid state chemistry*, pp (1), Consultant Bureau, New York.
- Mueller R. L. & Pronkin A. A. 1966 *Solid state chemistry*, pp 121, Consultant Bureau New York.
- Mueller R. L. 1968 *Glassy state* (collection), *Izd Akad. Nauk SSSR*, Moscow-Leningrad, pp. 67.
- Owen A. E. 1961 *Phys. Chem of Glasses* 2, 87
- Owen A. E. 1970 *Contemp. Phys* 11, 3, 227
- Janakirama Rao 1963 *Phys Chem of Glasses* 4, 1, 22.
- Schwartz M. & Mackenzie J. D. 1966 *J. Amer Ceram. Soc.* 49, 583.
- Wasfy N. 1965 *Some properties of silicate and borate glasses containing Ti in relation to structure*, M.Sc. Thesis U.A.C.