A transmission electron microscope study of some SnO_2-Sb_2O_5 semiconducting glazes

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A number of SnO_2—Sb_2O_5 semiconducting glaze samples have been examined by transmission electron microscopy. The distribution, morphology and size distribution of the SnO_2 particles have been determined, both for glazes used to control pollution flashover on electrical insulators and for glazes used to produce electrical resistors. Careful analysis suggests that in the insulator samples, point contact between SnO_2 particles is not achieved but each particle is surrounded by a rim of glass, typically a few tenths of a micron in thickness. It is shown that this model is in qualitative agreement with the results of measurements of glaze conductivity as a function of SnO_2 concentration. An estimate is made of the size of these rims as a function of concentration, from the known SnO_2 content of the glazes and from measured particle sizes. The distribution of shapes and sizes of the SnO_2 particles in the glaze are related to the distribution in the SnO_2 powder used to make the glaze. It is suggested that the smaller particles in the original powder are dissolved in the glaze during firing and recrystallize around the larger particles which are not fully dissolved. The influence of this process on the Sn distribution in the solution rims is discussed. In the resistor glazes, the wide range of SnO_2 particle sizes makes it more difficult to determine whether point contacts occur between the particles. Indirect evidence seems to suggest that percolation paths through the material do exist. It is shown that in a number of the glazes, fine-scale phase separation in the base glass occurs. Two distinct types of devitrified region in the insulator glazes have been observed, one of these types appears to correspond to the devitrified areas in the glass observed by scanning microscopy and the other type is α-quartz probably undissolved in the firing process.

1. Introduction

Semiconducting glazes are used on some high-voltage insulators to control pollution flashover, but their use has proved only partially successful as a result of deterioration of the glazes in service due largely, it is believed, to electrolytic action. The most promising and now most widely used glaze relies upon the semiconducting properties of Sb^{5+} doped SnO_2 incorporated in an alumino-silicate base glaze. This material is designed to give a surface resistivity of $10^7 \Omega$ and is applied to a thickness of about $200\,\mu m$. Similar glazes are also used for the production of high stability, high value resistors [1]. The purpose of the work described in this paper is to examine the internal structure of the glazes in order to gain a fuller appreciation of the factors that might control conduction mechanisms and service

performance in the insulator glazes and to compare the structure of these materials with that of the resistor glazes.

2. Experimental

The insulator glazes used in this study were produced by calcining analytical reagent grade SnO_2 with $2.5 \, mol\% \, Sb_2O_5$ at $1200°C$ for a few hours and the remilled powder was then mixed into a base glass of approximate composition $70\% \, SiO_2$, $9\% \, Al_2O_3$, $4.5\% \, (Na,K)_2O$, $9\% \, CaO$ and $7.5\% \, ZnO$. The proportions of $SnO_2 \, Sb_2O_5$ are expressed in this paper as percentages of the combined base glaze—tin oxide mixture. This was sprayed onto unfired electrical porcelain tiles and fired in air at $1200°C$ for 2 to 3 h. The samples were furnace cooled over a period of about 12 h. The resistor glazes of commercial origin were produced by feeding a Sn—Sb alloy in finely divided form into a vertical furnace and allowing it to burn in a stream of oxygen. This powder was then mixed with finely divided borosilicate or lead glass and the mixture suspended in an alcohol based resin. The dipped alumina resistor bodies were then sintered at $1100°C$ for 15 min and air cooled.

In a previous paper [2] the results of scanning microscopy and electron probe microanalysis on the materials was presented. In this paper the results of transmission microscopy will be shown to give a particularly clear impression of the distribution and morphology of the individual SnO_2 crystallites in the glazes and allow a considerable insight into the likely conduction mechanism in the materials.

For the purposes of transmission electron microscopy, samples were prepared from fired porcelain tiles by trepanning 3 mm diameter discs from the tiles with a diamond cutting tool and cutting and grinding away the porcelain. The flakes of semiconducting glazes obtained (about $200 \, \mu m$ thick) were polished on both sides with a diamond loaded wheel to a thickness of 10 to $20 \, \mu m$. Thinning from both sides ensured that the specimens were representative of the central portion of the glaze thickness. Specimens were then exposed in an Edwards Ion Thinning equipment to $6 \, kV \, Ar^+$ ions at near grazing incidence and penetration was effected in about 12 hours. Analyses were carried out on the thinned regions around the resultant hole in the glaze. The use of an AEI EM7 microscope operated at 1 MV enabled areas to be examined that were large enough to be representative of the material as whole.

3. Results
3.1. Insulator glazes

Fig. 1 shows a montage of the area around the hole in a $30\% \, SnO_2$ specimen at low magnification. The montage was obtained from an exceptionally large region of uniformly thinned glaze around the edge of the central hole. The extent of the thinned area enables a particularly clear impression to be obtained of the distribution of SnO_2 particles. Areas rich in Sn (high density of dark spots) are seen to cover perhaps 60% of the total area under view and these transmission microscope results confirm the impression of the Sn distribution
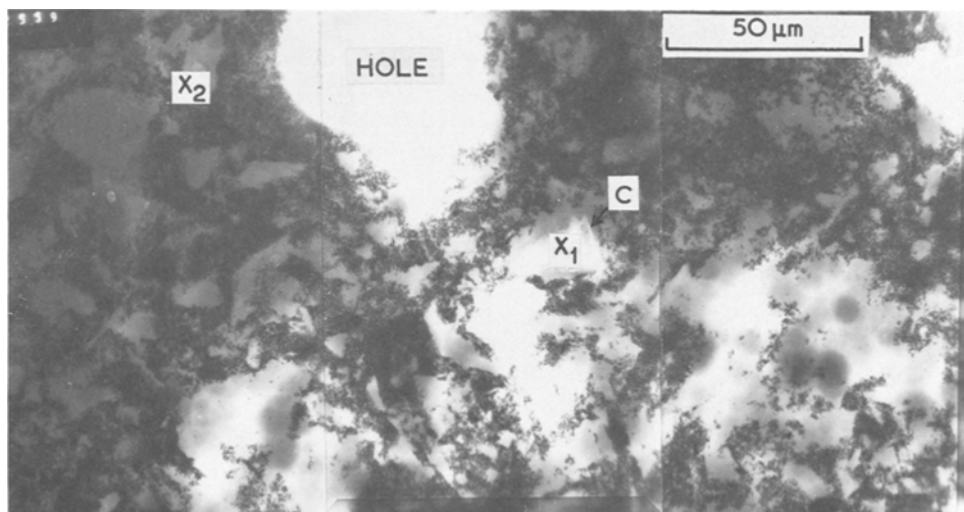

Figure 1 Montage from a 30% SnO_2 specimen.

obtained from the scanning microcope studies. Between these regions, areas of SnO_2 free base glass are to be observed, and these presumably correspond to the areas which were found to charge in the scanning microscope when the samples were not coated with a conducting surface film [2].

Fig. 1 also reveals a number of other interesting features. In the SnO_2 free areas, there are frequently found crystalline regions which appear to take two different forms (marked X_1 and X_2). The X_1 features comprise a central core edged with needle shaped crystals, whilst the X_2 features generally show the form of interpenetrating clusters of high aspect ratio crystals. The second type of feature we identify with the Ca–Sn rich needles reported in the scanning microscope analysis. Selected area diffraction patterns (SADP) have been obtained on these regions, but on the basis of the complex patterns obtained, no identification of this phase has yet been possible. The X_1 regions have been demonstrated by electron diffraction to be α-quartz and therefore are almost certainly residues of the quartz present in the constituents of the glaze material. They are frequently to be associated with small cracks (such as that marked C on the micrograph). Such cracks are common in whitewares and are caused by the tensile stresses induced by the high contraction of the quartz on cooling.*

Fig. 2 shows a somewhat higher magnification real image bright field (RIBF) view of an X_2-type region. In this micrograph, the general form is much closer to that of the needle shaped crystals observed in the scanning microscope. Although both crystal clusters lie in predominantly SnO_2 free "holes" in the glass, there is an overlying trail of SnO_2 particles present in both cases.

Fig. 3a shows an intermediate magnification picture obtained from a SnO_2 rich area and Fig. 3b shows a high magnification RIBF view of part of this field. Selected area diffraction patterns obtained from the individual particles have been indexed and confirm that they are indeed SnO_2 crystallites. The sizes of the rounded crystals are surprisingly uniform, being on average about $0.3\,\mu m$ in diameter. The relationship between the size of these particles and the range of particles in the starting materials will be discussed further
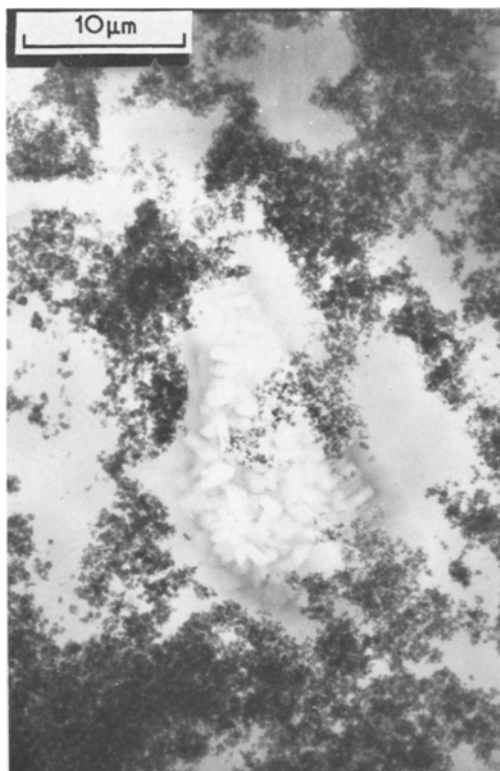

Figure 2 Real image bright field view of an X_2-type region.

in Section 4. The fringes parallel to the edges of the diffracting particles give a good indication of morphology. It is well known that Cassiterite twins easily and many of the particles comprise two or more portions; the composite particle, marked A in Fig. 3b, for example, is probably a multiple twin. This high magnification study also reveals a mottling in the matrix between the SnO_2 particles. This would seem to suggest phase separation in the base glass.

Further evidence of phase separation, but in an entirely glassy region, is revealed in Fig. 4. The contrast in this and similar micrographs is due to real differences in optical density between the dispersed and continuous phases and this is demonstrated by a through focus series. The phase separation was found to vary from one region to another; the size of the darker particles is about $60\,nm$ in Fig. 4 which is more than twice the size of those found in Fig. 3b for example. In yet other regions, the separation appeared to be absent, probably due to variations in the local SnO_2 con-

*Many of the crystals are surrounded by amorphous regions with angular boundaries. It is believed that these boundaries constitute the original shape of the crystals which have been partly invaded by diffusing alkali ions. Although amorphous, the regions have such a high viscosity at firing temperatures that no rounding occurs.
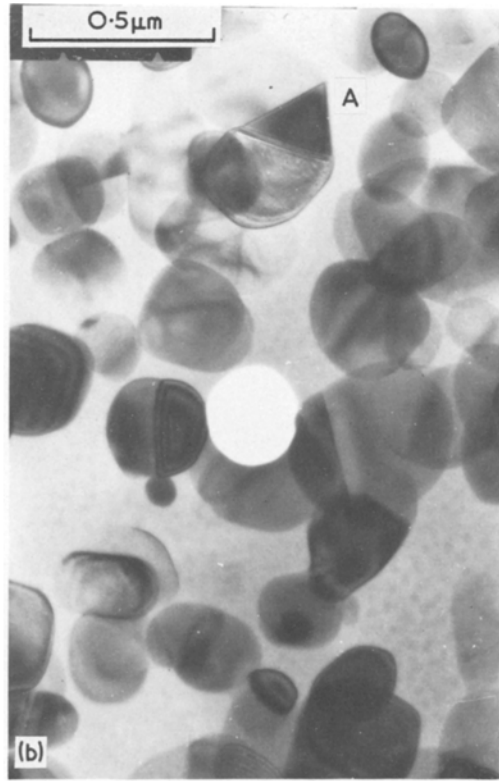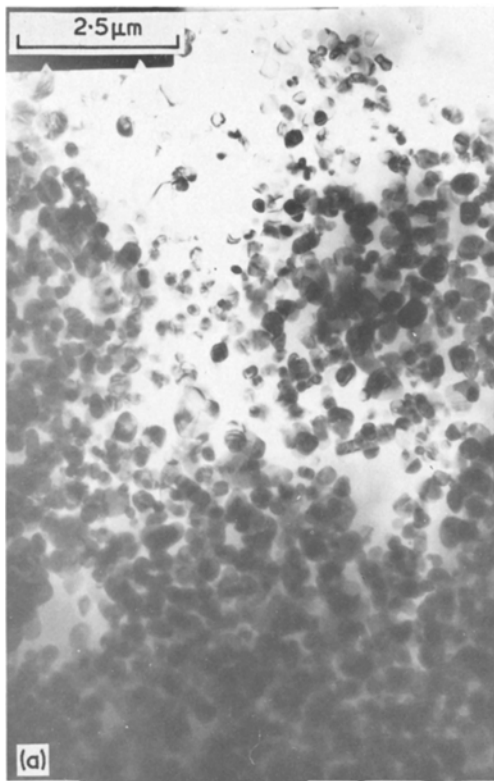
Figure 3 Real image bright field view of SnO$_2$-rich area (a) intermediate magnification (b) high magnification.
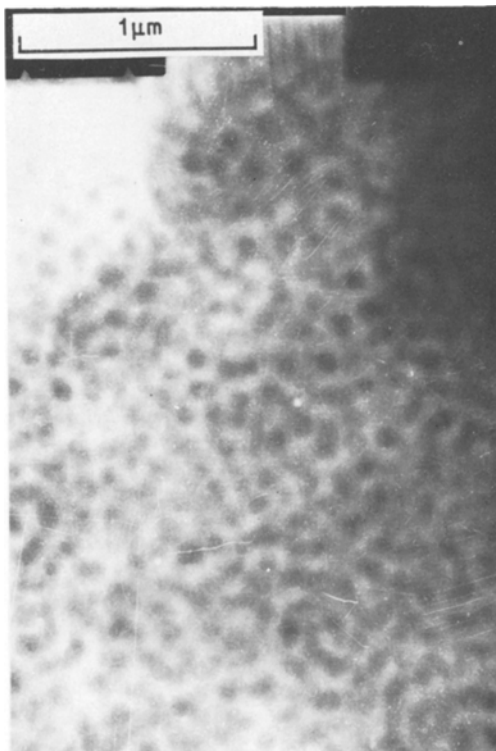

Figure 4 High magnification view of phase separation in a glassy region.

centration as discussed later. A systematic study to characterize the phase separation and to correlate it with other structural features has not been made.

Analysis of a 20% SnO$_2$ sample produced from the same starting materials as the 30% glaze and fired under identical conditions, showed a similar distribution of SnO$_2$ particles but the density of particles was much lower than equivalent areas in the 30% sample. It was difficult, however, to estimate to what extent this was due to a difference in thickness between the specimens. Transmission micrographs in this glaze again revealed phase separation and the presence of both X$_1$- and X$_2$-type features.

3.2. Resistor glazes

Two samples of the type of glaze used to produce high voltage, high stability resistors have been studied. A low magnification micrograph of a standard sample deposited on an alumina substrate is shown in Fig. 5. Away from the strongly thinned area (white on the plate), tin oxide particles are found to be evenly dispersed. Comparison with insulator samples shows that there are fewer areas of base glass between the clusters
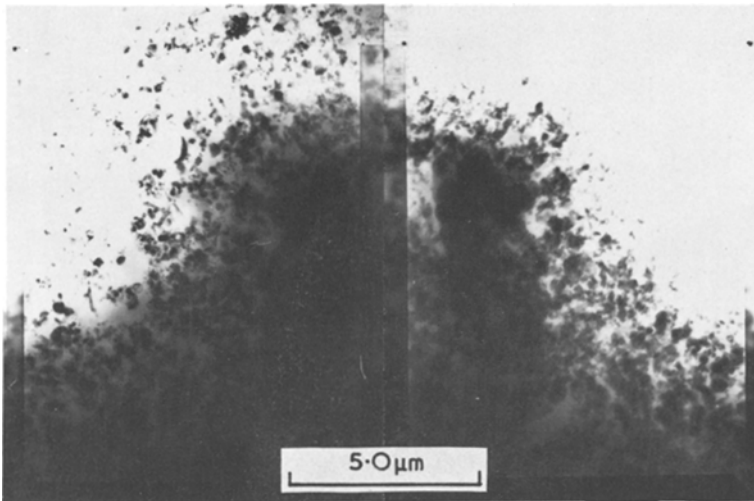
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of tin oxide particles, thus confirming the scanning electron microscope results on these glazes. Comparison of Fig. 6a with Fig. 3b shows that in the resistor glazes, the mean particle size is reduced compared with that of the insulator glazes. Measurements of particle size enlargements of Fig. 6a, gives a mean diameter of about 0.13 μm compared with the value of 0.3 μm for the in-sulator glazes. There would appear to be a wider range of particle sizes in the resistor material with some giant particles such as the twin lamella shown in Fig. 6b and a substantial number of particles with a diameter of less than 0.1 μm. SADP studies of a number of the giant particles in the resistor glaze show them to be SnO_2. It is not clear from these thinned section samples
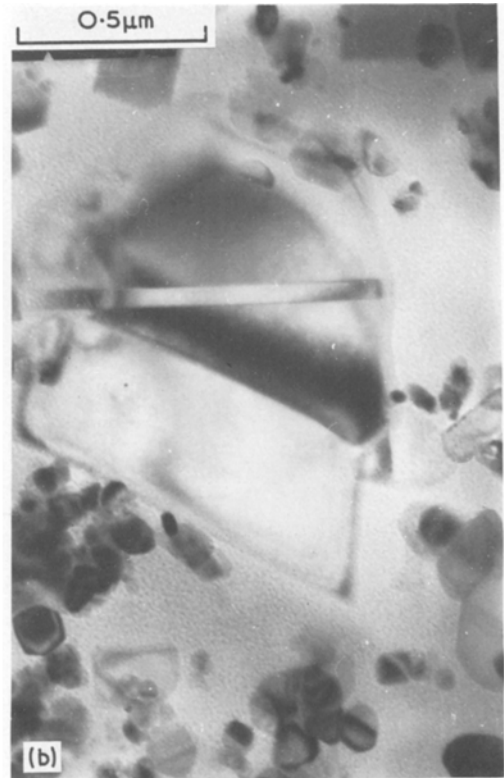

Figure 6 High magnification view of (a) a "typical" area from Fig. 5; (b) an area containing a "giant" twin lamella.
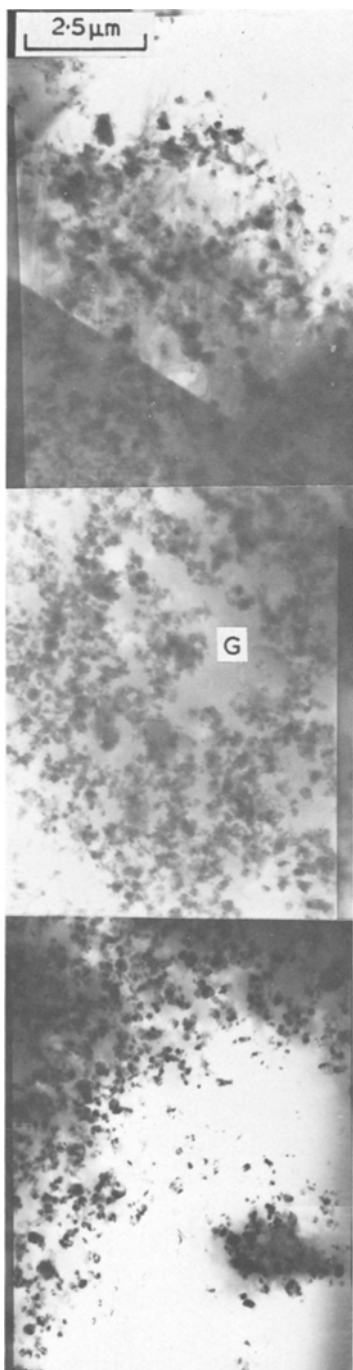
Figure 7 Montage from slow cooled resistor glaze.

by melting the glass/tin oxide mixture in an alumina crucible for 24 h at 1050° C and furnace cooling. The final glaze showed a honeycomb structure. Compared with the standard heat treatment, the glaze was held at a high temperature for a hundred times the normal period and cooled at about a hundredth of the normal rate for resistor glazes. This cooling rate is thus similar to that used commercially for insulator glazes.

A low magnification composite is shown in Fig. 7. This shows that there is, again, a fairly homogenous distribution of SnO_2 particles but SnO_2 free "holes" such as that at G, do exist. Careful examination shows the presence of faceted plate-like crystals and in some areas of the material these are at a high density. A zone depleted in SnO_2 is frequently observed round the perimeter of the crystals.

Micrographs of this sample (Fig. 8a) show that there are few very small SnO_2 particles present after the prolonged heat treatment and that the mean particle size appears larger than the standard resistor glaze. Moreover, there is no sign of phase separation in the glassy phase.

Fig. 8b shows an intermediate magnification view of one of the faceted platelets mentioned above with SnO_2 particles embedded in it. The large number of parallel bands of bend contours (marked B) imply a corrugated lattice and lead to the conclusion that the crystals are in a state of strain. An SADP from this area shows clear points which may be indexed to SnO_2 and which presumably arise from the embedded particles. The large crystal has not been identified.

4. Implications for possible conduction mechanisms in the glazes
4.1. Insulator glazes
Analysis of the limited extent of charging of the glaze surfaces in the scanning electron microscope [2] shows that contact between the clusters of SnO_2 particles is achieved at low SnO_2 concentrations (< 10 wt %) The connectivity between clusters is also apparent in Fig. 1 and they therefore form a conducting path through the material. It is clear from this that the conductivity is controlled by the structure within the clusters. The transmission microscope results are particularly useful in revealing the local environment of individual SnO_2 crystallites in the glazes. In particular the use of stereo pairs of intermediate magnification taken of areas containing clusters of SnO_2 crystal-

whether they are truly platelike or spheroidal particles sliced through by thinning. High magnification micrographs again show evidence of phase separation in the base glass, though in this case on a much finer scale.

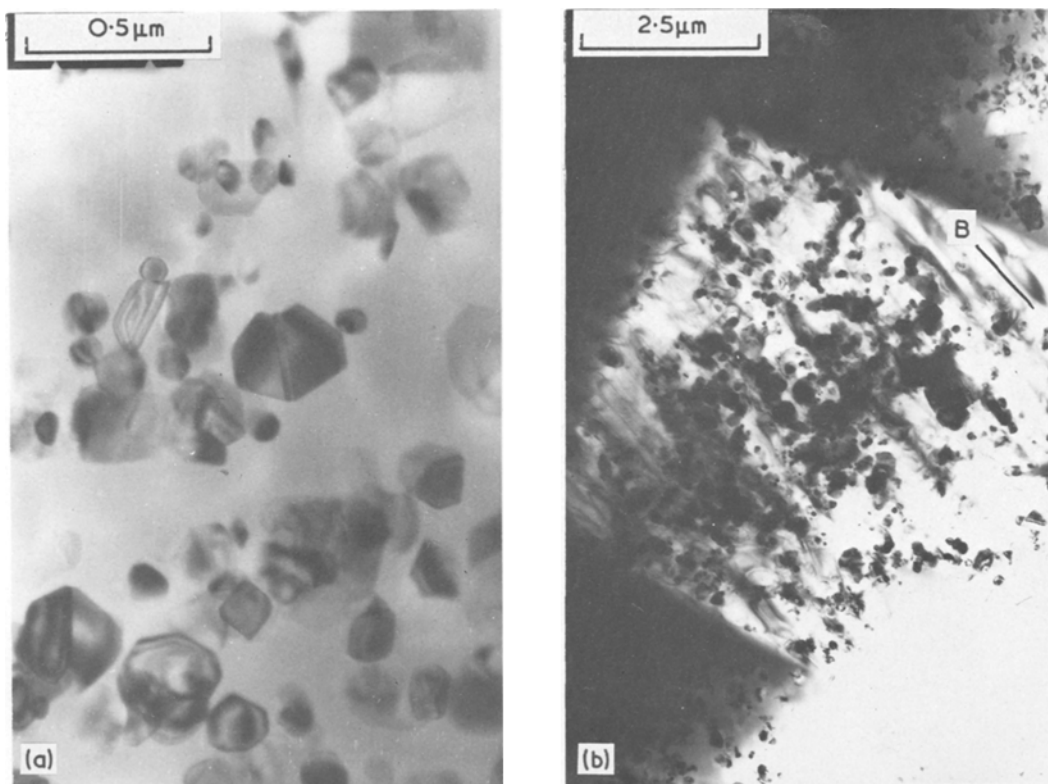The second resistor glaze sample was prepared

Figure 8 High magnification view of (a) a typical area from Fig. 7; (b) an area containing a faceted platelet embedded with SnO_2 particles.

lites, allows an estimate to be made of the proportion of particle—particle contacts within the clusters. Studies of numbers of such pairs for the 20% and 30% SnO_2 glazes shows that the SnO_2 particles in fact rarely come into contact but appear always to be separated by glass, the separation between nearest neighbours being seldom more than few tenths of a micron.

Since the conduction will be concentrated in the paths of minimum resistance, it will be the layers of glass between those SnO_2 crystals that are in close proximity that will tend to determine to a large degree the overall conduction characteristics of the material. It is unlikely that regions so close to the crystallites are uniform in composition; more probably they will be modified by dissolution of the SnO_2 from the particles into the glass and the reverse process of exsolution. The resultant

non-uniform distribution of SnO_2 in the interparticle regions (which we will subsequently describe as solution rims) will cause the conductivity to be non-uniform.

To form some appreciation of the magnitudes of the important quantities, it is instructive to make approximate calculations of the volume fractions of the particles and the separation between them. Table I shows the results obtained by taking the densities of the SnO_2 and the glass containing dissolved SnO_2 as 6.95 and 2.5 Mg m^{-3} respectively and assuming that the particles (diameter $0.3 \mu m$) are distributed in a primitive cubic lattice, but only over 80% of the glaze volume for the glass containing 30 wt % SnO_2 and only 70% for the glass containing 20 wt % SnO_2 [2]. In each case it is assumed that the concentration of SnO_2 dissolved in the affected

TABLE I

wt % SnO_2	vol % glaze affected	wt % SnO_2 dissolved	wt % SnO_2 undissolved	local vol % SnO_2 grains	grain separation (μm)
30	80	2.9	27.1	14.3	0.16
20	70	2.9	17.1	9.5	0.23

part of the glaze is 5 wt %. The calculated separations are then 0.23 μm and 0.16 μm respectively in good agreement with experimental observation.

Indirect evidence for the presence of the solution rims comes from the form of the room temperature conductivity as a function of SnO_2 concentration. The behaviour expected from percolation theory (see for example Shante and Kirkpatrick [3]) for the effect of the incorporation of particles of high conductivity in a low conductivity medium, is that at above a certain volume fraction, the conduction rises sharply. For example Binns [4] observed a change in conductivity of seven orders of magnitude when the concentration of iron carbonyl in a glass was increased from 12.5 to 15 vol %. In the SnO_2 insulator glazes, however, the conduction rises smoothly with concentration from 5×10^{-8} $(\Omega m)^{-1}$ at 10 wt % SnO_2 to 5×10^{-5} $(\Omega m)^{-1}$ at 35 wt % for a series of glazes fired and measured under identical conditions. Fig. 9 shows that the results obey the empirical relationship

$$\log \sigma = kc + \text{constant},$$

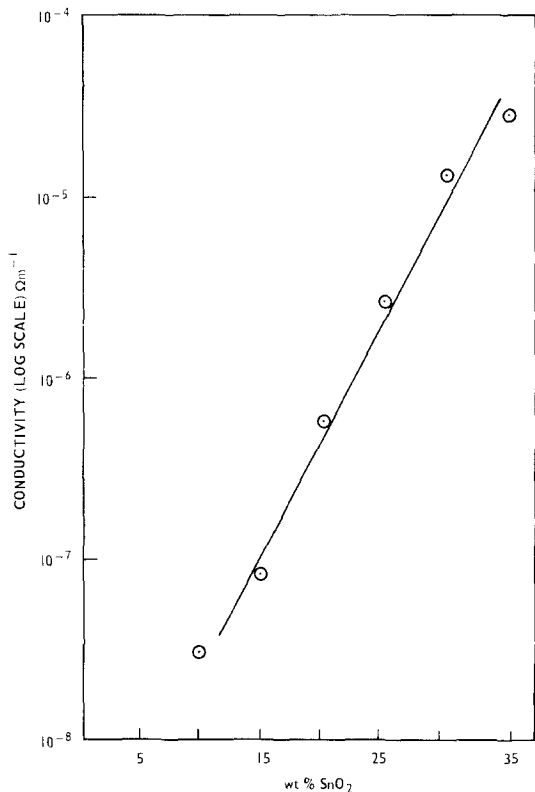where σ = conductivity and c = concentration.

Figure 9 Electrical conductivity versus concentration for standard SnO_2 glazes fired at 1200° C for 2 h.

This smooth relationship between conductivity and concentration implies that the SnO_2 particles tend to remain separated, in agreement with the microstructural observations. The reason for this separation may be found in the preparative process. It is clear from Fig. 3b that the size distribution of the SnO_2 particles in the fired 30% SnO_2 glaze is very narrow, with an average diameter of about 0.3 μm and few below 0.25 μm. On the other hand SnO_2 raw material for the glaze has a very broad size distribution, with 80 vol % of the grains having diameters below 0.25 μm. Since, as indicated by Table I, only about 10% of the SnO_2 originally added to this glaze is found ultimately to be dissolved, it is clear that something like 70 wt % must have coarsened by solution and regrowth onto larger particles.

Since growth can occur only from saturated solutions, it is probable that the solution of the smaller particles and re-precipitation on the larger ones, occurs at the maximum firing temperature of 1200° C. During cooling the melt will become supersaturated with SnO_2, which will tend to exsolve onto nearby particles leaving a low conductivity rim round each one. The thickness of each layer cannot readily be estimated, but it must be less than the inter-particle distance, because the diffusion distance decreases with decreasing temperature. Providing the layer is not so thin as to permit electron tunnelling, then it is this solution rim that largely controls the conductivity. The relatively low dependence of conductivity on applied voltage in these materials seems to imply that tunnelling is not important in the conduction mechanism.

This picture also seems to explain the somewhat puzzling observation that the Sb distribution in those glazes in which the SnO_2 and Sb_2O_5 have not been calcined before firing, seems to be similar to the distribution in glazes where the oxides have been chemically combined [2]. On the basis of the model under discussion, dissolved Sb (which presumably at the low concentrations employed would be largely dissolved in the glaze at 1200° C) would also crystallize on the SnO_2 particles which have remained partially preserved during the firing process.

Another feature of the incorporation of SnO_2, ZrO_2, TiO_2 and other transition metal oxides in glasses, is that the solubility of ions of high valency is greatest in alkali or alkali earth rich glasses, a factor which provides a driving force

for the phase separation of glasses containing them. The phenomenon for ZrO_2 in $MgO-Al_2O_2-SiO_2$ glasses is described by Nielson [5]. The high electron optical scattering of the droplets in Fig. 4 can be interpreted as due to the concentration in these droplets of the ZnO and CaO together with some of the Al_2O_3 and a relatively small proportion of silica. During cooling of the melt the driving force for separation increases, but the diffusion distance decreases. The structure that results therefore depends on the original concentrations and the rate of cooling. The SnO_2-rich material, although still glassy, is likely to be a semiconductor. Although the structure appears in Fig. 4 to comprise dispersed particles of dark material in a lighter background, it is probable that the two phases are continuous and interpenetrating. The regions depleted of SnO_2 near the crystallites are therefore likely to remain responsible for limiting the electrical conductivity.

4.2. Resistor glazes

The conduction mechanism in the resistor glazes subject to their normal firing cycle is less clear. Because of the existence of a wide range of particle size, it is much more difficult to ascertain analytically whether true point contact occurs. In these glazes small SnO_2 particles frequently appear to be interposed in the gaps between larger ones. It seems possible that the use of the low melting point base glass, and thus of a lower firing temperature, may reduce the Sn solubility to a very low level and thus as a corollary, this may lead to the retention of direct particle–particle contacts. It will be interesting to measure the concentration dependence of conductivity in these glasses. The resistor glazes show highly linear V–I plots and a notably low temperature coefficient or resistance and in these respects differ from the insulator materials.

5. Summary and conclusions

The transmission microscope studies of the $SnO_2-Sb_2O_5$ glazes have revealed a number of interesting features:

(1) The morphology, particle size distribution and extent of dispersion of the SnO_2 particles has been revealed for both the insulator and resistor glazes. Other structural features including phase separation in the glasses have been characterized.

(2) Stereoscopic micrograph pairs for the insulator glazes suggest that the SnO_2 particles do not achieve many particle–particle contacts but appear always to be separated by a thin region of glaze. An estimate has been made of the separation distance.

(3) The uniformity in size and shape of the SnO_2 crystallites in the fired insulator glaze indicates that the small SnO_2 particles in the original SnO_2 powder go into solution during firing and recrystallize on the cores of the surviving larger crystals. Further exsolution of SnO_2 particles during cooling probably leaves the rims of glass surrounding the particles deficient in SnO_2, thus reducing the conductivity.

(4) Conclusions 2 and 3 are consistent with the observed absence of a percolation limit in insulator glazes.

(5) In the resistor glazes the lower firing temperature leads to the retention of fine particles of SnO_2 and a wider particle size distribution.

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