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Two-Liquid Phase Structure of Photoconducting Oxide Glasses

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An electron microscopic study of a series of photoconducting oxide glasses in the systems $CdO/B_2O_3/SiO_2$, $CdO/B_2O_3/GeO_2$ and $PbO/Al_2O_3/SiO_2$, has shown the essential diphasic nature of these materials. The samples were examined by replica techniques, in transmission and by scanning electron microscopy. Two-liquid features have been identified, as has very fine-scale crystallisation, both on the basis of textures of fracture surfaces and of electron diffraction patterns. Physical models proposed to explain the electronic properties of glasses such as these must take account of this obvious two-phase nature of such materials.

1. Introduction

Recently Strickler and Roy [1] have described a new family of glassy oxide photoconductors containing no variable valence ions, chiefly in the system $CdO/B_2O_3/SiO_2$ and its obvious modifications. As part of that study, experiments were designed to attempt to crystallise from the glass a finely dispersed pre-selected photoconducting phase. Furthermore, it was imperative to study the structure of the new glasses in as great detail as possible in order to understand the crystallochemical basis for the existence of the photoconductivity.

It has become increasingly clear during the last several years that the structure of many glasses cannot be described simply by a consideration of the disposition of the first three or four shells of nearest neighbours. The common development of metastable liquid-immiscibility in the cooling of many (if not most) glasses is being increasingly recognised. In 1960, Roy [2] first explained the structure and the step-wise crystallisation [3] of the prototype glass-ceramic compositions by invoking the existence of two metastable liquids in the cooled glass or its "nucleated" state. This hypothesis has now been amply confirmed in dozens of papers e.g. [4, 5]. Furthermore, Phillips and Roy [6] were able to show that the "glass-ceramic" effect (finely dispersed bulk crystallisation) could be achieved in a wide variety of systems merely by selecting compositions bordering any primary phase field of two immiscible liquids.

The present study was, therefore, concerned with a detailed electron microscopic study of the structure of photoconducting glasses in the systems $CdO/B_2O_3/SiO_2$, $PbO/Al_2O_3/SiO_2$, $CdO/B_2O_3/GeO_2$, which could be reasonably expected to show possible two-phase separation, and also metastable crystallisation of specific phases with compositions rather far from the specific bulk composition.

2. Experimental

A large number of glasses were prepared in the systems $PbO/Al_2O_3/SiO_2$ [1], as well as $CdO/B_2O_3/SiO_2$ [1] with some additions [7], and $CdO/B_2O_3/GeO_2$ [7]. The components were homogenised by mixing in a Spex mill for 20 min. The glasses were melted in open platinum crucibles at temperatures about 100° above the melting point of the composition. Melts were homogenised by quenching in distilled water and remelting, before finally repouring and annealing. In some cases opalescence due to crystallisation appeared. Some compositions obviously crystallised after pouring, though the area of crystallisation was often localised on the surface of the glass. In most cases the crystalline material was a complex of unknown phases which could

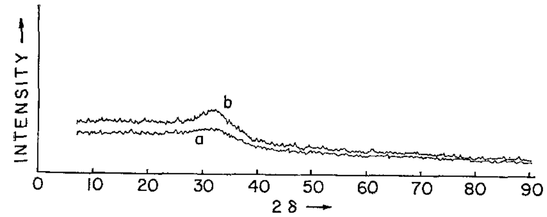
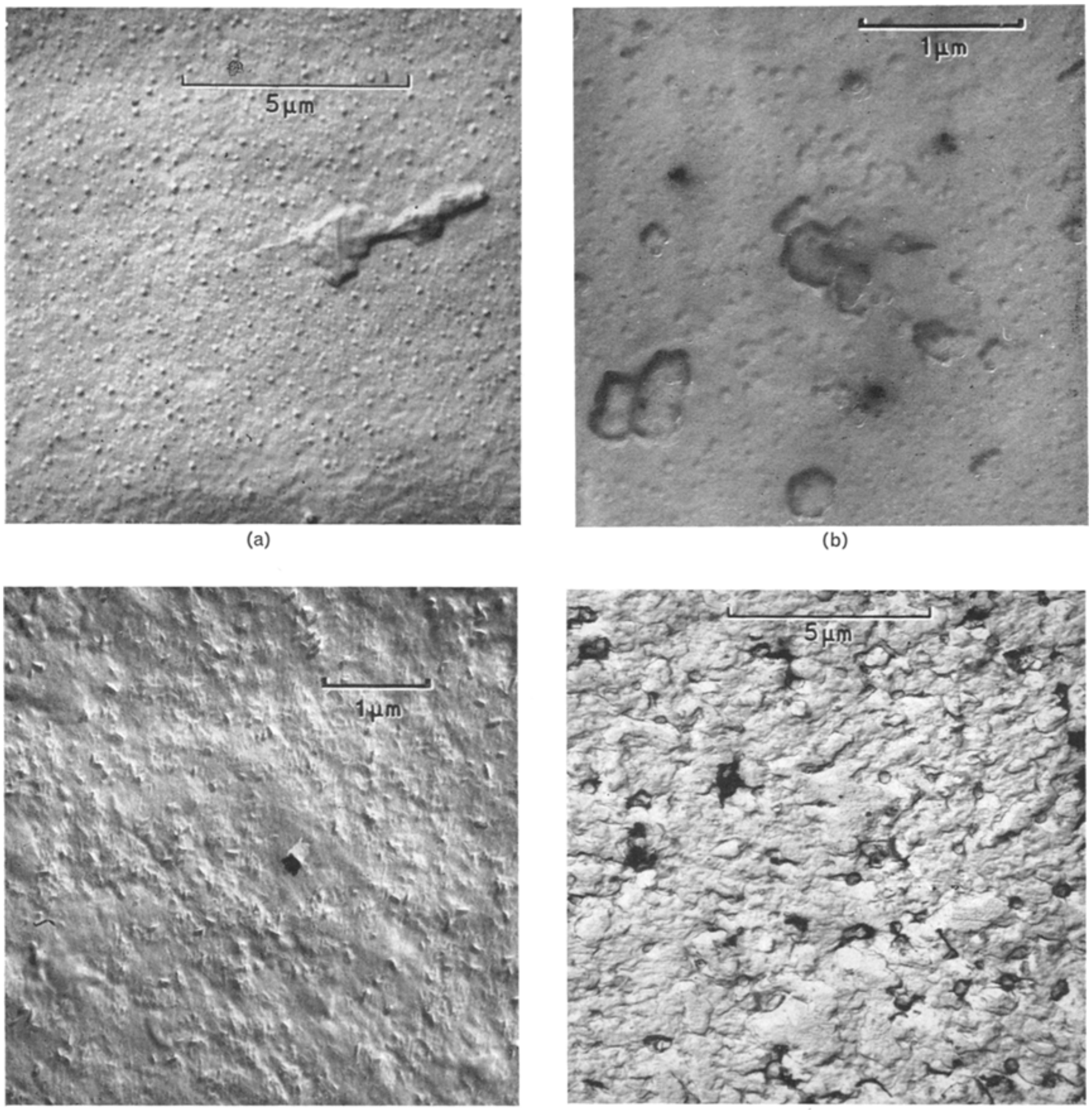


Figure 1 Automatically recorded diffraction pattern of: (a) 66.4% CdO/19.1% B_2O_3/14.5% SiO_2 glass powder; (b) 66.4% CdO/19.1% B_2O_3/14.5% GeO_2 glass powder. Filtered copper radiation.

not be identified. Optical microscopy, X-ray, and electron diffraction were used to check for crystals in these glasses. Fig. 1 shows a typical X-ray powder pattern of the $CdO/B_2O_3/SiO_2$ and $CdO/B_2O_3/GeO_2$ glasses.

The electron microscopy studies involved two techniques. Most of the work was done using single step platinum-shadowed carbon replicas. Samples were fractured in air or vacuum and replicated, or they were etched in HF or HNO_3 fumes and replicated. The second



(a) (b)

(c) (d)

Figure 2 Electron micrographs of samples of 70% PbO/5% Al_2O_3/25% SiO_2 crystallised for various lengths of time: (a) 0 h, glassy; (b) $\frac{1}{2}$ h, 450° C; (c) 1 h, 450° C; (d) 2 h, 450° C. All these electron micrographs are platinum shadowed carbon replicas of fresh fractured surfaces that were etched 10 sec in HF fumes.

technique consisted merely of grinding the glass and making observations of thin edges of fragments in transmission.

The scanning electron microscope was also used. Since this instrument requires a "rough" surface, the samples were extensively etched in HF before examination.

3. Results

From the range of compositions prepared in these systems [1, 7] three were selected as representative, as each of these compositions shows a phase separation and a tendency to crystallise when subjected to the proper experimental cycle. Glasses of these three compositions are described below (compositions given in mole per cent).

3.1. 70.0% Pb/5.0% Al_2O_3/25.0% SiO_2 Glass

This glass crystallises easily when heated in the 450 to 650° C temperature range. At temperatures below 500° C orthorhombic PbO precipitated while at higher temperatures (above 500° C) a mixture of orthorhombic and tetragonal PbO precipitated, as shown from the X-ray patterns of the partially crystallised glass. Typical electron micrographs of this composition glass are given in fig. 2. which shows unambiguously the presence of two phases which, since the material shows no evidence for Bragg diffraction, must be glassy. The development of the PbO crystals, as this glass crystallises, is clearly visible.

3.2. 66.4% CdO/19.1% B_2O_3/14.5% SiO_2 Glass

A high rate of quenching was necessary to avoid crystallisation of these glasses. A typical X-ray diffraction pattern of this composition glass has been shown in fig. 1 and clearly shows no crystallinity. An electron micrograph of one of these glasses is shown in fig. 3, and a scanning electron micrograph in fig. 4. Here again the unmixed-glassy structure is obvious, and is well confirmed in the SEM picture. The long periodicity ripple is a fracture pattern, but the finer scale structure is quite similar to that seen in the replica. Under special conditions, when $Cd(NO_3)_2$ partially replaced CdO in the initial composition mixture and such a glass was quenched in air and slowly annealed from 600° to room temperature to effect initial crystallisation, selected area diffraction patterns showed the three major diffraction maxima of CdO as very faint rings. However, more commonly (when major crystallisation occurred in these glasses) only yellow or white clusters of crystals of unknown composition and low symmetry could be found. As in the case of the glasses containing PbO, only by separation of a second glassy phase very rich in cadmium could the CdO crystallise out metastably from such compositions.

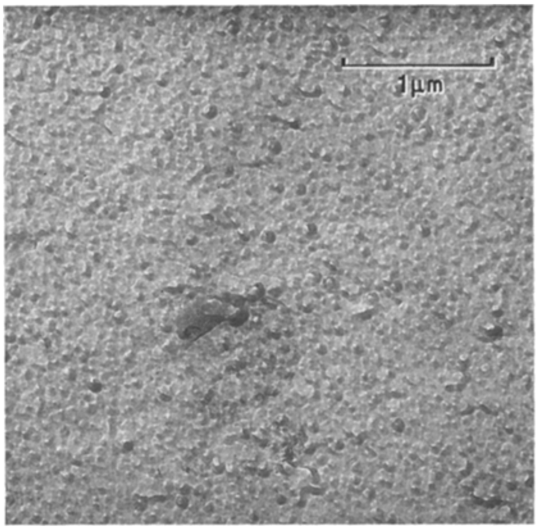


Figure 3 Carbon/platinum replica of vacuum-fractured 66.4% CdO/19.1% B_2O_3/14.5% SiO_2 glass showing phase separation.

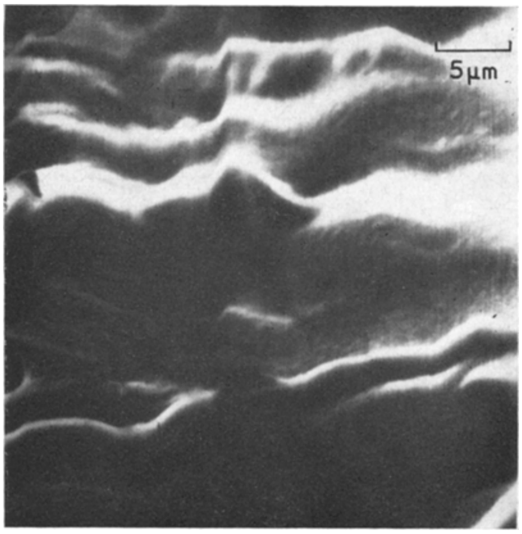


Figure 4 Scanning electron micrographs of the 66.4% CdO/19.1% B_2O_3/14.5% SiO_2 glass surface intensively etched in HF.

3.3. 65% CdO/19.1% B_2O_3/14.5% SiO_2/1.4% SnO_2 Glass

The glass of this composition always contained a milky-white fine dispersion of crystals which were identified by X-ray diffraction as SnO_2, rutile-structure, phase. Fig. 5 shows a typical electron micrograph of the knee-twin of the discrete SnO_2 crystals precipitated from this glass composition when annealed at 500° C in air for 1 h and then cooled slowly to room temperature.

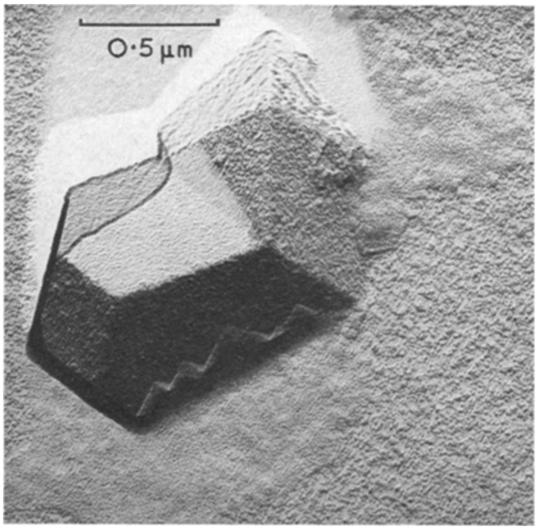


Figure 5 Carbon/platinum replica of fresh-fractured surface of 65% CdO/19.1% B_2O_3/14.5% SiO_2/1.4% SnO_2 glass showing crystals of SnO_2.

3.4. 66.4% CdO/19.1% B_2O_3/14.5% GeO_2 Glass

It is difficult to prepare a glass of this composition even by quenching the melt in water. An X-ray pattern of a successfully quenched glass is given in fig. 1. An electron micrograph of the same glass is shown in fig. 6 and a scanning electron micrograph is shown in fig. 7. Again the pronounced diphasic nature is clearly brought out. Evidently there are here two interpenetrating and interlacing phases, one of which is no doubt much richer in CdO.

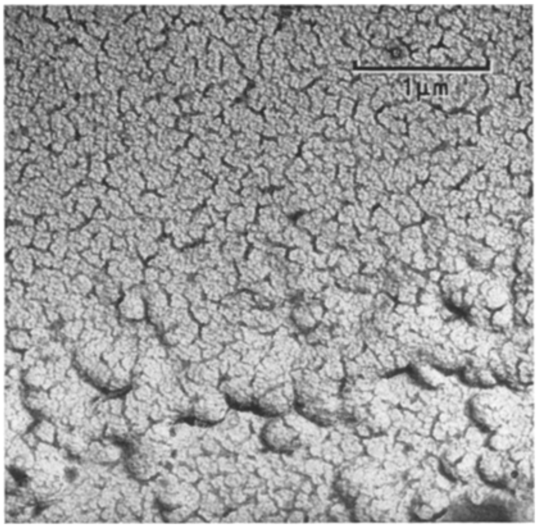


Figure 6 Carbon/platinum replica of fresh fractured surfaces of 66.4% CdO/19.1% B_2O_3/14.5% GeO_2 glass showing phase separation, and probable two-liquid structure. Vacuum-fractured samples showed an identical appearance.

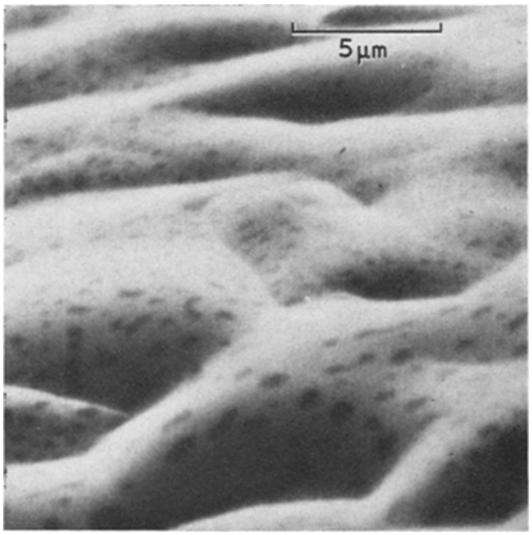


Figure 7 Scanning electron micrograph of the 66.4% CdO/19.1% B_2O_3/14.5% GeO_2 glass surface intensively etched in HF.

4. Discussion

4.1. Electron Microscopy

It is commonly difficult to distinguish between simple differences of scale and real texture differences in replicas of etched and unetched glasses. However, most differences in surface structure appear to be simply in scale, within a single glass type (see figs. 8 and 9). We do not attribute this difference to a chemical inhomogeneity in the glass. These two micrographs are of different areas in the same sample; the scale differences are caused by gradients in quenching rate across the sample. HNO_3-etched samples appeared very similar, distinguished only by less sharply defined interphase contacts.

The small scale roughness is undoubtedly indicative of a phase separation, and is commonly on a minimum scale of about 100 Å in unetched samples. In some samples there appear in fact to be two size groups, one being the individual separated phases, the other possibly being aggregates of these smaller particles or even a third immiscible phase (see fig. 8). Vacuum fracturing produces no real difference from fracturing in air. Several of the samples show some large dendrites on the surfaces. It is not known whether these dendrites are atmospheric etch products or if they formed during the heat treating of the samples.

4.2. Electron Diffraction

All $CdO/B_2O_3/SiO_2$ and $CdO/B_2O_3/GeO_2$ samples, no matter what the heat treatment or the composition, gave the typical diffraction pattern consisting of one diffuse halo, centered at about 2.8 Å.

Some samples gave scattered single-crystal patterns, the *d* spacings of which are given in table I. These appear to be related to the diffuse powder patterns mentioned above, in that strong spots closely coincide with the diffuse ring at 2.8 Å. In these cases other powder rings also appear at approximately 2.1 Å and 1.15 Å.

TABLE I Single crystal spots obtained in transmission electron diffraction studies of glasses.

$CdO/B_2O_3/GeO_2$ *d* spacings (Å)			$CdO/B_2O_3/SiO_2$ *d* spacings (Å)			
2.84	2.88	2.77	2.77	2.81	2.80	2.77
2.01		2.09	2.09		2.02	2.11
	1.72					
		1.15	1.17		1.15	1.13
1.01						

Note Small randomly oriented particles cause patterns to be quite diffuse and imperfect; therefore, measurement precise only to + 2%.

Thus while it is obvious that the unmixed-glass structure dominates the "macro" structure of the glass, the nature of the short range (first few spheres of co-ordination) order in each or both the glasses is still unknown. The occasional formation of small crystals of CdO within the cadmium-rich glass is to be expected, but how the glass structure is related to that of CdO is difficult to determine, although the resemblance within a short range is mandatory.

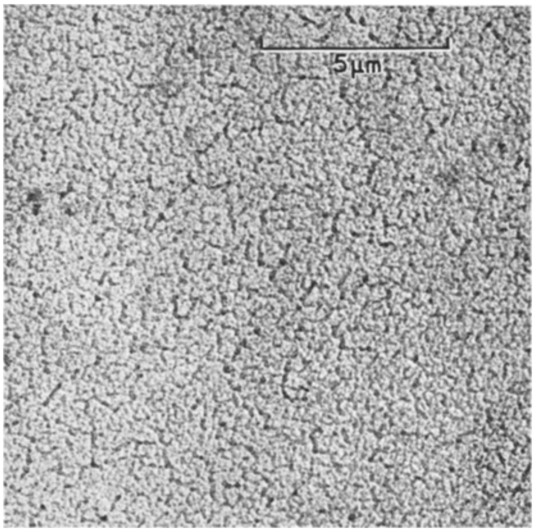


Figure 8 Carbon/platinum replica of HF-etched 66.4% CdO/19.1% B_2O_3/14.5% GeO_2 glass fracture surface, showing probable two-liquid structure.

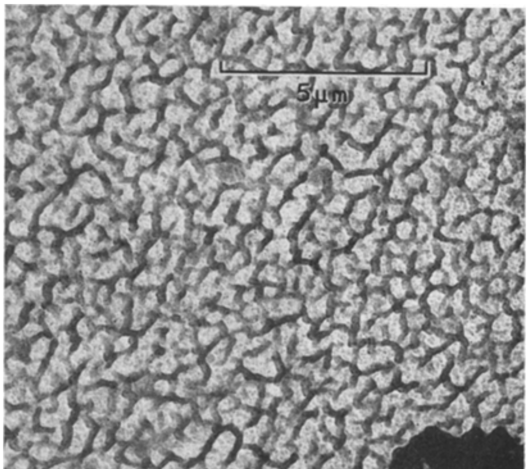


Figure 9 As fig. 8 showing identical texture and gross difference in scale of 66.4% CdO/19.1% B_2O_3/14.5% GeO_2 glass surface.

5. Conclusions

The importance of the demonstration of the possible diphasic nature of these glasses cannot be exaggerated. Physical models proposed to explain the electronic properties of glasses, commonly include an orderly structural bias inherited from the crystalline forbears, and even more generally assume an orderly compositional distribution. Such models are now seen to be inapplicable in this particular case. Moreover, suspicion is cast on all models explaining electronic conduction of glasses where the possibility of metastable two-liquid phase structures have been neglected.

Acknowledgement

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