

## Structure and physical properties of glassy lead vanadates

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The structure and physical properties of the lead-vanadate glasses of compositions  $(V_2O_5)_x(PbO)_{100-x}$  with  $x=50-90$  mol %, prepared by the roller-quenching technique have been studied. It has been shown by x-ray diffraction, scanning electron microscopy, density and oxygen molar volume measurements, etc., that single-phase homogeneous glasses with a random network structure can be obtained in this system. The network structure is built up of unaffected  $VO_5$  groups as in crystalline  $V_2O_5$  and affected  $VO_5$  groups. A gradual decrease in the coordination number of  $V^{5+}$  and  $V^{4+}$  ions and the formation of nonbridging oxygen atoms have been observed with increasing  $V_2O_5$  content in the glass compositions, consistent with the decrease in density. The nearly equimolar glass composition devitrifies to crystalline metavanadate  $PbV_2O_6$ . However, glasses with higher  $V_2O_5$  content devitrify to  $PbV_2O_6$  and a  $V_2O_5$ -rich amorphous phase. The fine structure of the electron spin resonance hyperfine lines observed when the glass composition is equimolar, gradually reduces to a two-component structure at the same effective  $g$  value and is interpreted as due to an increase of the hopping rate of polarons with increasing  $V_2O_5$  content in the glass compositions.

### I. INTRODUCTION

Oxide glasses containing transition-metal ions (Refs. 1–5) are of continuous interest because of their possible applications, such as electrical threshold and memory switching as well as optical switching devices.<sup>6–8</sup> These glasses exhibit semiconducting properties due to the presence of transition-metal ions in two different valence states.<sup>1–5,9,10</sup> Glasses containing vanadium are known to have both  $V^{4+}$  and  $V^{5+}$  ions present in them and the conduction process has been described by the hopping of an unpaired  $3d^1$  electron from a  $V^{4+}$  site to a  $V^{5+}$  site.<sup>1–5,9,10</sup> This unpaired electron induces a polarization of the lattice around it and the charge carrier is a small polaron.<sup>9,10</sup> Recently an equimolar glassy and polycrystalline lead-vanadate system has been studied by x-ray diffraction,<sup>11,12</sup> ESR,<sup>13</sup> magnetic measurements,<sup>14</sup> IR measurements,<sup>15</sup> etc. However, the compositional dependence of the various physical properties, except as determined by IR measurements,<sup>15</sup> of the lead-vanadate glasses has not been studied so far. Another source of interest in the lead-vanadate system comes from the study of its glass-forming ability. In fact there are only a few studies on glasses containing a large amount of  $V_2O_5$  as a unique network former,<sup>4</sup> though the analogous system containing  $P_2O_5$  has been widely characterized.<sup>1–3</sup> The objective of the present work is to study the compositional dependence of the structure and other physical properties of the lead-vanadate glasses prepared by fast quenching of the melt in a wide composition range (50–90 mol %  $V_2O_5$ ).

### II. EXPERIMENTAL PROCEDURE

Glassy samples were prepared from the reagent grade chemicals  $V_2O_5$  and  $PbO$ . These chemicals were melted in alumina crucibles in the temperature range

900–1200 °C depending on glass compositions. Vitrification was achieved by rapid cooling of the melt using a twin roller technique similar to one described by Chen and Miller.<sup>16</sup> X-ray-diffraction patterns of the samples were recorded in a Philips x-ray diffractometer (model PW 1050/51). Scanning electron micrographs of the polished surfaces of the samples were taken in a Hitachi (model S-200) scanning electron microscope attached with an energy-dispersive spectroscopy (EDS) microanalysis apparatus. A 150-Å-thick gold coating was deposited on the polished surfaces by vacuum evaporation to serve as the conduction layer. Differential thermal analysis (DTA) was performed for all samples using a Shimadzu thermal analyzer (model DT-40) with a heating rate of 20 °C/min in air atmosphere. The densities of the samples were measured at room temperature by the displacement method using acetone as the immersion liquid. The IR spectra at room temperature of the prepared glasses and the starting materials  $V_2O_5$  and  $PbO$  in KBr matrices were recorded in a Perkin-Elmer spectrophotometer (model 783) in the wave-number range 200–4000  $cm^{-1}$ . The magnetic susceptibility at room temperature was measured in an EG&G Parc vibrating sample magnetometer (model 155). The ESR spectra of the powdered samples were taken in a JEOL X band ESR spectrometer (model JES-RE1X) at room temperature. The final chemical compositions of all the prepared samples and the concentration of  $V^{4+}$  and  $V^{5+}$  ions were determined by redox-titration of the solution of the glasses in dilute  $HNO_3$  against potassium permanganate solution.<sup>17</sup>

### III. RESULTS AND DISCUSSION

#### A. X-ray diffraction and scanning electron microscopy studies

The x-ray-diffraction patterns of several compositions of the prepared samples are shown in Fig. 1. The

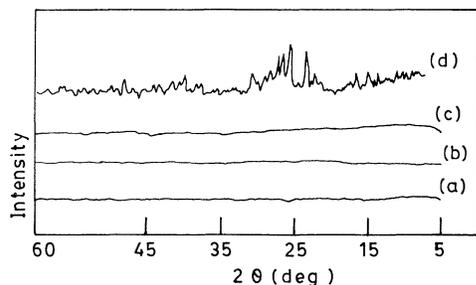


FIG. 1. X-ray diffractograms of different sample compositions. (a) 90 mol %  $V_2O_5$ , (b) 70 mol %  $V_2O_5$ , (c) 50 mol %  $V_2O_5$ , (d) 50 mol %  $V_2O_5$  heat treated at 320 °C for 20 h.

diffractograms do not present any peak, but only broad diffuse scattering at low angles characteristic of amorphous structures, i.e., a long-range structural disorder. Figure 1 also shows the diffractogram of a heat-treated sample of equimolar composition exhibiting crystalline peaks which are identified as the peaks of the stable polymorphic phase of a lead metavanadate crystal  $PbV_2O_6$ . Such a crystalline structure of the equimolar and high- $V_2O_5$ -content glass compositions has also been detected using x-ray analysis during thermal experiments by stopping the temperature rise.<sup>11</sup>

Figure 2 shows the scanning electron microscopy (SEM) micrographs of several samples as prepared and heat treated at 320 °C. The micrographs of the as-prepared samples exhibit a surface without any presence of microstructure which is again a characteristic of the amorphous phase. However, the heat-treated sample of equimolar composition shows crystalline structures, while heat-treated samples having higher  $V_2O_5$  content show crystalline structures embodied in amorphous phases. The EDS microanalysis showed that the crystalline phases observed in the heat-treated samples are lead

metavanadate  $PbV_2O_6$  as detected by x-ray analysis. The amorphous phase observed in the heat-treated samples with more than 50 mol %  $V_2O_5$  has been identified as  $V_2O_5$ -rich vitreous phases.

### B. IR spectra

The room-temperature IR spectra in the region 200–4000  $cm^{-1}$  of all glass compositions, and also of crystalline  $V_2O_5$  and  $PbO$  for comparison, are shown in Fig. 3. In the IR spectra, a water band at 3400  $cm^{-1}$  and an –OH stretching peak at 2920  $cm^{-1}$  have been observed. These peaks may be due to the hygroscopic character of the powdered samples.<sup>18,19</sup> Another absorption peak at 1640  $cm^{-1}$  is also observed for all glass compositions. The origin of the peak might be due to the –OH bending mode and absorbed water.<sup>19</sup> An intense high-frequency band at 1020  $cm^{-1}$  has been observed in crystalline  $V_2O_5$  and this band is assigned to the vibrations of isolated  $V=O$  vanadyl groups in  $VO_5$  trigonal bipyramids.<sup>20</sup> In the glasses containing 90–70 mol %  $V_2O_5$  this band becomes very weak and shifts towards lower wave number (1010  $cm^{-1}$ ). Also new bands appear in the range 950–970  $cm^{-1}$ . However, in the glass compositions containing 60 and 50 mol %  $V_2O_5$  the band at 1020  $cm^{-1}$  completely vanishes and new bands at 950  $cm^{-1}$  and 430  $cm^{-1}$  appear. According to the mechanism suggested earlier,<sup>21</sup> the  $Pb^{2+}$  ions occupy a position between the V–O–V layers. This is why they have a direct influence on the isolated  $V=O$  bonds of the  $VO_5$  groups according to the scheme  $Pb^{2+}-O=V^{5+}$ . Under that interaction the O atom of the vanadyl group is included in the Pb coordination polyhedron, leading to an elongation of the affected  $V=O$  bonds and a drop in wave numbers down to 970–950  $cm^{-1}$ . Thus in the glass containing 90–70 mol %  $V_2O_5$  (i.e., lower  $PbO$  content)  $VO_5$  groups with unaffected  $V=O$  bonds are preserved along with the

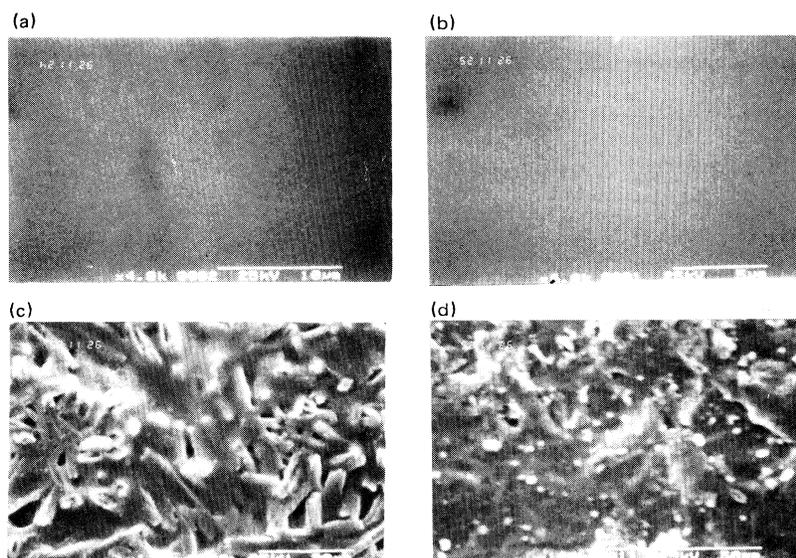


FIG. 2. Scanning electron micrographs of several glass compositions. (a) 50 mol %  $V_2O_5$  ( $\times 4000$ ), (b) 90 mol %  $V_2O_5$  ( $\times 6000$ ), (c) 50 mol %  $V_2O_5$  heat treated at 320 °C for 20 h ( $\times 1500$ ), (d) 90 mol %  $V_2O_5$  heat treated at 320 °C for 6 h ( $\times 1000$ ).

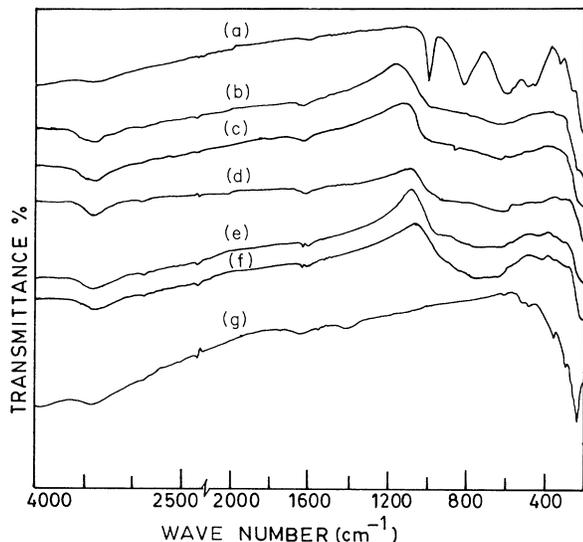


FIG. 3. Room-temperature infrared spectra of lead vanadate glasses. (a) Crystalline  $V_2O_5$ , (b) 90 mol %  $V_2O_5$ , (c) 80 mol %  $V_2O_5$ , (d) 70 mol %  $V_2O_5$ , (e) 60 mol %  $V_2O_5$ , (f) 50 mol %  $V_2O_5$ , (g) crystalline  $PbO$ .

affected  $VO_5$  polyhedra. With the increase of  $PbO$  (beyond 30 mol %) only affected  $VO_5$  polyhedra are obtained in the glass compositions containing 60 and 50 mol %  $V_2O_5$ . For the glass compositions containing 60 and 50 mol %  $V_2O_5$ , a new low-frequency band at  $430\text{ cm}^{-1}$  is observed in the IR spectra. The origin of this band is not clear and might be due to deformation vibrations of the distorted vanadyl group. In an earlier report<sup>15</sup> of the IR spectra of lead-vanadate glasses of similar compositions, two high-frequency bands at  $1020$  and  $970\text{--}950\text{ cm}^{-1}$ , except for glass containing 50 mol %  $V_2O_5$ , were observed. This slight variation is due to the different microstructure of the glasses prepared by quenching of the melt with a different cooling rate.

### C. Chemical compositions, density, and molar oxygen volume

Chemical analysis of all glass compositions shows that the analyzed compositions change slightly from the batch compositions due to evaporation loss during melting and

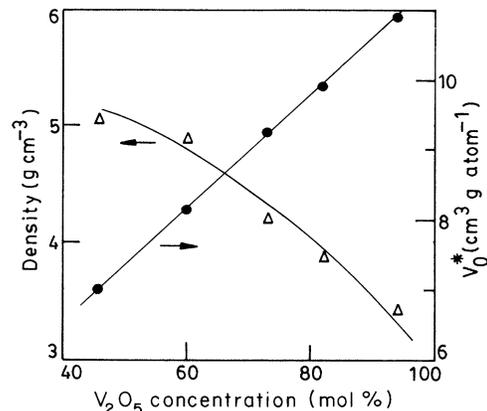


FIG. 4. Density and oxygen molar volume of lead-vanadate glasses shown as a function of  $V_2O_5$  content in the glass compositions.

that the vanadium ions exist in two oxidation states, e.g.,  $V^{5+}$  and  $V^{4+}$  in all glass compositions. Other oxidation states of vanadium have not been detected. The estimated concentrations of  $V^{4+}$  and total vanadium ions and their ratio  $C$  are shown in Table I. It is observed in Table I that the total vanadium ion concentration  $N$  increases, consistent with the increase of  $V_2O_5$  content in the glass compositions. However,  $V^{4+}$  concentrations and  $C$  values do not vary systematically with glass compositions. This is due to the fact that redox-reaction in the melts occurred for different durations of time, because the melts of different compositions were kept for different durations for homogenization at the melting temperature. Assuming the vanadium ions to be uniformly distributed in the glass matrix the average vanadium site separation  $R$  was estimated from the estimated total vanadium ion concentrations and is shown in Table I. The values of  $R$  decrease with the increase of  $V_2O_5$  content in the glass compositions.

The density of the glass samples, shown in Fig. 4 as a function of  $V_2O_5$  content in the compositions, decreases continuously with the increase of  $V_2O_5$  content in the glass compositions. The relationship between the density and the composition of a glass system is frequently expressed in terms of the apparent volume  $V_0^*$  occupied by

TABLE I. Compositions, concentrations of  $V^{4+}$ , and total vanadium ions and their ratio, density, average vanadium site separation, glass transition temperature, and crystallization temperature of lead-vanadate glasses.

| Nominal glass composition (mol %) |       | $[V^{4+}]$<br>( $10^{21}\text{ cm}^{-3}$ ) | $N$<br>( $10^{22}\text{ cm}^{-3}$ ) | $C = [V^{4+}]/N$ | Density<br>( $\text{g}/\text{cm}^{-3}$ ) | $R$<br>( $10^{-8}\text{ cm}$ ) | $T_g$<br>( $^{\circ}\text{C}$ ) | $T_c$<br>( $^{\circ}\text{C}$ ) |
|-----------------------------------|-------|--|-------------------------------------|------------------|--|--------------------------------|---------------------------------|---------------------------------|
| $V_2O_5$                          | $PbO$ |  |                                     |                  |  |                                |                                 |                                 |
| 50                                | 50    | 6.297                                      | 1.354                               | 0.064            | 5.045                                    | 4.195                          | 265                             | 320, 380 <sup>a</sup>           |
| 60                                | 40    | 0.751                                      | 1.779                               | 0.042            | 4.887                                    | 3.830                          | 250                             | 320, 380 <sup>a</sup>           |
| 70                                | 30    | 1.675                                      | 1.922                               | 0.087            | 4.210                                    | 3.733                          | 240                             | 275, 360 <sup>a</sup>           |
| 80                                | 20    | 3.017                                      | 2.005                               | 0.150            | 3.881                                    | 3.680                          | 235                             | 280, 390 <sup>a</sup>           |
| 90                                | 10    | 2.662                                      | 2.111                               | 0.126            | 3.433                                    | 3.617                          | 230                             | 260, 370 <sup>a</sup>           |

<sup>a</sup>Corresponding to the second exothermic peak.

1 g-at. of oxygen. The value of  $V_0^*$  has been determined from the formula given by Drake *et al.*<sup>22</sup> and its composition dependence is also shown in Fig. 4. The  $V_0^*$  changes monotonously with composition. This indicates that all the glass compositions appear to be in a single phase with random network structure, and that the geometry and topology of the random network do not change significantly with composition. These results are also consistent with the SEM micrographs (Fig. 2).

#### D. Thermal analysis

Figure 5 shows DTA curves of all the prepared glass samples. Each curve exhibits an endothermic dip due to glass transition, and two exothermic peaks corresponding to crystallization or phase transition. It is also observed in Fig. 5 that the intensity of the first peak increases and that of the second peak decreases with the increase of  $V_2O_5$  content in the glass compositions. The glass transition and crystallization temperatures are listed in Table I. The composition dependence of glass transition temperatures ( $T_g$ ) depicted in Fig. 6 indicates that the  $T_g$  decreases continuously with the increase of  $V_2O_5$  content in the glass compositions. DTA studies<sup>23,24</sup> on the structure of several glasses have already revealed that  $T_g$  shows a clear correlation with the change in the coordination number of the network former and with the formation of nonbridging oxygen atoms, which means destruction or depolymerization of the network structure. The  $T_g$ , in general, shows a distinct increase when the coordination number of the network former increases. Contrary to this, a formation of nonbridging oxygen causes a decrease in the  $T_g$ . The continuous and distinct decrease in the  $T_g$

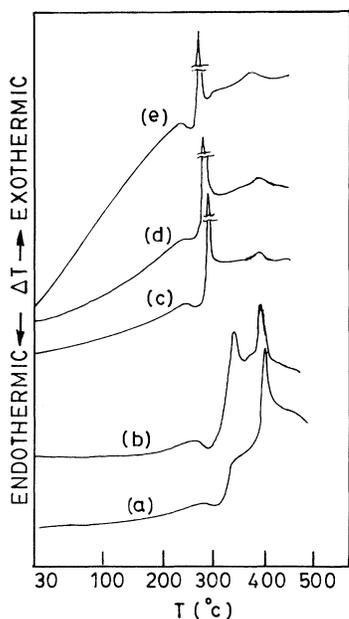


FIG. 5. Differential thermal analysis curves of the lead-vanadate glasses. (a) 50 mol %  $V_2O_5$ , (b) 60 mol %  $V_2O_5$ , (c) 70 mol %  $V_2O_5$ , (d) 80 mol %  $V_2O_5$ , (e) 90 mol %  $V_2O_5$ .

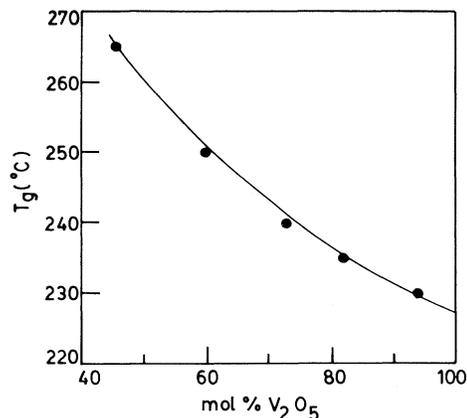


FIG. 6. Composition dependence of the glass transition temperatures ( $T_g$ ) of the lead-vanadate glasses.

from 265°C to 225°C observed in the present study, therefore, seems to suggest the gradual decrease in the coordination number of  $V^{5+}$  and  $V^{4+}$  ions and the formation of nonbridging oxygen atoms in the  $VO_4$  tetrahedral units. These results are consistent with the IR results<sup>21</sup> and density data. The decrease in  $T_g$  also suggests that the strength of the chemical bond between metal and oxygen atoms becomes weakened. This is ascribed to the increased interatomic distances between metal and oxygen ions leading to the decrease in density (Fig. 4).

Crystalline phases of equimolar glass composition (50 mol %  $V_2O_5$ -50 mol % PbO) has been studied earlier<sup>11</sup> using x-ray diffraction by stopping the temperature rise during the thermal experiment. It has been shown that the first exothermic peak corresponds to the transition of homogeneous glassy phase to unstable crystalline lead metavanadate  $PbV_2O_6$  and the second exothermic peak corresponds to the phase transition of the unstable  $PbV_2O_6$  to a stable polymorphic crystalline phase of  $PbV_2O_6$ .

The DTA results of the equimolar glass composition of the present study completely coincide with the reported one. Glasses with higher  $V_2O_5$  content devitrify giving rise to the stable crystalline metavanadate  $PbV_2O_6$  phase and  $V_2O_5$ -rich vitreous phase at temperatures corresponding to the first exothermic peaks, which depend on glass compositions. The second exothermic peaks are due to the devitrification of  $V_2O_5$ -rich vitreous phases. The vitreous  $V_2O_5$ -rich phases have also been detected by the SEM studies in the heat-treated (at 320°C) glass compositions containing more than 50 mol %  $V_2O_5$ .

#### E. ESR and magnetic susceptibility

Magnetic susceptibility of the prepared glasses measured at room temperature varied consistently with the  $V^{4+}$  ion concentrations determined by chemical analysis (cf. Sec. III C). This is due to the fact that magnetic properties of these glasses arise from the paramagnetic unpaired  $3d^1$  electron whose concentration is similar to

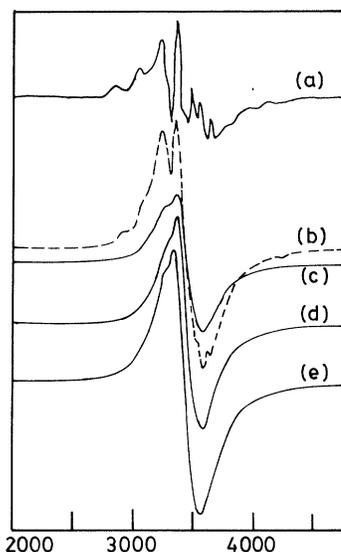


FIG. 7. Room-temperature ESR spectra taken at 9.44 GHz of lead-vanadate glass compositions. (a) 50 mol %  $V_2O_5$  (gain=5), (b) 60 mol %  $V_2O_5$  (gain=10), (c) 70 mol %  $V_2O_5$  (gain=1.25), (d) 80 mol %  $V_2O_5$  (gain=1.6), (e) 90 mol %  $V_2O_5$  (gain=1.25).

the  $V^{4+}$  ion concentrations. The estimated  $V^{4+}$  ion concentrations from the measured susceptibility agreed, within experimental error, with those determined from chemical analysis.

The room-temperature ESR spectra of the glasses are shown in Fig. 7. It is observed that glass containing 50 mol %  $V_2O_5$  [Fig. 7(a)] shows a complex ESR spectrum made up of resolved hyperfine component of the  $V^{51}$  isotope. The observed spectra can be described by the axially symmetric spin Hamiltonian

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y),$$

where  $S = \frac{1}{2}$ ,  $I = \frac{7}{2}$ , and all other parameters have the usual meanings. Such a spectrum is characteristic of tetravalent vanadium ions  $V^{4+}$  ( $3d^1$ ) and has been studied in other vanadate systems.<sup>25,26</sup>

As the  $V_2O_5$  content increases in the glass compositions, the ESR lines broaden with a partially resolved hyperfine spectrum and finally for  $V_2O_5$  content more than 60 mol %, the ESR spectra show two lines of

different widths, but within the experimental error, at the same effective  $g$  value ( $g_e$ ). Both lines are strongly narrowed by exchange interaction.

The experimentally determined spin Hamiltonian parameters are listed in Table II. For the samples for which no resolved hyperfine structure has been observed, the effective  $g$  value is given together with the linewidth ( $\Delta H$ ). It might be noted that the parameters for the equimolar glass are close to those reported earlier.<sup>13</sup> It might also be noted that the effective  $g$  values and the linewidths for glass compositions containing more than 60 mol %  $V_2O_5$  are nearly equal.

The composition dependence of the observed ESR line shapes for the vanadate glasses reported earlier<sup>25-29</sup> has been explained previously on the basis of different  $V^{4+}$  concentrations or phase segregation. However, for the lead-vanadate system (Fig. 7) the ESR line shapes vary systematically with compositions and cannot be attributed to the irregular variation of  $V^{4+}$  concentrations. Also the glasses show (Figs. 2 and 4) no sign of phase separation. The variation of line shapes can be explained by considering the difference in the hopping rate of charge carriers (polarons) in different glass compositions. It has been shown<sup>9,10</sup> that the hopping frequency of the polarons in the glasses is proportional to  $\exp(-W/kT)$ , where  $W$  is the activation energy for the hopping process which can be written as  $W = W_H + W_D/2$ , where  $W_H$  is the hopping energy of polarons between two identical sites and  $W_D$  is the average energy difference between adjacent vanadium sites due to the disordered nature of the glass. Analysis of the dc electrical conductivity of the lead-vanadate glasses shows<sup>30</sup> that  $W$  is higher for low  $V_2O_5$  content glasses. Thus the hopping rate of polarons is low for low- $V_2O_5$  content glass compositions. The higher value of  $W$  allows the observation of a well-resolved hyperfine component in the equimolar glass system. The resolution of the hyperfine component decreases with the increasing  $V_2O_5$  content in the glass composition due to a decrease in the value of  $W$ .

#### IV. CONCLUSIONS

Various investigations such as x-ray diffraction, scanning electron microscopy, density and oxygen molar volume, infrared spectroscopy, differential analysis, etc., on the lead-vanadate glasses in the composition range 50–90 mol %  $V_2O_5$  suggest that single-phase homogeneous glasses are obtained by the rapid quenching of the melt. Chemical analysis of the glasses shows that vanadi-

TABLE II. ESR parameters for the lead-vanadate glasses.

| Sample composition<br>mol % $V_2O_5$ | $g_{\parallel}$   | $g_{\perp}$       | $g_e$             | $A_{\parallel}$<br>(Gauss) | $A_{\perp}$<br>(Gauss) | $\Delta H$<br>(Gauss) |
|--------------------------------------|-------------------|-------------------|-------------------|----------------------------|------------------------|-----------------------|
| 50                                   | $1.916 \pm 0.007$ | $1.979 \pm 0.007$ |                   | $170 \pm 5$                | $58 \pm 5$             |                       |
| 60                                   | $1.918 \pm 0.010$ | $1.959 \pm 0.010$ |                   | $172 \pm 5$                | $56 \pm 5$             |                       |
| 70                                   |                   |                   | $1.957 \pm 0.007$ |                            |                        | $225 \pm 5$           |
| 80                                   |                   |                   | $1.957 \pm 0.007$ |                            |                        | $212 \pm 5$           |
| 90                                   |                   |                   | $1.957 \pm 0.007$ |                            |                        | $208 \pm 5$           |

um ions exist in two valence states, namely  $V^{5+}$  and  $V^{4+}$ , in all glass compositions. The trends in the IR spectra show that the two types of  $VO_5$  polyhedra build up the network structure: unaffected  $VO_5$  groups and affected  $VO_5$  groups. The metavanadate chain structure formed by  $VO_5$  polyhedra with V-O bonds are affected by the  $Pb^{2+}$  ions for the high-PbO-content glasses. The decrease of glass transition temperatures with the increase of  $V_2O_5$  content in the glass compositions indicates the gradual decrease in the coordinate numbers of  $V^{5+}$  and  $V^{4+}$  ions and the formation of nonbridging oxygen, consistent with the decrease of density. The equimolar glass composition devitrifies to crystalline lead metavanadate,

while glass compositions with higher  $V_2O_5$  content devitrify to a crystalline phase and an amorphous phase rich in  $V_2O_5$ . The fine structure of the ESR line shapes observed in the equimolar glass composition diminished with the increase of  $V_2O_5$  content in the glass compositions and this is attributed to an increase of the hopping rate of polarons with the increasing  $V_2O_5$  content in the glass compositions.

#### ACKNOWLEDGMENTS

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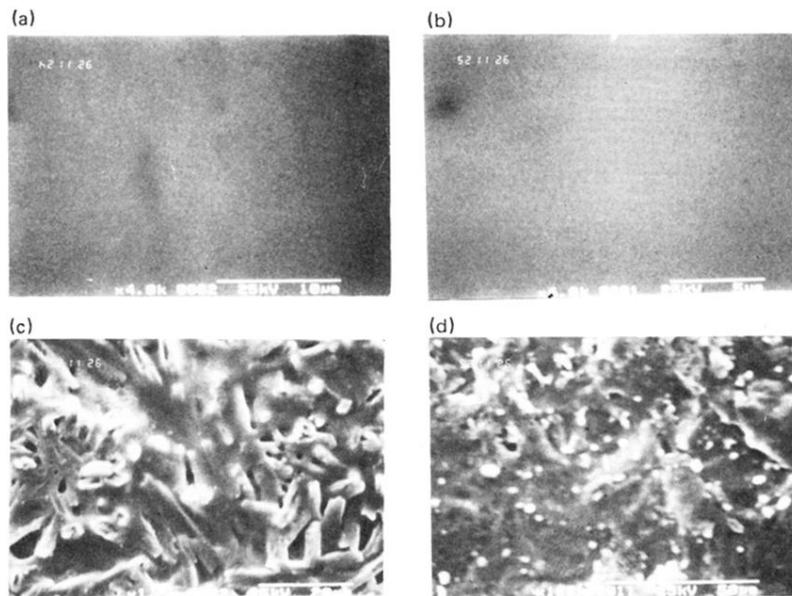


FIG. 2. Scanning electron micrographs of several glass compositions. (a) 50 mol %  $V_2O_5$  ( $\times 4000$ ), (b) 90 mol %  $V_2O_5$  ( $\times 6000$ ), (c) 50 mol %  $V_2O_5$  heat treated at  $320^\circ\text{C}$  for 20 h ( $\times 1500$ ), (d) 90 mol %  $V_2O_5$  heat treated at  $320^\circ\text{C}$  for 6 h ( $\times 1000$ ).