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Preparation and properties of rapidly quenched glasses in the V_2O_5–PbO system

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Rapidly quenched glassy films in the V_2O_5–PbO system were prepared using a twin-roller type apparatus. The glass formation region was 0–60 mol% PbO. The first crystallization temperature increased from 210 °C for the V_2O_5 glass to 292 °C for the glass of 60 mol% PbO. The metastable unknown phase was first crystallized in the glasses around 50 mol% PbO. Infrared absorption spectra of the glasses were measured. Electrical conductivity of the glasses decreased with increasing of PbO content. The electrical behaviour of the glasses is discussed based on the glass structure estimated from the infrared spectral data.

1. Introduction

Vanadate glasses containing glass-forming oxides, such as P_2O_5 [1], GeO_2 [2], TeO_2 [3], with a wide composition range have been prepared by a normal quenching method and their semiconductivity investigated. The conduction mechanism in the vanadate glasses is based on the electron hopping between V^{5+} and V^{4+} ions. Other vanadate glasses, including glass-modifying oxides such as BaO [4], ZnO [5], with a narrow composition range, have also been obtained by the same method. Pure V_2O_5 glass was first prepared by splat cooling [5]. The application of a rapid quenching technique to binary vanadate systems enabled glasses to be prepared with novel compositions [7]. The rapidly quenched glasses in the V_2O_5–ZnO system were studied in detail [8].

In the V_2O_5–PbO system, five compounds, i.e. PbV_2O_6 [9], $Pb_2V_2O_7$ [10], $Pb_3V_2O_8$ [11], $Pb_4V_2O_9$ [12] and $Pb_8V_2O_{13}$ [13] were reported. The glasses containing about 50 mol% PbO were prepared by a normal quenching method [4, 13]. By a rapid quenching technique, glasses with the compositions of 20 and 50 mol% PbO were obtained [7, 14]. However, the properties of the rapidly quenched glasses in this system have not yet been fully revealed.

In the present work, glasses in the V_2O_5–PbO system were prepared by a twin-roller apparatus. The thermal stability, crystallization process, infrared (IR) spectrum and electrical conductivity were investigated in order to understand basic properties of the quenched glasses. From the viewpoint of glass structure, changes in electrical conductivity with the composition have been explained.

2. Experimental procedure

Reagent-grade V_2O_5 and PbO were used as starting materials. The powder mixtures were fired at 450–600 °C in air, depending on the composition. Five compounds were confirmed to form by solid state reaction. Rapid-quenching treatments were carried out by the apparatus which consisted of a thermal image furnace with a halogen lamp as a light source and metallic twin rollers (50 mm diameter) [15]. The rollers rotated at 3000 r.p.m. and the cooling rate was estimated to be about 10^6 K s^{-1}. The powder samples were pressed into rods (5 mm × 5 mm × 30 mm) and sintered in air. The sintered rods were placed individually into the thermal image furnace and melted at the lower end. The molten droplets fell between the rotating rollers and were quenched. The quenched films were about 20 μm thick.

X-ray diffractometry was used to identify the phases in the as-quenched and heat-treated films. Differential thermal analysis (DTA) and thermogravimetry (TG) measurement was conducted at a heating rate of 10 °C min^{-1} to investigate the thermal behaviour of the quenched films. Infrared absorption spectra between 2000–400 cm^{-1} were measured for the ground films dispersed in a pressed KBr pellet. D.c. electrical conductivity of the as-quenched films was measured in the temperature range 25–300 °C. Evaporated gold electrodes which make good ohmic contacts with vanadate glasses [16] were used. The activation energy for conduction was then calculated.

3. Results and discussion

3.1. The glass-formation region and crystallization process

The compositions are indicated by x in $(1 - x)$ V_2O_5–xPbO. The colour of the as-quenched films changed from dark brown for $x = 0$, through reddish brown to yellow with increasing x. Table I shows the phases existing in the samples before and after rapid-quenching treatment. Amorphous haloes around $2\theta = 25°$–$30°$ (CuK_α) appeared for the films with $x = 0$–0.60, but crystalline phases were contained in the films with $x > 0.60$. The glass-formation region ranged from $x = 0$–0.60 and was slightly wider than $x = 0$–0.50 as in the previous report [7]. In the $(1 - x)V_2O_5$–xZnO or $(1 - x)V_2O_5$–xCdO system,

TABLE I Compositions, phases in the samples before and after quenching and crystallization processes of the quenched samples in the $(1-x)V_2O_5$–xPbO

x	Phase	Phase	Phase transition sequence
	Before quenching	After quenching	
0	V_2O_5	Glass	$(210)^aV_2O_5$
0.20	$V_2O_5 + PbV_2O_6$	Glass	$(241)V_2O_5$ + glass $(375)V_2O_5 + PbV_2O_6$
0.40	$V_2O_5 + PbV_2O_6$	Glass	$(274)A^b$ + glass $(308)A + V_2O_5$ $(360)PbV_2O_6 + V_2O_5$
0.50	PbV_2O_6	Glass	(290)A $(392)PbV_2O_6$
0.60	$PbV_2O_6 + Pb_2V_2O_7$	Glass	$(292)Pb_2V_2O_7$ + glass $(366)Pb_2V_2O_7 + PbV_2O_6$
0.667	$Pb_2V_2O_7$	Glass + $Pb_2V_2O_7$	$(246)Pb_2V_2O_7$

[a] ( ) indicates transition temperature (°C).

[b] A: unknown phase.

glasses with the composition $x = 0.75$ could be obtained [8, 17]. The glass-formation region in the V_2O_5–PbO system was narrower than that in these systems. Zinc or cadmium ions could be partially located in the glass network. However, the lead ion could not be incorporated into the network as much as these ions, because the ionic radius of lead is larger than that of zinc or cadmium.

For all the as-quenched films, no appreciable weight change was detected in the TG measurements. This means that the partial reduction of V^{5+} to V^{4+} during melting took place only to a very small amount. Fig. 1 shows the DTA curves of the glassy films. All the glassy films except for that of $x = 0$ showed a glass transition before crystallization. The first crystallization temperature rose with increasing x, ranging from 210 °C for $x = 0$ to 290 °C for $x = 0.60$. The crystallization processes in the glasses are shown on the right-hand side of Table I. The crystallization processes in the glass with $x = 0$, 0.20 and 0.60 were simple. Crystalline V_2O_5 formed first in the glasses with $x = 0$ and 0.20, and stable PbV_2O_6 appeared at higher temperature in the case of $x = 0.20$. $Pb_2V_2O_7$ was first crystallized and then PbV_2O_6 formed in the glass with $x = 0.60$. On the other hand, the unknown phase (A) was crystallized as a intermediate phase in the glasses with $x = 0.40$ and 0.50. The formation of two metastable phases in the normally quenched samples of $x = 0.50$, has been reported [13]. The X-ray diffraction pattern of the A phase formed in this work agreed with that of one of the reported phases. In the glass with $x = 0.40$, first the A phase and second V_2O_5 were crystallized, and stable PbV_2O_6 formed associated with the disappearance of A phase. Fig. 2 shows the change of the X-ray diffraction pattern for the glass of $x = 0.50$ with heat treatment. The A phase appeared and changed to stable PbV_2O_6. No structural analysis of the A phase has yet been carried out.

3.2. Infrared absorption spectra of crystalline phases and glasses

Infrared absorption measurements have been used in studying the structure of both crystalline and glassy

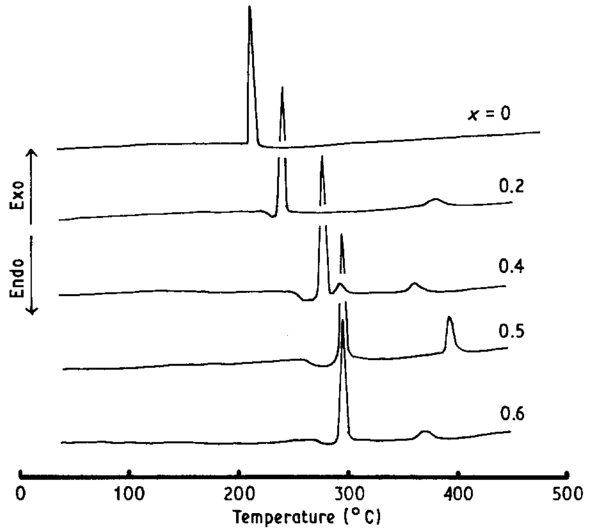

Figure 1 DTA curves of the as-quenched glasses in the $(1-x)$ V_2O_5–xPbO system.

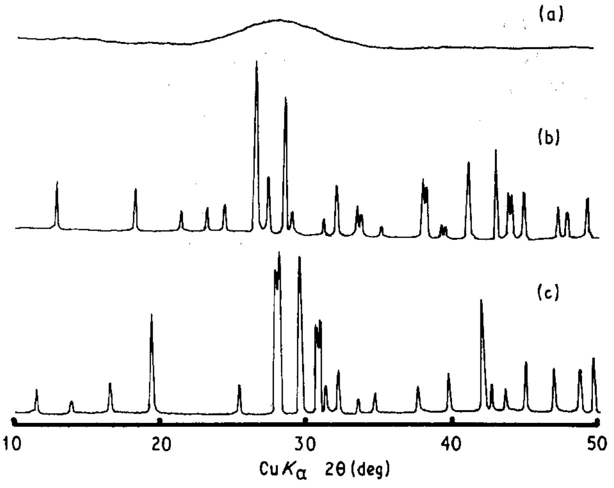

Figure 2 Changes of X-ray diffraction profiles for the glass with $x = 0.50$ on heat treatment: (a) as-quenched glass, (b) unknown A phase after heating to 320 °C, (c) stable PbV_2O_6 after heating to 450 °C.

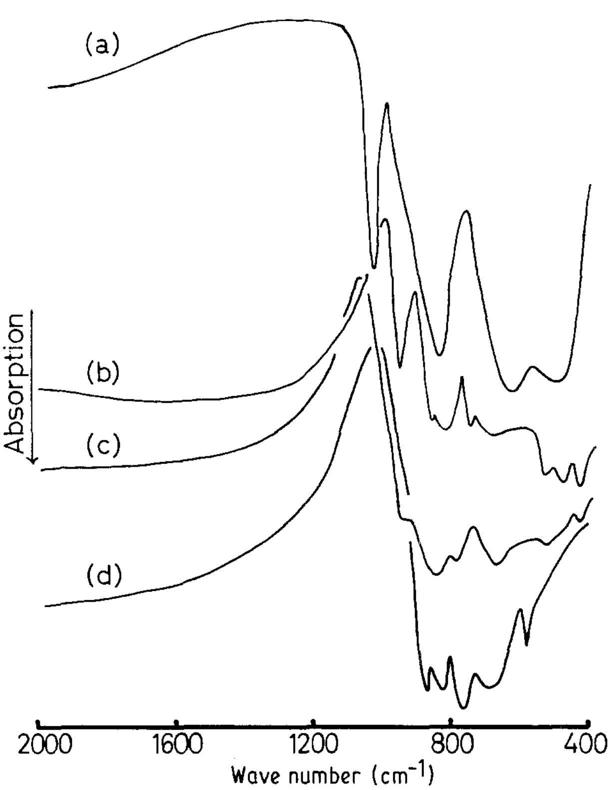

Figure 3 Infrared absorption spectra of crystalline phases: (a) V_2O_5, (b) PbV_2O_6, (c) unknown A phase, (d) $Pb_2V_2O_7$.

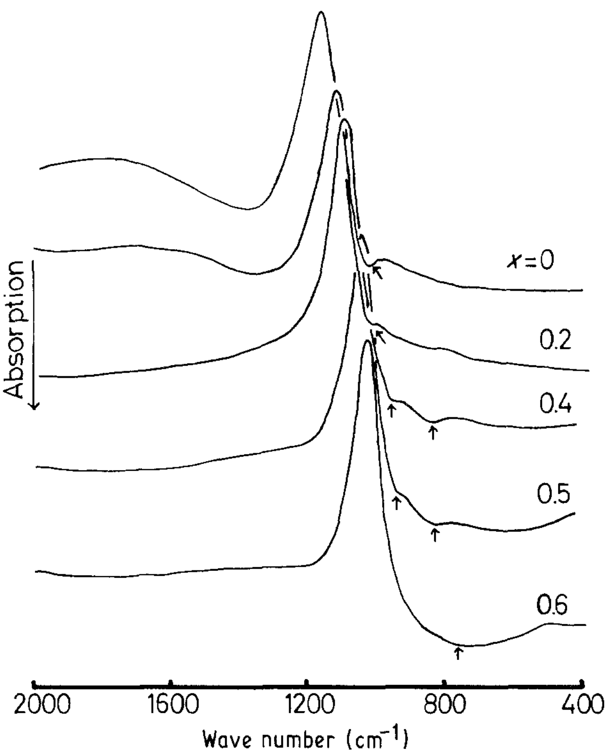

Figure 4 Infrared absorption spectra of the as-quenched glasses in the $(1-x)V_2O_5$–xPbO system.

phases. Fig. 3 shows the infrared absorption spectra of the crystalline phases formed in the crystallization processes. Crystalline V_2O_5 showed four absorption bands at 1020, 830, 620 and 500 cm^{-1}. The sharp band at 1020 cm^{-1} was assigned to the vibration of isolated shorter V–O bonds in VO_5 polyhedra [18]. PbV_2O_6 had a sharp band at 960 cm^{-1} and rather broad bands at 860, 830, 750, 700, 530, 480 and 430 cm^{-1}. The band at 960 cm^{-1} was assigned to the vibration of the rather short V–O bond in VO_5 polyhedra in PbV_2O_6 structure [9]. $Pb_2V_2O_7$ showed bands at 870, 830, 770, 700 and 580 cm^{-1}, which agreed well with the reported value [19]. The spectrum of the unknown A phase was similar to that of PbV_2O_6 rather than $Pb_2V_2O_7$.

Fig. 4 shows the infrared absorption spectra of the quenched glasses. The absorption bands of the glasses were much broader than those of the corresponding crystalline phases. Vanadate glasses had a very transparent band around 1100 cm^{-1} [8, 14]. This band shifted to the lower wave number side with increasing x. The glassy V_2O_5 ($x = 0$) showed a small band at 1020 cm^{-1}. This band was very sharp in the crystalline state (Fig. 3). The VO_5 polyhedra with one short V–O bond remained in the glassy state. With increasing x, this band became weaker and disappeared in the glass with $x = 0.40$. Instead, two new absorption bands, at 960 and 850 cm^{-1}, were observed in the glass with $x = 0.40$ and 0.50. As shown in Fig. 3, PbV_2O_6 and the unknown A phase showed bands at these wave numbers. The lead ion was located between the network consisting of the VO_5 polyhedra as a glass modifier. By the addition of lead ion to the glassy V_2O_5, the coordination around vanadium ions in the glassy state changes from the VO_5 polyhedra, similar to those constructing the layer structure of V_2O_5 with one short V–O bond (0.158 nm), to the VO_5 polyhedra with one slightly longer V–O bond (0.161 nm) in metavanadate PbV_2O_6 [20]. These cause the changes in the absorption band from 1020 cm^{-1} to 960 cm^{-1}. The glass with $x = 0.60$ showed a broad band at 760 cm^{-1}. $Pb_2V_2O_7$ contained the VO_4 tetrahedra-constructing V_2O_7 group and had several absorption bands between 900 and 700 cm^{-1}, as shown in Fig. 3. The spectrum for the glass with $x = 0.60$ showed some similarities to that for $Pb_2V_2O_7$. Corresponding to the structural changes of the crystalline state from the layer type of VO_5 in V_2O_5 through the chain type of VO_5 in PbV_2O_6, to the V_2O_7 group of VO_4 in $Pb_2V_2O_7$, the glass structure of the quenched glass changed with increasing x. The number of continuous V–O–V bonds gradually decreased, according to the structural change in the glasses.

3.3. Electrical conductivity of quenched glasses

Fig. 5 shows the temperature dependence of the d.c. conductivity for the glasses. The conductivity decreased with increasing x. The activation energy for conduction rose from 0.40 eV for the glass with $x = 0$ to 0.92 eV for that with $x = 0.60$. Deviations from the linear relation between $\log \sigma$ and $1/T$ were observed for the low-conductive glasses and attributed to the adsorption of H_2O in air on the surfaces.

In the lead vanadate glasses, as in the case of other vanadate glasses containing glass-modifying ions, the conduction mechanism is based on the electron hopping between V^{5+} and V^{4+} ions through the V–O–V

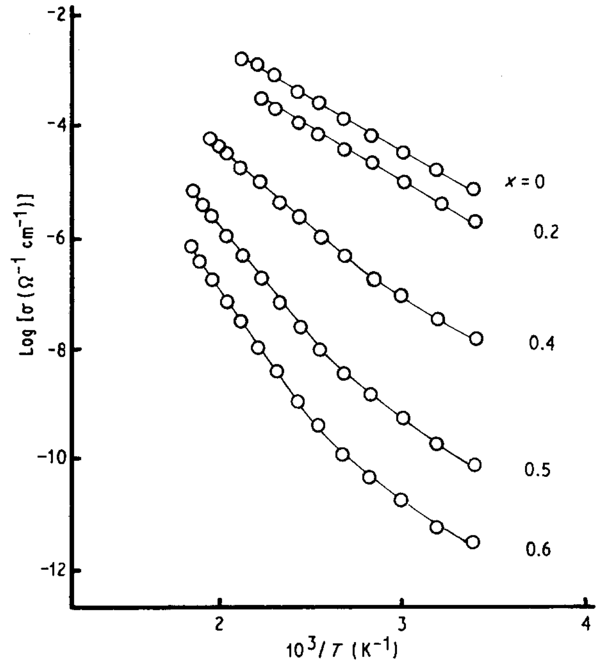

Figure 5 Electrical conductivities of the as-quenched glasses in the $(1-x)V_2O_5$–$xPbO$ system.

bonds in the glass network. The existence of the V^{4+} ion is indispensable for electronic conduction. Although no weight change caused by the re-oxidation of V^{4+} to V^{5+} ion was detected in the TG measurements, a certain number of V^{4+} ions must exist in the glasses. The drop in the conductivity on the addition of PbO became much larger for glasses with $x > 0.40$. This behaviour corresponds to the infrared spectral data which indicate that the network structure of V_2O_5 glass remains in the glasses up to $x = 0.20$ and then changes through the metavanadate type to the pyrovanadate type with increasing x. In addition to the decrease in the number of vanadium ions, the reduction in the number of continuous V–O–V bonds in the glass for the conduction path causes a large fall in the conductivity in the glass with $x > 0.40$.

4. Conclusion

The glasses with $x = 0$–0.60 in the $(1-x)V_2O_5$–$xPbO$ system, which had a wider composition range than that reported, were prepared by a twin-roller quenching method. The thermal stability of the glasses increased with increasing PbO content. A metastable unknown phase formed as an intermediate phase in the crystallization process of the glasses with $x = 0.40$ and 0.60. Lead ions were located between the glass network as a glass modifier. The electrical conductivity of the glasses was lowered with increasing x. This behaviour has been explained on the basis of the glass structure estimated from the infrared spectral data.

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