Structural and physical properties of Fe_2O_3-doped lead vanadate glass

S. Mandal[a)] and S. Hazra[b)]

Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032, India

The role of Fe_2O_3 in the structural and physical properties of ternary lead vanadium iron glass system has been studied in comparison with the binary lead vanadate glasses. X-ray diffraction, scanning electron microscopy, and differential thermal analysis show that homogeneous glasses of composition $10Fe_2O_3 \cdot xV_2O_5 \cdot (90 - x)PbO$ can be obtained for $x = 50$ to 80 mol%. Observation from the infrared spectroscopy shows that the basic building blocks of these glasses are same as those of crystalline V_2O_5, while differential thermal analysis and electrical conduction of these glasses suggest that there is a strong role of iron, both in the glass network and in the conduction mechanism for the glasses containing a low percentage of vanadium.

I. INTRODUCTION

Oxide glasses containing transition metal ions are of great interest because of their possible application in the field of optical switching and memory switching devices.[1,2] They show semiconducting properties due to the presence of two different valence states of the transition metal ions. Glasses containing vanadium are of particular interest since vanadium itself forms the glassy network and hence a large amount of vanadium can be incorporated. The glasses containing vanadium are highly conductive, which makes them more suitable for applications in electrical switching devices. Some work on the vanadate glasses has been done recently[3–5] in which vanadium oxide plays the unique role of network former. Recently, we have studied some structural[5] and electrical properties[6] of the lead vanadate glass system.

In the present work, iron oxide was used to dope the lead vanadate glasses in a fixed proportion, and the role of iron on the structural and electrical properties of the prepared glass samples was studied in comparison with the lead vanadium glasses with the change of glass composition. It was attempted to correlate the results from the structural studies with the results of the electrical studies.

II. EXPERIMENT

Glass samples of compositions $10Fe_2O_3 \cdot xV_2O_5 \cdot (90 - x)PbO$ with $x = 50$ to 80 mol% have been prepared from reagent grade chemicals V_2O_5, PbO, and Fe_2O_3. The chemicals mixed in desired proportions were melted in pure alumina crucibles. The melts were kept for 1 h in the temperature range 900–1000 °C depending on the glass composition for homogeneous mixing. The vitrification was achieved by subsequent rapid cooling of the melts between two brass plates. Chemical analyses were done to find out any trace of aluminum in the glass samples. The results, however, were negative.

The x-ray diffraction patterns of the as-prepared and of the heat-treated samples were taken in a Philips x-ray diffractometer (model PW 1050/51). The scanning electron microscopy of the polished surface of the as-prepared and heat-treated samples were taken in a Hitachi scanning electron microscope (model S-200). The differential thermal analysis (DTA) of the powdered samples was carried out in air in a Shimadzu thermal analyzer (model DT-40). The infrared (IR) spectra of the powdered samples and of the starting materials in KBr matrices were taken in a Perkin-Elmer spectrophotometer (model 783) in the wavenumber range 200–4000 cm^{-1}. A 200-Å-thick gold coating was deposited as electrode material on both surfaces of the samples by vacuum evaporation. The electrical measurements of the samples were carried out by using a Keithley electrometer (model 617) in the temperature range 100–450 K in dry conditions.

[a)]Present address: Depto. Solidos Ionicos, Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Cientificas, Cantoblanco, 28049-Madrid, Spain.
[b)]Present address: Surface Physics Division, Saha Institute of Nuclear Physics, Sector 1, Block-AF′, Bidhannagar, Calcutta 700064, India.
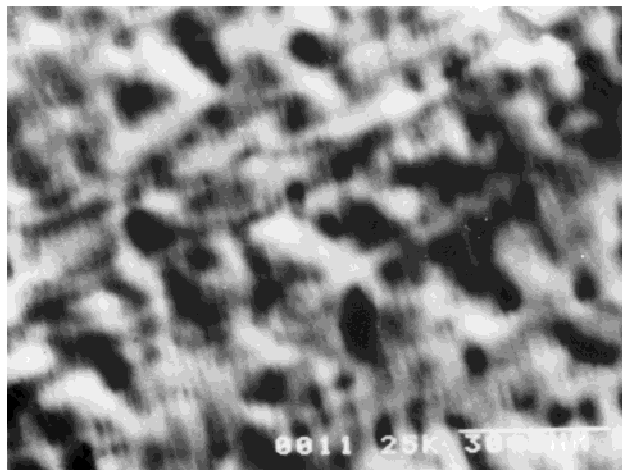
III. RESULTS AND DISCUSSION

A. Glass formation domain

X-ray diffraction patterns (not shown here) of the glassy samples show broad diffuse scattering at low angles which confirm the amorphous nature of the samples. The scanning electron micrograph of as-prepared samples, shown in Fig. 1(a), shows no sign of microstructure, confirming the amorphous and homogeneous nature of the samples. However, the micrograph [Fig. 1(b)] of the samples heat treated near the crystallization temperature shows the distinct presence of a microstructure at the surface of the samples. Differential thermal analysis curves for two glass compositions are shown in Fig. 2, which exhibit an endothermic peak due to the glass transition followed by a prominent exothermic peak due to crystallization. Similar observations for the samples of composition $10Fe_2O_3 \cdot xV_2O_5 \cdot (90 -$

$x)PbO$ were obtained for $x = 50$ to 80 mol%, which represents the homogeneous glass formation domain for the present system.

B. Glass network and structure

The glass transition (T_g) and crystallization (T_c) temperature were estimated within an error of ± 5 °C and are shown in Table I. The variations of T_g with glass compositions are shown in the inset of Fig. 2. The T_g of binary lead vanadate glasses are also included for comparison. It can be noted that in the ternary glasses the change of T_g is more rapid than in the binary glasses. The

TABLE I. Parameter obtained by fitting Schnakenberg's model to the experimental conductivity data of the ternary glasses along with T_g and T_c.

Glass compositions (mol%)		W_H (eV)	W_d (eV)	ν_0 (10^{13} s^{-1})	T_g (°C)	T_c (°C)
V_2O_5	PbO					
50	40	0.47	0.28	1.7	310	390
60	30	0.43	0.27	1.8	300	360
70	20	0.43	0.27	1.9	255	350
80	10	0.39	0.20	1.6	255	340

(a)

(b)

FIG. 1. Scanning electron micrographs of (a) as-prepared 50 mol% V_2O_5 and (b) heat-treated 80 mol% V_2O_5 glass compositions.
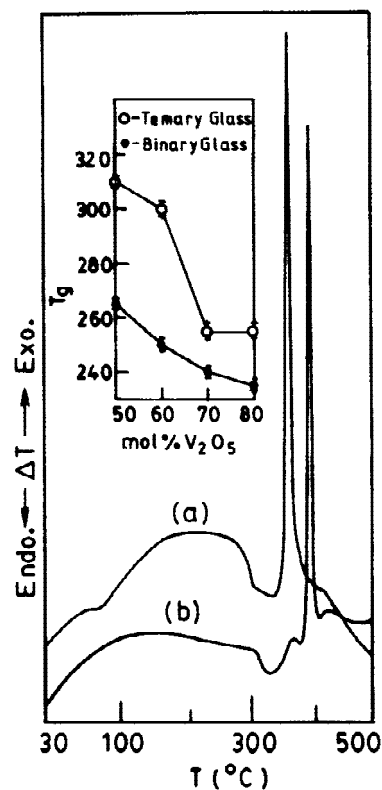

FIG. 2. Differential thermal analysis curves of (a) 80 mol% V_2O_5 and (b) 50 mol% V_2O_5 glass compositions of the ternary glasses. The inset shows the variation of glass transition temperature (T_g) with the variation of mol% V_2O_5 for ternary vanadate glasses along with the binary lead vanadate glasses.

T_g for ternary glasses containing 50 and 60 mol% V_2O_5 are ~310 and 300 °C, while for those containing 70 and 80 mol% V_2O_5, T_g is ~255 °C. Such a large change (~45 °C) in T_g with composition cannot be accounted for the formation of nonbridging oxygen in the glass network. This can only happen if some of the iron goes into the V–O–V chain leading to a V–O–Fe chain which will strengthen the network leading to an increase in T_g. This is a marked difference of this system with the binary lead vanadate system.

The infrared spectra at room temprature of all the glasses are shown in Fig. 3. IR spectra of the crystalline V_2O_5, PbO, and Fe_2O_3 are also included in the figure [3(a)–3(c)] for comparison. In the IR spectra a water band at 3400 cm⁻¹ and an –OH stretching band at 2920 cm⁻¹ have been observed. Another band at 1640 cm⁻¹ is also observed which may be due to the –OH bending mode of absorbed water. These bands are due to the hygroscopic character of the powdered samples. However, the bulk glass samples are very stable and not hygroscopic in nature. An intense high-frequency band at 1020 cm⁻¹ has been observed for crystalline V_2O_5. This band is assigned to the vibrations of isolated V=O vanadyl groups in V_2O_5 trigonal bipyramids.[6] In the glass samples this band becomes weak and a shoulder. This weak band shifts toward the low-frequency region (950–980 cm⁻¹) with the increase of PbO content. According to the mechanism suggested earlier,[8] the Pb^{2+} ions occupy a position between the V–O–V layers. Thus

Pb^{2+} has a direct influence on the isolated V=O bonds leading to a drop in wavenumber. This is more pronounced in the glass composition where the percentage of PbO is greater [Fig. 3(f) and 3(g)]. This shows that the basic network building block in the glasses remain the same as in crystalline V_2O_5. The weakness of the bands appears due to the randomness in the structure of the materials.

C. Electrical conductivity

The temperature dependence of the logarithmic conductivity is shown in Fig. 4 as a function of reciprocal temperature for three glass compositions. The inset of Fig. 4 shows the conductivity at 300 K with the change of composition for both the ternary and binary glasses. The conductivities were measured within an error of 5–10%. The sublinear change in conductivity with reciprocal temperature indicates a temperature-dependent activation energy, characteristic of small-polaron-hopping conduction,[9] which is confirmed later in the text. It is clear from the inset of Fig. 4 that for higher V_2O_5 content glasses the conductivity is higher in both the glass systems. The conductivity of the two systems is almost the same for the glasses containing 80 and 70 mol% V_2O_5, which indicates that the conduction of these glasses is due to hopping of charge carriers between two vanadium states only. But as is evident from the other compositions, this is not true. The ternary glasses have a higher conductivity over their binary counterpart. We propose
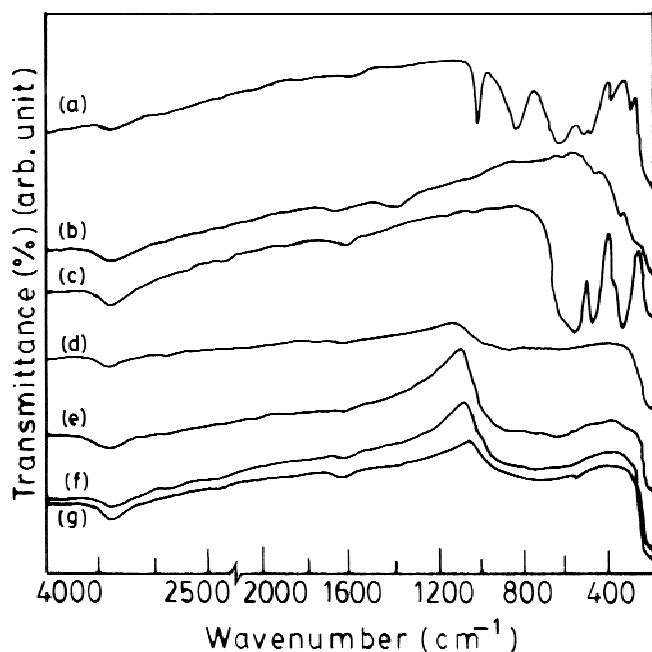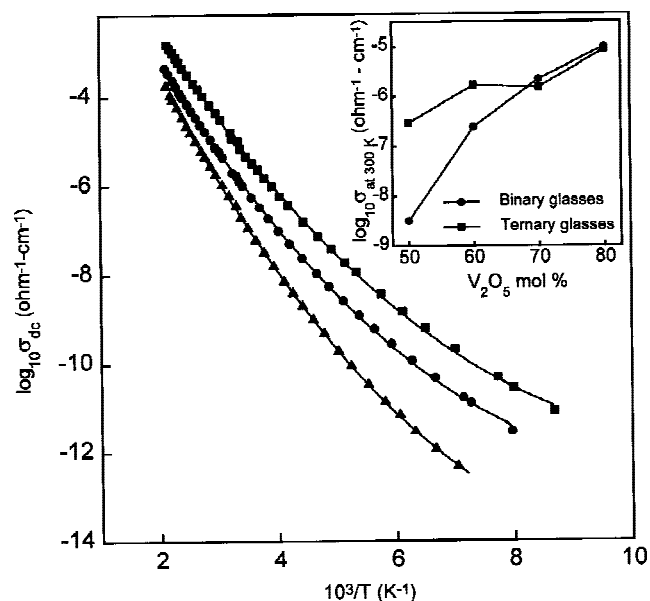

FIG. 3. Room-temperature infrared spectra of the ternary glasses. The spectra of starting materials are also included for comparison: (a) crystalline V_2O_5, (b) crystalline PbO, (c) crystalline Fe_2O_3, (d) 80 mol% V_2O_5, (e) 70 mol% V_2O_5, (f) 60 mol% V_2O_5, (g) 50 mol% V_2O_5.

FIG. 4. Dependence of the logarithmic conductivity is shown as a function of reciprocal temperature for three glass compositions, (■) 80 mol% V_2O_5, (●) 70 mol% V_2O_5, and (▲) 50 mol% V_2O_5. The solid line is the best fit to Schnakenberg's generalized polaron-hopping model. The inset shows the conductivity at 300 K with the change of composition for both the ternary and binary glasses.

that iron also takes part in the conduction mechanism giving a higher conductivity, since we have earlier seen in the DTA; the most probable case here is the formation of a V–O–Fe bridge so that hopping of polaron from the vanadium site to the iron site and vice versa take place.

To account for the conductivity in a wide temperature range Schnakenberg[10] has considered a general polaron-hopping model in which an optical multiphonon process determines the conductivity at higher temperature, while at low temperatures charge carrier transport is an acoustical one-phonon-assisted hopping process. The temperature dependence of the conductivity in this model has the form

$$\sigma \sim T^{-1}[\sinh(h\nu_0/k_BT)]^{1/2} \exp[-(4W_H/h\nu_0) \tanh(h\nu_0/4k_BT)] \, exp(-W_D/k_BT) \quad ,$$

where W_H is the polaron hopping energy, W_D is the disorder energy resulting from the variation of local environment of ions, and ν_0 is the optical phonon frequency. This model predicts a temperature-dependent hopping energy which decreases with the decrease of temperature consistent with the data presented in Fig. 4. The experimental data were fitted with the theory, and the best fit is shown in Fig. 4. The best fit values of the parameters ν_0, W_H, and W_D are shown in Table I. The W_D values show that disorderliness is greatest for 50 mol% V_2O_5 glass composition.

IV. CONCLUSION

Various investigations such as x-ray diffraction, scanning electron microscopy, differential thermal analysis, infrared spectroscopy, and electrical conductivity of the ternary lead vanadium iron glasses have been done to see the effect of iron in the structure of the glasses. The study reveals that it is possible to prepare a wide composition range of glasses. It was seen that while only vanadium take part in the conduction mechanism for the two highest V_2O_5 content glasses, in the other two glass compositions both vanadium and iron took part in the conduction mechanism. This is due to the fact that a chain like V–O–Fe is formed along with V–O–V, which is also confirmed from the DTA study.

REFERENCES

1. Y. Sakuri and J. Yamaki, J. Electrochem. Soc. **132,** 512 (1985).
2. J. Livage, J.P. Jolivet, and E. Tronc, J. Non-Cryst. Solids **121,** 35 (1990).
3. V. Fares, M. Magini, and A. Montero, J. Non-Cryst. Solids **99,** 404 (1988).
4. V. Dimitrov and Y. Dimitriev, J. Non-Cryst. Solids **122,** 133 (1990).
5. S. Mandal and A. Ghosh, Phys. Rev. B **48,** 9388 (1993).
6. S. Mandal and A. Ghosh, Phys. Rev. B **49,** 3131 (1994).
7. E. Dachille and R. Roy, J. Am. Ceram. Soc. **42,** 78 (1965).
8. Y. Dimitriev, V. Dimitrov, M. Arnaudov, and D. Topalov, J. Non-Cryst. Solids **57,** 147 (1983).
9. I.G. Austin and N.F. Mott, Adv. Phys. **18,** 41 (1969).
10. J. Schnakenberg, Phys. Status Solidi **28,** 623 (1968).