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A New Family of Photoconducting Oxide Glassy Materials

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By a systematic variation of the crystal-chemical parameters, we have found a new family of photoconducting materials that are glassy oxides containing no variable valency ions. The "best" compositions group around the general formula 65 MO-20 R_2O_3-15 XO_2. Electronic conduction and near-ohmic behaviour are established. The spectral response shows a peak at 380 nm corresponding to the absorption edge of the glass. Very small (~10 ppm) concentrations of impurities nearly destroy the photo effects. A conduction model based on Goodenough's d-orbital overlap is presented to account for the data.

1. Introduction

1.1. Relevant Literature

Many authors [1-4] have established the existence of electronic conduction in glasses containing a variable valency ion, but to date no oxide glasses containing ions with only one stable oxidation state have been proven to be electronic conductors. The question of electronic conduction in these glasses is of considerable importance from both theoretical and applied points of view, for electronic conduction cannot occur by the hopping mechanism.

Most of the previous work on electronic conduction in oxide glasses is based on the system V_2O_5-P_2O_5 with various additions. Such glasses have been established as electronic conductors by 1) nonpolarisation in a d.c. field and 2) no EMF when the glasses are used as an electrolyte in a galvanic cell.

Lambert [5] has pointed out the importance of space-charged-limited currents (SCLC) in insulators and discussed these SCLC in detail. Such currents are characterised by a nonlinear variation of the current with voltage; i.e., $I \alpha V^n$ where n is greater than one.

Most semiconductors exhibit photoconductivity and this property has been extensively studied in these materials. Bube [6] presented a general review of photoconductivity as well as results on the materials aspect of photoconducting insulators – all of them crystalline. Sharma and Rieckhoff [7] studied photoconduction of quartz, fused silica and sodium silicate glass with a Q-switching laser. They explain their results by multiphoton interaction.

In this study we have attempted to design and prepare photoconducting, noncrystalline, oxide solids. This could lead to a whole new family of particularly useful materials, and also establish the presence of electronic conduction in oxide glasses containing no variable valency ions.

2. Experimental Procedure

2.1. Preparation of Glasses

Details of the experimental procedure are given in the dissertation [8] and hence only special points will be raised here.

Since relatively large quantities of glass were needed to equilibrate and modify the glass, conventional glass-making processes have been used. The "reagent grade", or better, components were mixed, melted in air in platinum crucibles, fritted twice in deionised water and finally poured. The glasses were then annealed from the approximate strain point to room temperature in about four hours. A typical spectrographic analysis of a 65 CdO-20 B_2O_3-15 SiO_2 glass is given in table I.

TABLE I Typical spectrochemical analysis of a 65 CdO-20 B_2O_3-15 SiO_2 glass.

Major elements (> 1%)	Cd, B, Si
Minor elements (1.0 to 0.01 %)	None
Trace elements (.01% to 10 P)	Mg
Not detected (< 10 PM)	V, Ti, Ge, Co, Ni, Pt, Mo

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Systematic variations of M, R and X glass compositions included the ions shown in table II(a). It is interesting to note that various glasses containing high concentrations of HgO were prepared for the first time. Mercury-rich glasses cannot be melted in air since the HgO evaporates, hence these glasses were made by sealing the glass components in platinum capsules and melting them under hydrostatic nitrogen pressures of about 2500 psi. Due to the release of oxygen by dissociation of HgO, this results in an effective oxygen pressure of 2500 psi, repressing further dissociation. Some of the glasses were equilibrated with different oxygen activities by bubbling gases or gas mixtures with controlled oxygen fugacities through the melt. This is the only method which allows one to make "large" quantities of glass corresponding to different controlled oxidation conditions in a reasonable time (see Nair, White and Roy [9]).

Since all of the glasses prepared in this work were transparent in the visible, every sample was examined microscopically. X-ray diffraction was also used to determine crystalline species in the partially crystallised glasses.

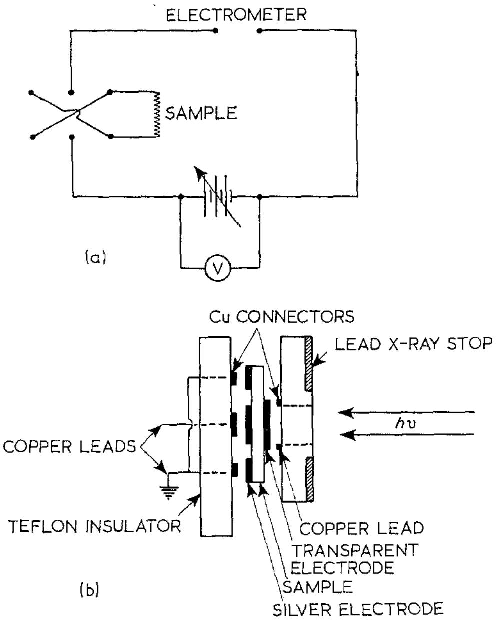

Figure 1 Schematic diagram of the measuring circuit (*a*) and sample holder (*b*) used in this study.

2.2. Electrical Measurements

The electrical measurements were made in a shielded, light-tight box using a guarded, two-electrode, d.c. method. Fig. 1 shows the sample holder and a schematic diagram of the measuring circuit. The current through the sample was reversed and two readings always agreed within 10%. The back electrode was a silver paint air dried at 100°C while the transparent electrode was a water soluble polyvinyl quaternary amine*. In several cases an evaporated gold film was used for the transparent electrode. The transmission qualities of these two films are compared in fig. 2. For general photoconductivity measurements a mercury lamp was used, while for the spectral sensitivity and other special measurements a xenon high intensity lamp was used. The intensities of both lamps were calibrated using a standardised thermopile. A shutter on the light-tight box controlled the exposure of the samples to the light. Glass samples used for the electrical measurements were ground to a thickness of 1.0 to 1.5 mm and one surface was polished with 3 μm diamond paste. The surfaces were carefully cleaned in warm soapy water, rinsed with deionised water and finally rinsed with acetone before applying the electrodes.

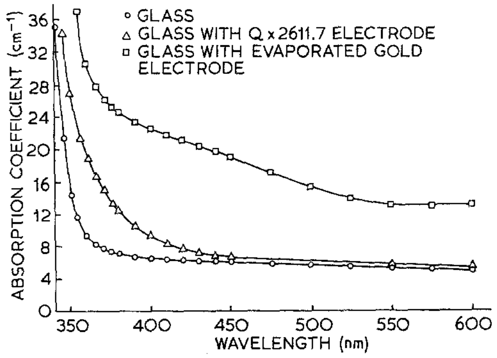

Figure 2 Effect of the transparent electrode on the optical transmission of 65 CdO-20 B_2O_3-15 SiO_2 glass.

The reproducibility of the electrical measurements was about ± 50% which included errors in the area of the electrodes, instrumental errors (± 1 VDC and ± 0.02 decade for the current measurement), light intensity and surface perfection of the samples.

Absorption spectra in the range 200 to 3500 nm were measured on a Beckman DK-2 spectrophotometer.

*Dow Chemical QX 2611.7

3. Results

3.1. Systems Studied

The principal ideas underlying the selection of compositions were derived from Goodenough's [10] hypothesis of narrow d-band conduction in certain metal oxides. This argument requires that a very high concentration of the cations be present in as low a co-ordination as possible. Therefore, only systems capable of yielding glasses with a high concentration of heavy metal oxides were considered. The systems studied are listed in Table II and the pertinent electrical data are given in table II (b). The survey was intended to uncover not only the *existence* of photoconduction, but also the trends in these properties as a function of the basic crystal-chemical parameters. Of the systems studied, glasses containing PbO and CdO gave by far the highest photocurrents with the CdO-containing glasses being much higher than the PbO analog.

TABLE II (a) Summary of systematic variations in compositions.

Ion substituted in M site	R site	X-site
Sn	Al	Si
Cd	Bi	Ge
Hg	B	
Pb		

TABLE II (b) Summary of electrical properties in selected systems.

Systems	Maximum mole % heavy metal oxide in glass	Remarks
PbO-Bi_2O_3-SiO_2	85 (PbO + Bi_2O_3)	Very weakly photoconductive
PbO-B_2O_3-SiO_2	70	Very weakly photoconductive
PbO-Al_2O_3-SiO_2	70	Very weakly photoconductive
SnO-B_2O_3-SiO_2	—	Could not form glasses with SnO content > 50%
HgO-B_2O_3-SiO_2	~ 65	Can be melted in sealed containers under hydrostatic pressure. Not photoconductive
CdO-B_2O_3-SiO_2	65	High photocurrents
CdO-B_2O_3-GeO_2	55	High photocurrents
PbO-B_2O_3-GeO_2	55	Not photoconductive

3.2. Electrical Properties

The first issue concerning the data is to decide between electronic and ionic conduction mechanisms in the glasses. Most oxide glasses are ionic conductors with the alkali metal ions carrying the currents. Ionic conduction is characterised by a decreasing current with time under a constant d.c. field, best explained by transport of the mobile ions away from one electrode leaving a high resistivity barrier. Conversely electronic conduction should show no current decay with time under a constant d.c. field. Several glasses were subjected to a d.c. field of 10^3 V/cm for up to 15 hours with the currents showing no change. The very flat curves in fig. 3 demonstrate that the glasses are indeed electronic conductors.

In electrical studies on insulators the question of ohmic or SCLC conduction must also be considered. The most common method of deciding between these two types of conduction is to study the current-voltage characteristics. Current-voltage curves were run on all of the samples prepared in this work. Some typical curves are presented in fig. 4. These curves show a linear relation between the current and voltage characteristic of ohmic behaviour.

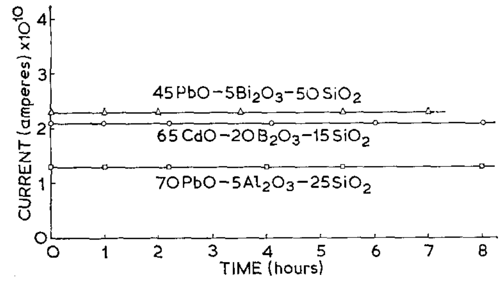

Figure 3 The change in d-c dark currents with time for several glasses.

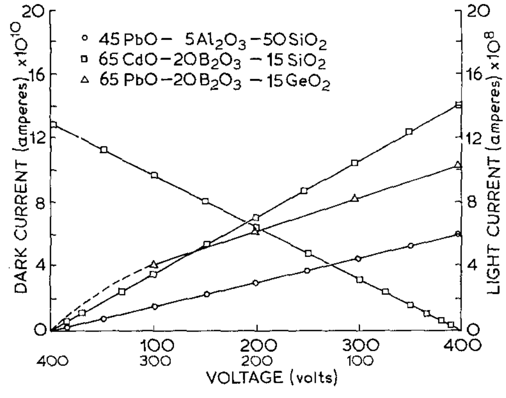

Figure 4 Current-voltage curves for several glasses.

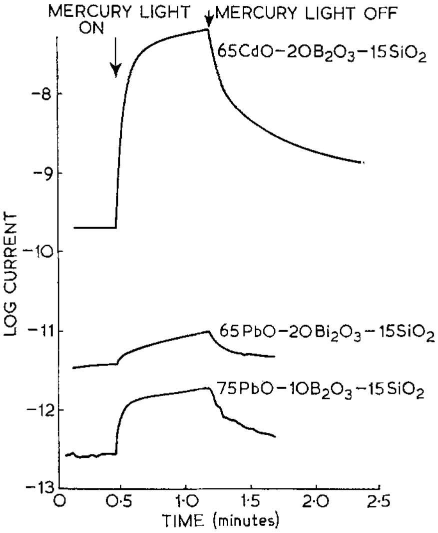

Figure 5 Photocurrents of several glasses.

Another important characterisation of photoconductors is their spectral sensitivity, the number of electron-hole pairs generated by one photon as a function of wave length. These measurements were made using a grating monochromator in conjunction with a high intensity xenon lamp to measure the photocurrent as a function of wave length. The results obtained for several glasses are shown in fig. 6, and one notes a sharp peak in the photoresponse at about 360 nm. This can generally be related to the absorption edge of the glass as can be seen by comparing these data with the optical absorption curves of the glasses shown in fig. 7.

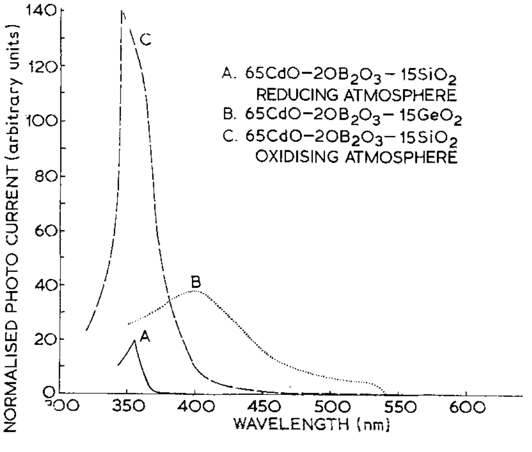

Figure 6 Spectral response of several glasses.

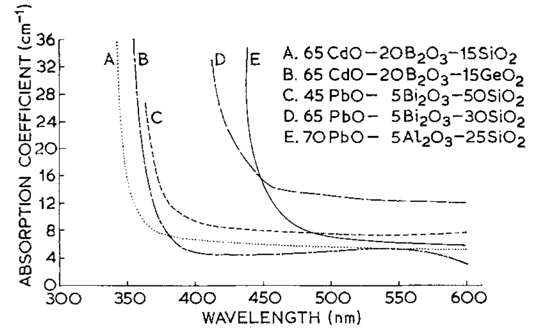

Figure 7 Absorption curves of several glasses.

3.3. Importance of High Purity of the Glasses

Since it was hypothesised that changing the ratios of two valence states in the glass could affect the electrical properties, a detailed study of the influence of the redox condition of the glass (changing the oxygen partial pressure from 1 to 10^{-10} atm.) was made. A measurable but very small effect was noted on the photocurrents. The results of these controlled atmosphere studies are summarised in fig. 8 and will be discussed in greater detail later.

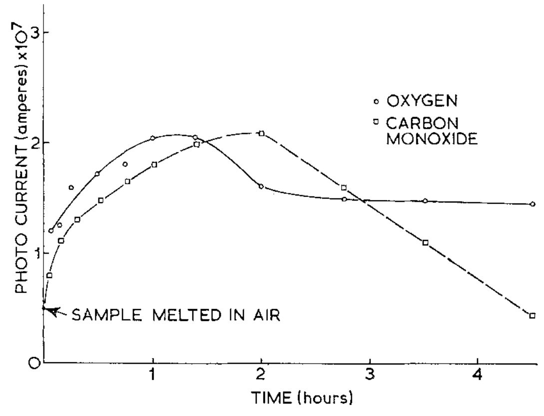

Figure 8 Effect of time gases were bubbled through the glasses on the photocurrents.

Perhaps the most important general finding of the study was that we established that impurity levels in the range of 1 to 10 PPM of 3 d ions quench all photostimulated currents. It had been noted that with one lot of CdO we were unable to find any photoconductivity in the glasses. Spectrographic analysis of this lot of CdO showed 0.1 to 0.01 % Fe as the only difference between this and the other lots of CdO. To establish the role of Fe, we added Fe_2O_3 to glasses made from the high purity components. At a concentration of 100 PPM Fe_2O_3, the absorption curve of the Fe-containing glass cannot be distinguished from that of the pure glass. In this series of glasses only the glass with the 10 PPM of Fe_2O_3 addition still showed any measurable photocurrents and it was at least one order of magnitude lower than that for the pure glass. These results are summarised in table III. Analogous experiments where Ni, Cu, Mn and Co were added gave the same results.

TABLE III Effect of Fe_2O_3 concentration on the photocurrents in a 65 CdO-20 B_2O_3-15 SiO_2 glass. Experimental conditions: sandwich cell, 100 VDC across sample, 4×10^{15} eV per cm^2 sec illumination, sample thickness 1.0 to 1.2 mm.

Weight % Fe_2O_3	Dark current (Amperes)	Ratio of light to dark current
1.0	1.2×10^{-10}	1.0
0.1	2.0×10^{-10}	1.0
0.01	2.1×10^{-10}	1.0
0.001	1.8×10^{-10}	5.0

3.4. Structure of the Glasses

The atomic level structure of glasses containing very high percentages of "heavy" metal atoms has been of considerable interest for several decades. Whether the Pb^{2+} (for instance in high lead glasses) is a "modifier" (high c.n.) or a glass-former (4 c.n. or lower) is of great importance. Attempts were made to determine the nearest neighbour (first sphere of co-ordination) structure by calculating the molar refractivity (MR). Dachille and Roy [11] have shown that as the cation coordination number of changes from 6 to 4, the MR increases substantially. Thus if one compares the MR of a glass with values calculated from a linear combination of the MR of the constituent oxides (with known structures and co-ordination) one can estimate whether the co-ordination number in the glass is the same as that in the oxides. These data, compared in table IV, show no evidence for a co-ordination number change in going from the crystalline oxide to the glass. It is an unexpected and unlikely result that the Cd^{2+} and Pb^{2+} ions are predominantly 6-co-ordinated in the glass. With the high concentration of these ions it seems inconceivable that they play exclusively the role of a glass modifier. However, in an earlier paper (Caslavska *et al* [12]) we have shown that many of these compositions consist of phase separated or microheterogeneous materials. It is possible that the Cd or Pb rich regions are in fact still 6-co-ordinated.

TABLE IV Molar refractivity data for several glasses.

Glass composition (Mole %)	MR of glass	MR of linear combination of oxides
65 CdO-20 B_2O_3-15 SiO_2	9.40	9.56
60 PbO-20 Bi_2O_3-20 SiO_2	17.65	17.38
50 PbO-10 Bi_2O_3-40 SiO_2	14.32	14.46

4. Discussion

The nature of the electronic structure of these glasses and the conduction mechanism are not completely understood at this time. Following the ideas of Goodenough [10] it is possible that conduction occurs in these compositions by narrow "d" orbital overlap of the cations or, possibly, by the interaction between a strongly polarizing cation and the oxygen "p" orbitals. In the former case, crystallographic considerations and interatomic distances will determine the probability of overlap. Goodenough derived the following empirical formulas to define the critical interatomic distance which would determine whether or not overlap occurs.

$$R_c(3d) = 3.15 - 0.03\,(Z - Z_{Ti}) - 0.04\Delta\,[J(J+1)] \qquad (1)$$

where $\Delta[J(J +)] = J_e(J_e + 1) - J_c(J_c + 1)$; J_e and J_c are the quantum numbers for localised and collective electrons Z and Z_{Ti} are the atomic numbers of the 3d equivalent atom in question and Ti respectively.

$$R_c(4d) = 0.88 + R_c(3d) \qquad (2)$$

Using these formulas the critical separation for Cd^{2+} was calculated assuming the super exchange interaction is very small. Then from the assumed octahedral co-ordination of Cd^{2+}, it is possible to calculate the Cd-Cd separation in the glass. These results are given in table V. From this table one can see that the Cd-Cd separation in the glass is very close to the critical separation and depends on the orientation of the cadmium octahedra. Since a glassy structure is aperiodic, there is no restriction placed on the orientation of these octahedra, and one would expect irregular chains in which the Cd^{2+} ions are separated by 3.69A or less.

As with the Cd-Cd separation, the Pb-Pb separation depends upon the orientation of the octahedra and may approach the critical separation with corner shared octahedra which are joined at an angle of less than 180°. Table V gives calculated values of the separation of the Cd and Pb anions. Since the Pb-Pb separation is greater than the Cd-Cd, the interaction on the electrons would be smaller and the conduction band would be narrower. This may explain the reduced photocurrents in the Pb-containing glasses than in the Cd-containing glasses.

TABLE V Separation of anions assuming a regular octahedron,. O^{2-} radius of 1.40 Å and no rattling of the cation.

Cd-Cd separation (A)	Pb-Pb separation	Orientation of octahedra	Anion separation calculated from equations 1 and 2
2.29	3.02	Face shared	Cd = 3.69
2.80	3.70	Edge shared	Pb = 4.21
3.96	5.23	Corner shared	

The second requirement for conduction, in the Goodenough theory, is that the "d" orbitals must be only partially filled. Both Cd^{2+} and Pb^{2+} have filled 4d and 5d shells respectively. Hence, the glasses should be, and are insulators in the dark. For conduction to occur in the narrow band, the incident photons must promote electrons to the higher s or p levels. This is born out by the increase in photocurrents as the energy of the incident radiation is increased. Beyond the adsorption edge, the photocurrents decrease due to the shallow penetration of the incident radiation.

In the cases where the impurity ions are present in the glass, the variable valency ions must act as recombination centres. With a high concentration of these recombination centres, the lifetimes of the holes and electrons are so short they cannot contribute to the photocurrents.

If the photocurrents were thermally activated by absorption of light, then one would expect the dark-coloured glasses, which absorb a higher percentage of the radiation, to be better photoconductors than the light-coloured glasses. Hence addition of Fe_2O_3 to the 65 CdO-20 B_2O_3-15 SiO_2 glass should increase the photoconductivity. Also if the temperature of the sample is increased by the proximity of the sample to the incandescent lamp, then all glasses should show about the same photocurrents. The organic electrode begins to decompose at temperatures in excess of 90°C. Since this electrode showed no degradation after 8 hours of exposure in the measuring apparatus, we can assume the temperature of the sample did not exceed 90°C. Thus we conclude that the photocurrents observed in this study are not thermally activated.

The microstructure also plays an important role in the electrical properties of the glasses. In the samples through which various gases were bubbled, both O_2 and CO cause an initial increase in the photocurrents. These results are best explained by the microstructure of the glasses The glasses show phase separation (see fig. 9a) in which one glassy phase is totally surrounded by a second glassy phase. Both phases are glassy, for no sign of crystallinity can be detected by either microscopic or X-ray diffraction examination. As the gas was bubbled through the glass, it reduced the size of the phases and broke up the particle boundaries. Since the large smooth areas (fig. 9a) have the largest volume, we assume this is a CdO-rich phase and should be a good photoconductor with lower resistivity. In this state the SiO_2-rich phase (high resistivity and poor photoconductor) acts as phase boundary insulators and prevents the photocurrent from moving one phase "grain" to another. Then after the bubbling gas broke up these phase boundaries, the CdO-rich phase was the continuous phase and the sample gave a higher photocurrent. The decrease in photocurrent with bubbling time for CO is probably due to the contamination of the glass with platinum. An analysis of the glass after 2 hours of CO bubbling showed 0.01 % Pt whereas Pt was undetected in any of the other melts.

Although the current voltage data indicates the ohmic nature of conduction, it is conceivable that conduction may be SCL. With the two phase microstructure as shown in fig. 9, space charges could develop along the silica-rich glassy phase. Since this phase is distributed uniformly through the glass sample and the space charge builds up on a very small particle, the bulk conduction appears to be ohmic rather than SCLC.

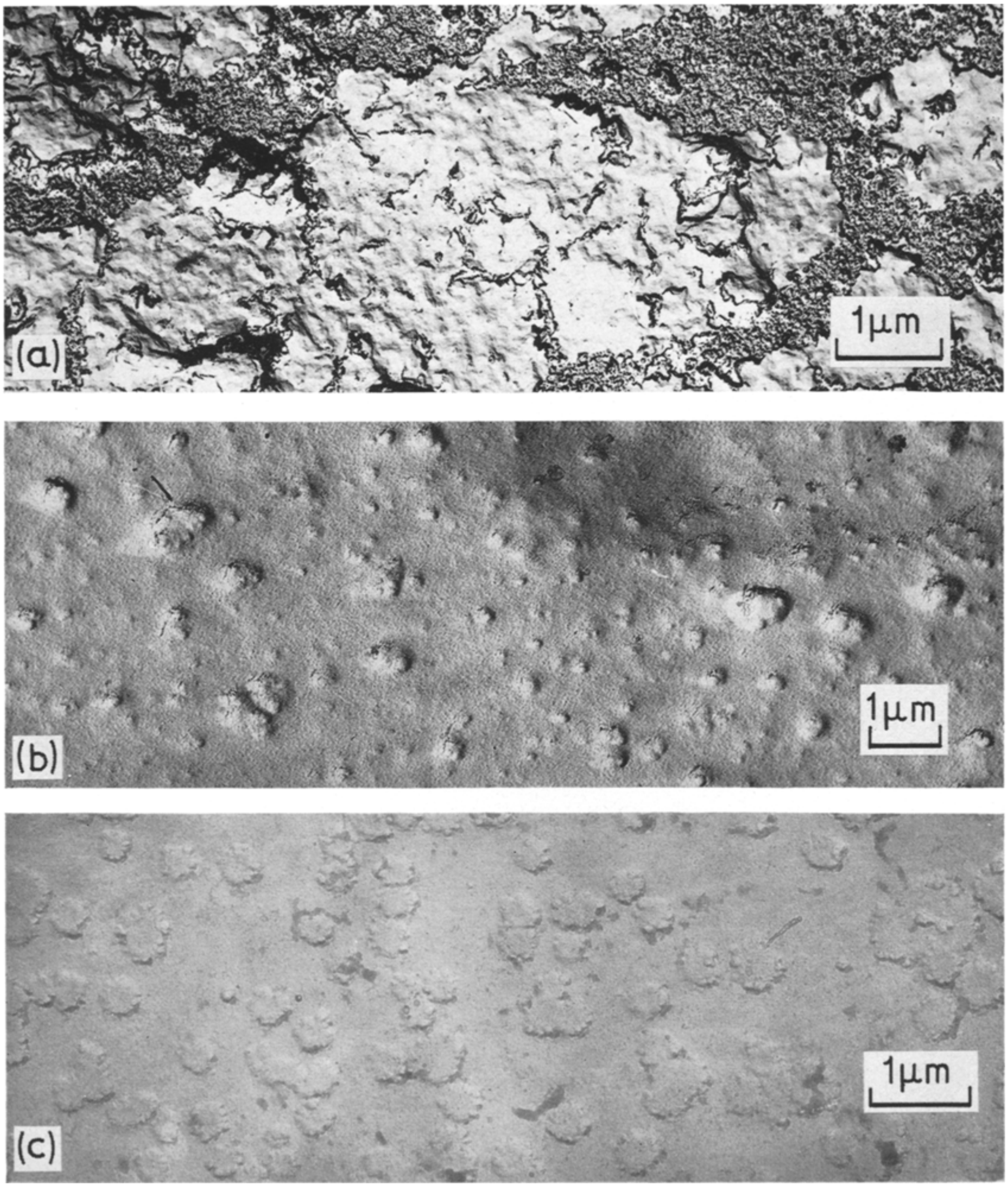

Figure 9 (*a*) As cast glass. (*b*) O_2 bubbled through glass for 80 minutes. (*c*) CO bubbled through glass for 80 minutes. Platinum shadowed carbon replicas of fresh fractured glass surfaces etched 10 seconds in HF fumes.

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