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# Electrical properties of $V_2O_5$–PbO–$GeO_2$ glasses

C. H. CHUNG*, D. LEZAL†, J. D. MACKENZIE
*Materials Department, School of Engineering and Applied Science, University of California, Los Angeles, CA 90024, USA*

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Glasses in the $V_2O_5$–PbO–$GeO_2$ system containing 55 mol % $V_2O_5$ were found to undergo a droplet-type phase separation. The dispersed phase is rich in $GeO_2$. The volume per cent of this phase increases with increasing $GeO_2$/PbO ratio in the glass. When the volume per cent of dispersed phase is small, the direct current conductivity depends mainly on the continuous phase. When the dispersed phase reaches about 42 vol %, a second kind of phase separation appears in the continuous phase and thus alters the conductivity dramatically. Providing that the heterogeneity is taken into consideration, all the conductivities of phase-separated glasses can be explained by the theory proposed by Mott.

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## 1. Introduction

Semiconducting oxide glasses based on $V_2O_5$ were first reported by Denton *et al.* in 1954 [1]. Since that time, a great deal of experimental results have been reported. Comprehensive theoretical treatises have been published by Mott and his co-workers [2, 3]. However, discrepancies still exist between theory and experimental results [4]. Attempts to explain these discrepancies can be found in the literature, but none of them have been completely successful. An obvious possible cause of such discrepancy is phase separation, although, the only experimental evidence of phase separation was reported by Kinser and Wilson [5] on $V_2O_5$–$P_2O_5$ glasses. There is no known theoretical treatment of the effects of phase separation on the electronic properties of oxide semiconducting glasses. Since Mal'tsev *et al.* [6] have shown that a region of liquid immiscibility exists in the phase diagram of the $V_2O_5$–PbO–$GeO_2$ system (Fig. 1) and glasses based on this system have been reported to exhibit switching behaviour [7], a study on how phase separation affects electronic properties was considered desirable.

## 2. Experimental procedure

Reagent grade chemicals ($V_2O_5$, PbO and $GeO_2$) were well-mixed and melted in quartz crucibles at a temperature of 1150° C in an electric furnace for 30 minutes. The temperature was then decreased to 1000° C, and maintained at this temperature for another hour before quenching onto an aluminium mould. All the glasses were annealed at 200° C for one hour. Table I lists the molar compositions, densities and the notation of the glasses studied. There was a significant loss of PbO, but no dissolution of $SiO_2$ was observed from chemical analysis. The *C* values, i.e., the $V^{4+}/V_{\text{total}}$ ratio, determined from the measurement of magnetic susceptibility, are also included. Magnetic susceptibility was measured by the Gouy method [8] for which an AL7500 precision magnet, an AL7500R series current regulator, and an electric micro-balance with sensitivity of 0.01 mg were used. The *C* value was then calculated from the number of unpaired electrons and the total amount of vanadium present. The refractive index was calculated from the reflectance, measured using light of wavelength 3.5 $\mu$m, of a

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*Present Address: Kylex Inc., 420 Bernardo Avenue, Mountain View, CA 94043, USA.

†Present Address: Institute of Radio Engineering and Electronics, Czechoslovakia Academy of Science, Prague, Czechoslovakia.

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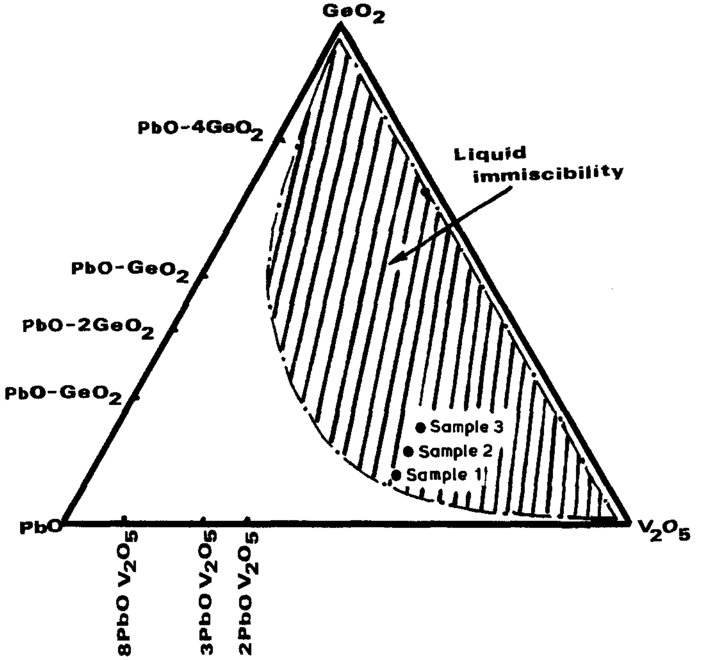

*Figure 1* Phase diagram of the $V_2O_5$–$PbO$–$GeO_2$ system [6].

well-polished glass sample using a Perkin–Elmer model 137 IR-spectrophotometer and a Barnes model 126 micro-specular reflectance unit. No dispersion was observed over a fairly wide range of wavelengths. Scanning electron microscope (SEM) pictures were taken from the polished surface of samples etched for one minute with 1% HCl. A platinum coating of thickness 300 Å was deposited by argon ion sputtering to serve as a conductive layer. Electrical conductivity was measured in a cryogenic unit. Vapour-deposited gold was used as electrodes. Ohmic behaviour was ascertained from linearity of current–voltage curves; a three-terminal method with guard ring was used. Differential thermal analysis (DTA) results were obtained from a Theta differential thermal analyser using a heating rate of 10° C min$^{-1}$. X-ray powder diffraction analyses from the powdered samples were performed using a Philips diffractometer using CuK$\alpha$ radiation. Sample compositions were determined from chemical analyses performed by Pacific Spectrochemical Analysis Co., Los Angeles, California.

## 3. Microstructure

Scanning electron micrographs are shown in Fig. 2 and from them it is evident that droplet-type phase separation occurred in these glasses. The volume per cent of the dispersed phase for glass Samples 1, 2 and 3 was determined, by a point-counting method, to be 9%, 20%, and 42%, respectively, [8]. X-ray analysis showed total absence of crystallinity from Samples 1 and 2. However, there were traces of a crystalline phase in Sample 3. The chemical durability of the dispersed phase in a 1% HCl solution was found to be poorer than that of the continuous phase. This fact permitted the chemical analysis of the dispersed phase easily and helped to clearly reveal the microstructure of the glass under SEM analysis. The composition of the dispersed phase was deter-

TABLE I Composition and properties of $V_2O_5$–$PbO$–$GeO_2$ glasses

| Sample number | Batch composition (mol%) | Analysed composition (mol%) | Density (gm cm$^{-3}$) | $C$ ratio ($V^{4+}/V_{total}$) |
|---|---|---|---|---|
| 1 | 55 $V_2O_5$–36 PbO–9GeO$_2$ | 57.9 $V_2O_5$–32.4 PbO–9.7 GeO$_2$ | 4.50 | 0.28 |
| 2 | 55 $V_2O_5$–31.5 PbO–13.5 GeO$_2$ | 56.9 $V_2O_5$–29.2 PbO–13.9 GeO$_2$ | 4.33 | 0.31 |
| 3 | 55 $V_2O_5$–27 PbO–18 GeO$_2$ | 56.5 $V_2O_5$–25.1 PbO–18.4 GeO$_2$ | 4.23 | 0.19 |
| 4 | 60 $V_2O_5$–35 PbO–5 GeO$_2$ | – | 4.59 | 0.16 |
| 5 | 34 $V_2O_5$–1 PbO–65 GeO$_2$ | – | 3.54 | 0.56 |

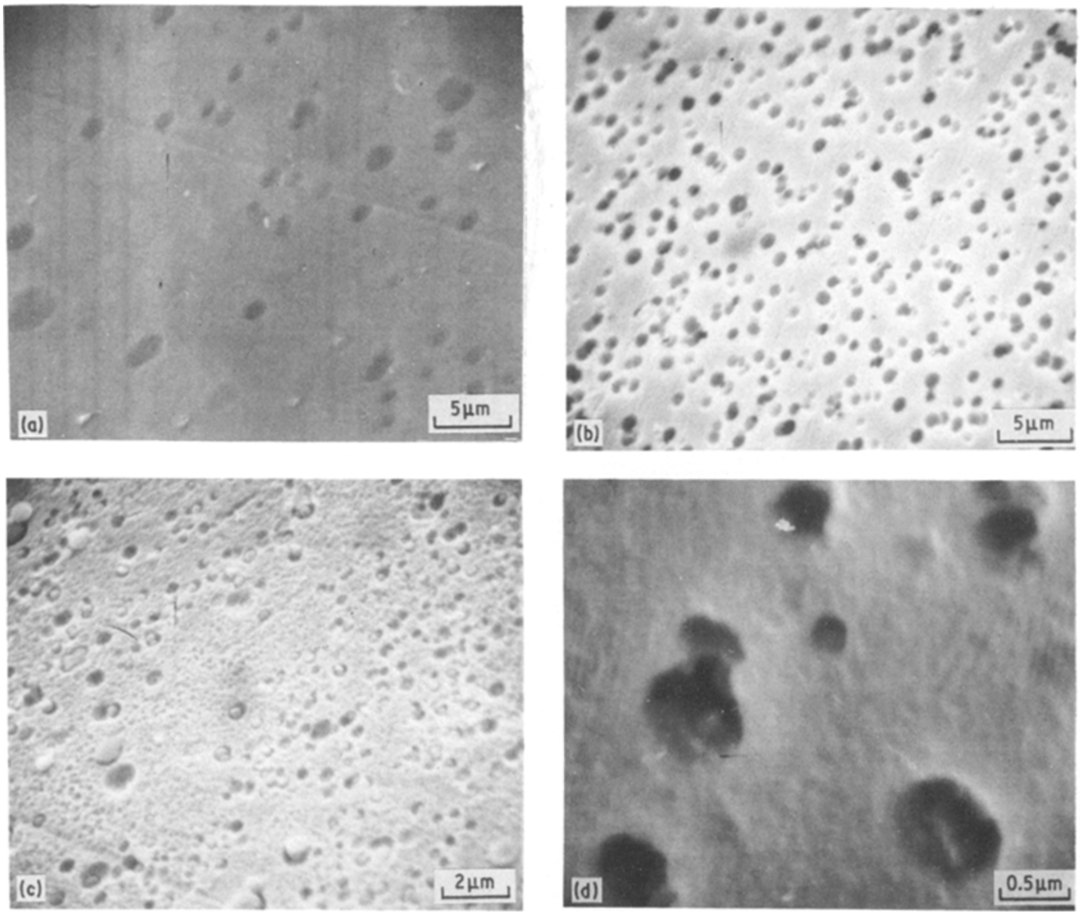

*Figure 2* Scanning electron micrographs of $V_2O_5$–PbO–$GeO_2$ glasses. (a) 55 mol% $V_2O_5$–36 mol% PbO–9 mol% $GeO_2$ system; (b) 55 mol% $V_2O_5$–31.5 mol% PbO–13.5 mol% $GeO_2$ system; (c) 55 mol% $V_2O_5$–27 mol% PbO–18 mol% $GeO_2$ system; (d) the microstructure of the system in (c), shown in greater detail.

mined from a chemical analysis as follows. The glass powder was etched in 1 % HCl solution. The *etchant* was then filtered and evaporated to dryness. The residue was then analysed. The analysis showed that the composition of the residue was close to 34 vol% $V_2O_5$–65 vol% $GeO_2$–1 vol% PbO. The composition of the continuous phase in Sample 2 was deduced from the phase diagram shown in Fig. 1 to be close to 60 vol% $V_2O_5$–5 vol% $GeO_2$–35 vol% PbO. In Sample 3 a second kind of inhomogeneity in the continuous phase can be seen from the high magnification micrograph of the glass shown in Fig. 2. This, however, is not seen in the continuous phases of Samples 1 and 2.

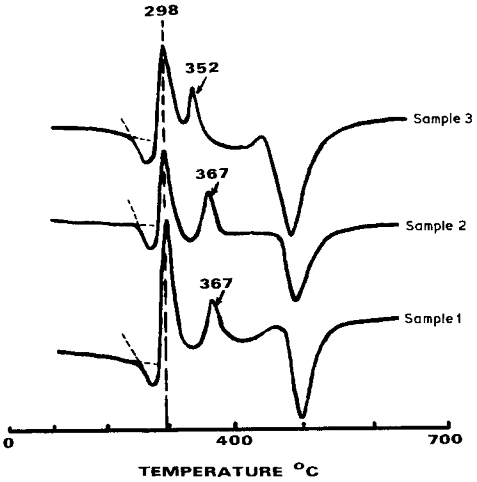

*Figure 3* DTA curves of Samples 1, 2 and 3.

## 4. Differential thermal analysis

The results of differential thermal analysis of Samples 1, 2 and 3 are shown in Fig. 3. All glasses

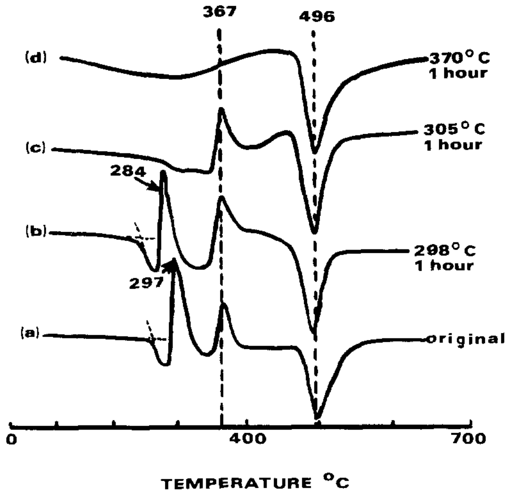

*Figure 4* DTA curves of Sample 2 under a sequence of heat treatment.

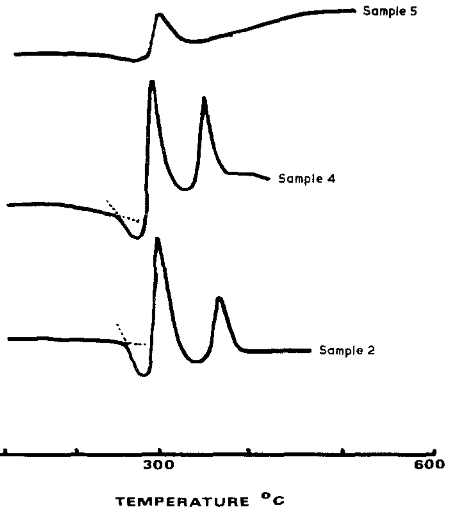

*Figure 5* DTA curves of Samples 2, 4 and 5.

showed two exothermic peaks. The first peak for all three glasses occurred at a temperature of about 298° C. Subsequent X-ray analysis of samples treated at 298° C for one hour showed that this peak was the result of the precipitation of $V_4O_9$ crystals [9]. The second peaks from Samples 1 and 2 were both at about 367° C, whereas that for Sample 3 appeared at a lower temperature of 352° C. X-ray diffraction data from all three samples heat-treated at 370° C were highly complex. It is possible that $2V_2O_5$–6PbO–$GeO_2$ and $V_2O_5$–17PbO–$2GeO_2$ were formed [6]. Fig. 4 shows that DTA results of Sample 2 after undergoing a sequence of heat treatments. It is interesting to note that the treatment of Sample 2 at 298° C for as long as one hour was insufficient to complete crystallization. Curve b in Fig. 4 shows that crystallization occurred at 284° C, probably as a result of enhanced nucleation. After the sample has been heat treated at 305° C for one hour, crystallization was evidently completed, as seen in Fig. 4c. Heat treatment of Sample 2 at 370° C for one hour resulted in complete crystallization as seen from the disappearance of the exothermic peak in Fig. 4d. Fig. 5 shows the DTA results of Samples 2, 4 and 5. Samples 4 and 5 had compositions similar to those of the continuous and dispersed phases of Sample 2, respectively, as described in Section 3. The disappearance of the second exothermic peak for Sample 5 indicated that the second peak for Sample 2 was a consequence solely of the crystallization of the continuous phase. The first peak, then, was the combined effect of both the continuous and dispersed phases. The lowering of the temperature of the second exothermic peak to 352° C for Sample 3 was probably due to the presence of the additional inhomogeneity, as seen in Fig. 2d.

## 5. Electrical Properties

The dependence of the direct current (d.c.) conductivity of $V_2O_5$–PbO–$GeO_2$ glasses on temperature is shown in Fig. 6. Despite the differing PbO/$GeO_2$ ratios in the compositions of Samples 1 and 2, the d.c. conductivities and the activation energies (0.34 eV) for these glasses are not too different. Sample 3, however, has an activation energy of only $0.22 \pm 0.02$ eV. Since the electrical properties of 55 mol% $V_2O_5$–45 mol% $GeO_2$ glass ($C = 0.10$) and 55 mol% $V_2O_5$–45 mol% PbO glass ($C = 0.12$) are almost identical [10] (Fig. 6), the oxides in these glasses, $GeO_2$ and PbO must play similar roles in the hopping conduction. The effect of PbO/$GeO_2$ ratio on the d.c. conductivity of $V_2O_5$-containing glasses could therefore be less important than the effect the equivalent ratio has been observed to have in iron-containing glasses [11, 12]. It would appear that the difference in electrical properties in Sample 3 must be the result of microstructural effects (Fig. 2d) and/or the presence of the crystalline phase.

According to Mott [2, 3] the electrical conductivity, $\sigma$, of semiconducting oxide glasses is given by

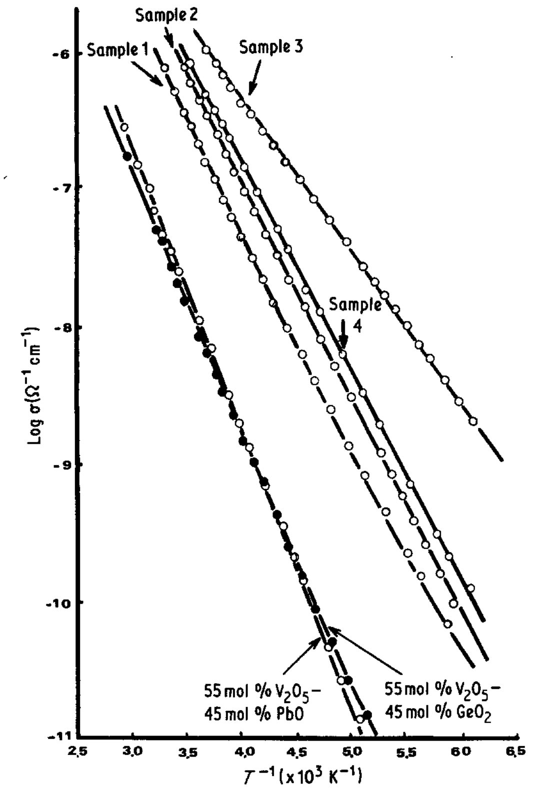

*Figure 6* Plot of log conductivity against $1/T$ for $V_2O_5$–PbO–$GeO_2$ ternary glasses and equivalent plots for $V_2O_5$–PbO and $V_2O_5$–$GeO_2$ glasses.

$$\sigma = \frac{\nu_{\text{ph}} e^2 C(1-C)}{kTR} \exp(-2\alpha R) \exp\left(-\frac{W}{kT}\right), \tag{1}$$

where $\nu_{\text{ph}}$ is the phonon frequency, $e$ is the electronic charge, $\alpha$ is the rate of the wave function decay, $C$ is the ratio of the ion concentration in the low valency state to the total concentration of transition metal ions, $R$ is the average hopping distance, $k$ is the Boltzmann constant, $T$ is the temperature, $W$ is the activation energy given by

$$W = W_{\text{H}} + \tfrac{1}{2} W_{\text{D}}, \tag{2}$$

where $W_{\text{H}}$ is the hopping energy and $W_{\text{D}}$ is the disorder energy arising from the energy difference of neighbours between two hopping sites [13]. A typical value of $W_{\text{D}}$ calculated from theory [2] is approximately 0.1 eV for $V_2O_5$–$P_2O_5$ glasses and usually less than 0.1 eV [13] for other glass systems.

The $W_{\text{H}}$ term can be calculated from theory [3], and is given by

$$W_{\text{H}} = \frac{1}{4} \frac{e^2}{\epsilon_{\text{p}}} \; \frac{1}{\gamma_{\text{p}}} - \frac{1}{R}, \tag{3}$$

where $\epsilon_{\text{p}} = (1/\epsilon_\infty - 1/\epsilon_{\text{s}})^{-1}$ and $\epsilon_{\text{s}}$ and $\epsilon_\infty$ are the static and high frequency dielectric constants of the glass, respectively. $\gamma_{\text{p}}$ is the polaron radius which was found for crystalline solids to be

$$\gamma_{\text{p}} = \tfrac{1}{2}(\pi/6N)^{1/3}, \tag{4}$$

where $N$ is the number of sites per unit volume. $W_{\text{H}}$ can be calculated from Equations 3 and 4, given the approximation $\epsilon_{\text{p}} \simeq \epsilon_\infty = n^2$, where $n$ is the refractive index of the glass. Table II summarizes the calculated $W_{\text{H}}$ values and the important parameters for Samples 1, 2 and 3. Evidently, discrepancies do exist in most glasses between the theoretical $W_{\text{H}}$ values and experimentally determined $W$ values, particularly in the case of Sample 3. It should be noted that Mott's theory was developed from the assumption of a continuous random network in the glass. Special care should be taken when the theory is applied to a glass which has the microstructure shown in Fig. 2.

Equations for the electrical conductivity of heterogeneous crystals have been proposed for a small volume fraction of dispersed phase [14] as well as for a large volume fraction of dispersed phase [15]. In the former case,

$$\sigma = \sigma_1 \frac{\sigma_1(2-2V_2) + \sigma_2(1+2V_2)}{\sigma_1(2+V_2) + \sigma_2(1-V_2)} \tag{5}$$

TABLE II Physical parameters of $V_2O_5$–PbO–$GeO_2$ glasses

| Sample number | $C$ ratio ($V^{4+}/V_{\text{total}}$) | $\sigma_0$ ($\times 10^{-1}\ \Omega^{-1}\ \text{cm}^{-1}$) | $\sigma_{25°\text{C}}$ ($\times 10^{-6}\ \Omega^{-1}\ \text{cm}^{-1}$) | $n$* | $N$ ($\times 10^{22}\ \text{cm}^{-3}$) | $R$ (Å) | $\gamma_{\text{p}}$ (Å) | $W_{\text{H}}$ (eV) | $W$ (eV) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.28 | 6.7 | 0.9 | 2.26 | 1.57 | 4.00 | 1.61 | 0.25 | 0.35 ± 0.02 |
| 2 | 0.31 | 5.8 | 1.7 | 2.17 | 1.56 | 4.01 | 1.62 | 0.26 | 0.33 ± 0.02 |
| 3 | 0.19 | 0.15 | 2.0 | 1.99 | 1.56 | 4.01 | 1.62 | 0.33 | 0.22 ± 0.02 |
| 4 | 0.16 | 5.1 | 2.2 | 2.00 | 1.08 | 3.91 | – | 0.33 | 0.32 ± 0.02 |
| 5 | 0.56 | – | – | – | – | – | – | – | – |

*$n$ is the refractive index for incident wavelength of 3.5 μm.

and

$$\bar{W} = \frac{W_1(1-V_2)\{2(2+V_2)+4\beta(1-V_2)+\beta^2(1+2V_2)\}+9\beta V_2 W_2}{2(2-V_2-V_2^2)+\beta(4+V_2+4V_2^2)+\beta^2(1+V_2-2V_2^2)}\,; \tag{6}$$

in the latter case,

$$\frac{\sigma-\sigma_2}{\sigma_1-\sigma_2}\left(\frac{\sigma_1}{\sigma}\right)^{1/3} = 1-V_2 \tag{7}$$

and

$$\bar{W} = \frac{(1-V_2)\{2\sigma_1^{2/3}W_1+\sigma_1^{2/3}\beta(W_1-3W_2)\}+3\sigma_1^{2/3}\beta W_2}{2\sigma^{2/3}+\sigma_1^{-1/3}\sigma_2}\,, \tag{8}$$

where $\sigma$ and $\bar{W}$ are the d.c. conductivity and activation energy of the heterogeneous glass, respectively, $\sigma_1$ is the d.c. conductivity of the continuous phase, $\sigma_2$ is the d.c. conductivity of the dispersed phase, $V_2$ is the volume fraction of the dispersed phase and $\beta$ is the ratio $\sigma_2/\sigma_1$.

As mentioned earlier, the chemical compositions of the continuous and dispersed phases for Sample 2 have been analysed and found to be 60 vol% $V_2O_5$–5 vol% $GeO_2$–35 vol% PbO and 34 vol% $V_2O_5$–65 vol% $GeO_2$–1 vol% PbO, respectively. Stable glasses of both compositions could be readily made. The d.c. conductivity of 34 vol% $V_2O_5$–65 vol% $GeO_2$–1 vol% PbO glass was too low to be measured. The electrical properties of 60 vol% $V_2O_5$–35 vol% PbO–5 vol% $GeO_2$ glass is shown in Table II. Good agreement of the experimentally determined and theoretically determined values for the activation energies is evident for Sample 4. Applying Equation 5 and Equation 6 to the results for Sample 2, it was found that $\sigma = 0.73\sigma_1$, and $\bar{W} = W_1$. These values are in good agreement with the results shown in Table III.

Although a chemical analysis of the Sample 1 was not performed, the phase diagram in Fig. 1 shows that the compositions of the dispersed phases in Samples 1, 2 and 3 should not be too different. Thus, if it is assumed that the total amount of $GeO_2$ has been formed into the dispersed phase, in each case, with the approximate composition of $V_2O_5$–$2GeO_2$ in all glasses, the calculated compositions for the continuous phase in Samples 1, 2 and 3 would be 59 vol% $V_2O_5$–41 vol% PbO, 60 vol% $V_2O_5$–40 vol% PbO and 63 vol% $V_2O_5$–37 vol% PbO, respectively. Therefore, very similar compositions exist in the continuous phase of Samples 1 and 2. Moreover, the theoretical calculation of the density of Sample 1 from the densities of Samples 4 and 5 agreed quite well with the experimental value (see Table III). Therefore, substituting the results from Samples 4 and 5 and the volume per cent of the dispersed phase in Sample 1 into Equations 5 and 6, it is found that $\sigma = 0.87\sigma_1$, and $\bar{W} = W_1$. This again is in agreement with the results from Sample 1 (see Table III). The slight difference can be attributed to the difference in $C$ values of the continuous phases between Samples 1 and 2 (see Table II).

Sample 3 contained 42 vol% of the discontinuous phase; therefore, Equations 7 and 8 should be used. The calculated results at room temperature for $\sigma$ and $\bar{W}$ are $9.73 \times 10^{-7}\,\Omega^{-1}\,\text{cm}^{-1}$ and 0.15 eV, respectively. Evidently, in this case, agreement between the theory and experimental results is unsatisfactory. The microstructure shown in Fig. 2d clearly indicates the existence of a

TABLE III Comparison of experimental and theoretical results of the physical properties of $V_2O_5$–PbO–$GeO_2$ glasses

| Sample number | Density (gm $cm^{-3}$) | | Conductivity, $\sigma_{25^\circ C}$($\times 10^{-6}\,\Omega^{-1}\,cm^{-1}$) | | $W$ (eV) | |
|---|---|---|---|---|---|---|
| | Experimental | Theoretical | Experimental | Theoretical | Experimental | Theoretical |
| 1 | 4.50 | 4.50 | 0.9 | 2.0 | 0.35 | 0.32 |
| 2 | 4.33 | 4.37 | 1.7 | 1.6 | 0.33 | 0.32 |
| 3 | 4.23 | 4.15 | 3.0 | 0.97 | 0.22 | 0.15 |
| 4 | 4.59 | – | 2.2 | – | 0.32 | – |
| 5 | 3.54 | – | – | – | – | – |

*The theoretical values were calculated from the experimental densities of Samples 4 and 5 and the volume per cent of the dispersed phase in Samples 1, 2 and 3.

second kind of phase separation in the continuous phase of Sample 3. This difference in the microstructure of the continuous phase of Sample 3 from those of Samples 1 and 2 is also reflected in the second exothermic peak of Sample 3 (Fig. 4). As pointed out earlier (see Section 4), the second exothermic peak of Sample 3 (Fig. 4) is due solely to the crystallization of the continuous phase. It is believed that the lowering of the temperature for the second exothermic peak is a consequence of phase separation in the continuous phase of Sample 3.

## 6. Conclusion

$V_2O_5$–PbO–$GeO_2$ glasses containing 55 mol% $V_2O_5$ have been shown to exhibit droplet-type phase separation. The concentration of the dispersed phase increases with increasing $GeO_2$/PbO ratio. The inconsistency of d.c. conductivity measurements with Mott's theory is due to the presence of phase separation. The conductivity is seen to be compatible with Mott's theory if the theories of electrical conductivity for heterogeneous systems developed by Hanai [15] and Dryden *et al.* [16] are applied. When 42 vol% of a dispersed phase exists in $V_2O_5$–PbO–$GeO_2$ glass, a second kind of phase separation from the preliminary crystallization of a vanadium oxide phase can occur, which dramatically alters the conductivity.

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