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Electrical properties of a partially crystallized aluminosilicate glass containing TiO_2 and Nb_2O_5

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A two-stage heat treatment of an aluminosilicate glass containing both TiO_2 and Nb_2O_5 may be used to precipitate a fine dispersion of doped TiO_2 crystals within a glassy matrix. The resulting partially crystalline product exhibits the properties of a semiconducting material with activation energies for conduction ranging from 0.2 to 0.35 eV. The d.c. conductivity of the specimens has been shown to be related to the size of the TiO_2 crystals. With prolonged crystallization treatment a second non-conducting crystalline phase, anorthite, reduces the conductivity of the glass–ceramics.

1. Introduction

The use of semiconducting glazes for coating the surface of high-tension insulators was first proposed by Forrest [1] over forty years ago. The application of a conducting glaze would enable the manufacturer to control the surface resistivity and thus provide a more uniform voltage distribution. This in turn would reduce the likelihood of flashover occurring in a polluted environment, where electrical discharges in damp atmospheric conditions produce unwanted radio and TV interference.

Over the years a number of different types of glaze have been developed and site trials have been conducted. The first glazes were based on a glass containing semiconducting ferrite crystals [2], while other glazes containing reduced titania [3], and more recently tin oxide doped with pentavalent antimony oxide [4], have also been tried. The last glaze has been the most successful so far but even this has shown a tendency to deteriorate while in service.

The doped SnO_2 glazes have been the subject of an intensive study by Taylor [5], Morgan *et al.* [6], and Taylor *et al.* [7], in an attempt to relate the microstructure with the electrical properties. The glazes contained needles of SnO_2 associated with the antimony. The existence of both relatively conducting and relatively insulating areas was established and the conductivity of the glazes was postulated as being due to the existence of overlapping solubility rims surrounding the doped SnO_2 crystals. In service these glazes were found to deteriorate over a period of several years, and Taylor suggested [5] that this was due to an electrolytic reaction within the glaze together with micro-discharging. One of the reasons for this possibly lay in the technique used for producing the glaze and the method of application. Briefly, SnO_2 with an added 2.5 mol % Sb_2O_5 was first calcined and then mixed with a finely ground glass powder. A slurry of the glaze powder was then sprayed on to the surface of the porcelain insulator, which was then fired to 1200° C in the normal manner. A microstructural study [5] revealed an uneven distribution of the SnO_2 crystals within the glaze, with some areas relatively lean in conducting particles. While a conducting network of crystals was produced, resistive areas could build up a local charge which eventually led to an electrical breakdown within the glaze structure.

It seems unlikely that an even distribution of SnO_2 crystals within the glaze could be produced

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by any method based on mechanical mixing. This has led to the present study in which a homogeneous glass containing both TiO_2 and Nb_2O_5 was first produced and then, with a controlled heat treatment, the glass was induced to crystallize to give a fine, even distribution of TiO_2 crystals doped with the pentavalent oxide. The method used is very similar to the production of glass–ceramic materials [8], in which TiO_2 is frequently used as the nucleating agent for the promotion of uniform crystallization of the glass. By careful control of the heat treatment it is possible to vary both the size and the nucleation density of the precipitating crystalline phase.

The conversion of a homogeneous glass to a fine-grained glass–ceramic involves two distinct stages. The first stage, known as the nucleation step, involves a heat treatment to produce microscopic nucleating particles. In practice this is usually achieved at a temperature of about 700 to 800° C. This stage is followed by raising the temperature some 100 to 150° C to enable crystals to grow on the nuclei produced at the lower temperature. Many commercial glass–ceramic compositions are seen to undergo spinodal decomposition, a glass-in-glass phase separation, at the nucleation temperature, in particular those compositions containing TiO_2 as the nucleating agent. Glass-in-glass phase separation, which may be seen by direct transmission electron microscopy, or by replication techniques, effectively separates a homogeneous glass into glassy phases, one rich in TiO_2 and the other rich in SiO_2. Separation starts on an atomic scale and grows with extended length of nucleating heat treatment. As the size of the separated regions grows they eventually reach proportions with the same dimensions as the wavelength of visible light, and at this point as light is scattered the glass takes on an opalescent appearance. TiO_2 regions may be induced to precipitate crystalline needles of rutile (TiO_2) by raising the temperature to the crystal-growing regime.

It is therefore possible to produce an extremely fine and even distribution of crystalline particles within a glassy matrix; the size and distribution of the crystalline particles is finer and more regular than any mechanical method could be expected to achieve.

2. Experimental details

A homogeneous glass of composition 51% SiO_2, 16% Al_2O_3, 16% CaO, 5% ZnO, 10% TiO_2 and 2 wt % Nb_2O_5, was prepared by fusing the appropriate oxides or carbonates in a platinum crucible at 1500° C. The melt was quenched, crushed to a fine powder and remelted three times to ensure homogeneity. The glass was finally cast on to a brass plate, then annealed from 700° C and cut into small pieces (1 to 2 cm square). Heat treatments were performed in electric muffle funaces with a thermocouple placed alongside the specimens. Typical two-stage heat treatments at 800 and 1000° C are shown in Table I, with the crystalline phases as identified by X-ray powder diffraction techniques shown alongside.

TABLE I Heat treatment of glass and crystalline phases produced

Sample number	Heat treatment		Crystalline phases present*
	Time at 800° C (h)	Time at 1000° C (h)	
1	18	0.25	Rutile
2	18	0.5	Rutile
3	3	0.5	Rutile
4	0	1.0	Rutile + trace anorthite
5	3	1.0	Rutile + trace anorthite
6	3	3.0	Rutile + anorthite

*Rutile = TiO_2; anorthite = $CaO \cdot Al_2O_3 \cdot 2SiO_2$.

The crystallized glasses were examined by preparing thin polished sections and observing the crystallinity directly with an optical microscope. The samples were seen to crystallize in a uniform manner throughout the specimen. Fractured surfaces were examined in the scanning electron microscope (SEM) where the size of the rutile needles could be measured directly. It was found that a light etch in 0.5% HF solution increased the contrast between the crystalline needles and the glassy matrix. Electron microprobe analysis (EPMA) of the needles revealed both titanium and niobium, but with needles less than 1 μm across it was not possible to say if the niobium was in the TiO_2 or in the glass.

d.c. conductivity measurements were made on specimens approximately 2 cm × 2 cm, thinned down to about 3 mm. The polished surfaces of the specimens were coated with evaporated gold to act as good electrical contacts. The conductivity of the samples was measured from room temperature to about 500° C with applied voltages of up to 40 V d.c. Current values were recorded and from voltage–current

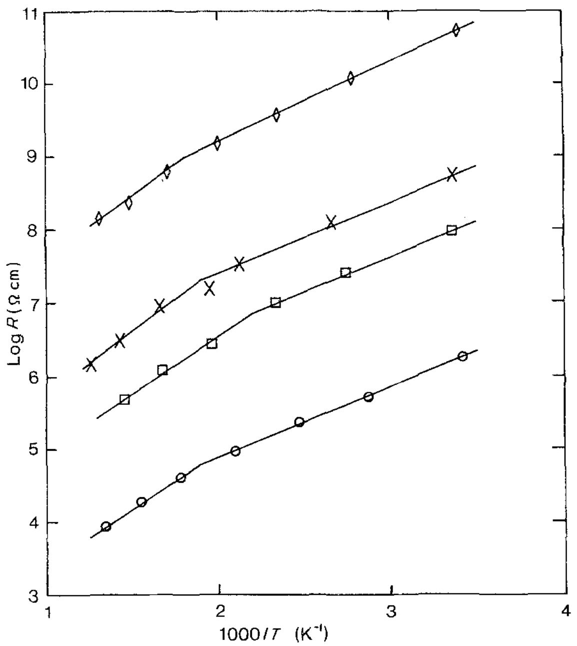

Figure 1 The change in resistivity as a function of heat treatment of the glass. (◊) J1/1, 1 h 1000° C; (x) J1/2, 3 h 800° C + 0.5 h 1000° C; (□) J1/3, 3 h 800° C + 1 h 1000° C; (○) J1/4, 3 h 800° C + 3 h 1000° C.

plots the resistance values obtained. The resistance was then converted to a resistivity value from a knowledge of the thickness of the specimen and the area of the electrodes.

3. Results

The glass before heat treatment is essentially non-conducting, with a room-temperature resistivity of $10^{14.1}$ Ω cm. Partial crystallization of the glass produces a semiconducting material. Conductivity was assumed to be entirely electronic, as no sign of polarization was observed during the conductivity measurements. Typical results are shown in Fig. 1 in which $\log_{10} R$ is plotted as a function of $1/T(\mathrm{K}^{-1})$. For a given heat treatment the values for the resistivity as a function of temperature are seen to lie on two intersecting straight-line curves. The activation energy for conduction was calculated from the slope of the graphs using the Arrhenius equation. At low temperatures the activation energy was approximately 0.2 eV, rising to 0.35 eV for the high-temperature conductivity.

The heat treatments shown in Table I produced rutile needles of different sizes. When the average length of the needles is plotted against the room-temperature resistivity of the samples (Fig. 2) the resistivity falls rapidly at first as the needles increase in length. Once the needles exceed 6 to 7 μm in length the rate of change in resistivity is much reduced.

4. Discussion

TiO_2 is readily soluble in the glass melt at 1500° C and glasses containing up to 15 wt % have been prepared with no difficulty. At subsolidus temperatures TiO_2 is much less soluble and the glass rapidly becomes supersaturated with respect to TiO_2. A single-stage heat treatment at, say, 1000° C produces relatively few large needles (Fig. 3), while by comparison a two-stage heat treatment at 800 and 1000° C produces a fine distribution of rutile needles (Fig. 4). The difference in microstructure is entirely due to the heat treatment at 800° C. X-ray powder diffraction of samples heat treated for up to 18 h at 800° C has shown the absence of detectable crystallization. Transmission electron microscopy of ion-beam thinned specimens revealed the presence of "droplet type" phase separation which starts as a fine sub-micron dispersion and grows with length of heat treatment. A fine dispersion of TiO_2-rich droplets in a silicate matrix enables a very fine dispersion of rutile needles to form when the temperature is raised to 1000° C. Both the initial glass and the phase-separated glass are non-conducting. However, once the rutile needles start to grow the conductivity increases rapidly. It has been shown that a glass prepared without the niobium pentoxide and crystallized in a similar manner remains non-conducting after heat treatment.

Niobium is therefore responsible for

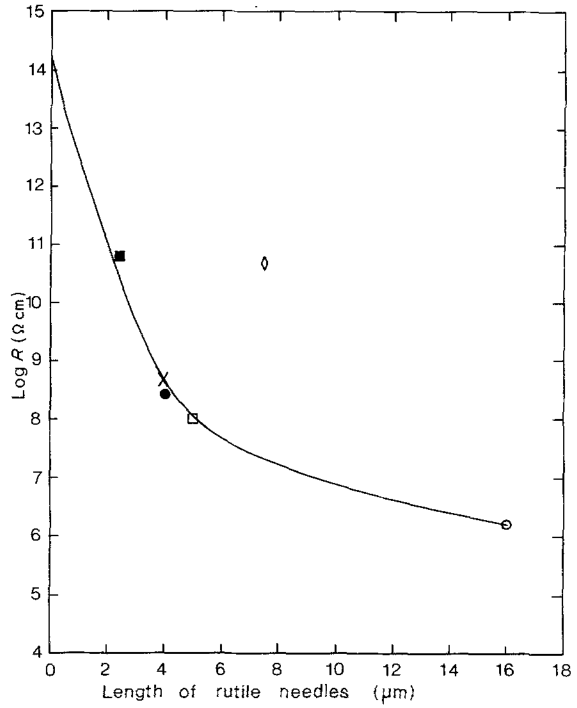

Figure 2 Room-temperature resistivity of the crystallized glasses as a function of length of rutile needles. All samples except J1/1 underwent phase separation prior to crystallization. (◊) J1/1, 1 h 1000° C; (x) J1/2, 3 h 800° C + 0.5 h 1000° C; (□) J1/3, 3 h 800° C + 1 h 1000° C; (o) J1/4, 3 h 800° C + 3 h 1000° C; (■) J1/5, 18 h 800° C + 0.25 h 1000° C; (●) J1/6, 18 h 800° C + 0.5 h 1000° C.

producing a semiconducting material although its actual role remains unknown. A separate study [9] has shown that solid solutions of TiO_2 containing up to 9 mol % Nb_2O_5 may be prepared by solid-state diffusion reaction. However, the change in lattice parameters with solid solution is extremely small and attempts to confirm that the rutile needles are solid solutions have been unsuccessful. Nevertheless, it is not unreasonable to assume that even trace amounts of Nb_2O_5 in solution in TiO_2 would produce a defect lattice structure. During the crystallization of the glass the rutile needles grow rapidly at first, then the growth rate slows down as the diffusion distance for Ti^{4+} ions to the advancing crystal growth interfaces increases. The longest rutile needles observed have been just over 20 μm in length.

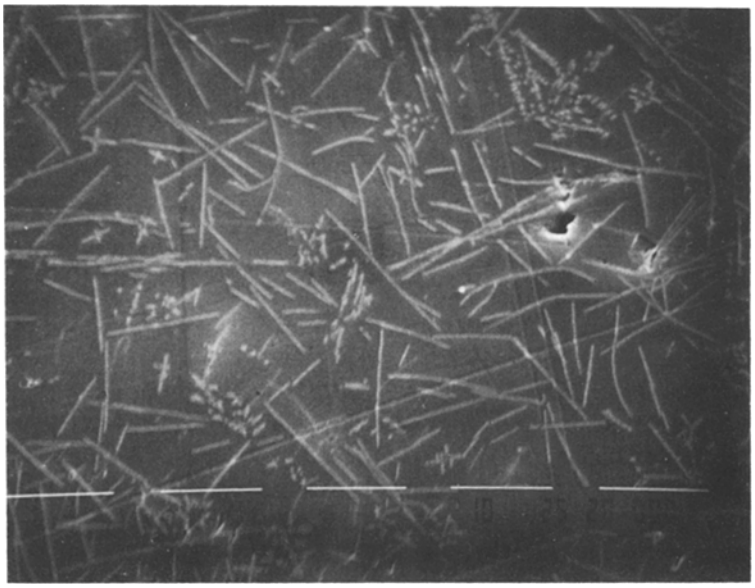

Figure 3 Rutile needles grown by crystallizing the glass for 0.5 h at 1000° C. White bar = 10 μm.

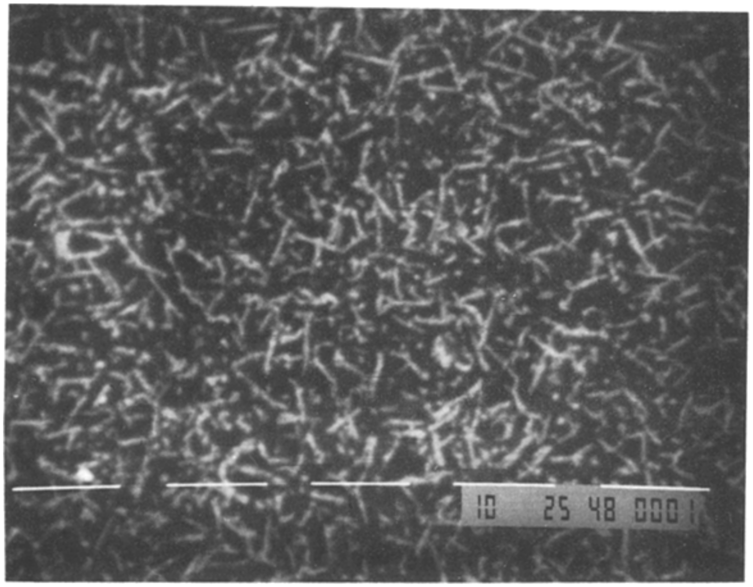

Figure 4 Fine dispersion of rutile needles grown by a two-stage heat treatment of 3 h at 800° C, followed by 0.5 h at 1000° C. White bar = 10 μm.

Prolonged heat treatment of the glass produced a second crystalline phase, $CaO \cdot Al_2O_3 \cdot 2SiO_2$, namely anorthite. Since the composition of the base glass lies within the primary field of anorthite in the $CaO{-}Al_2O_3{-}SiO_2$ system, it is not surprising that this phase also crystallized from the glass. Anorthite is a non-conducting phase and the resistivity of samples with a prolonged crystallization was seen to increase as the relative amount of anorthite to rutile increased.

A semiconducting material is produced when a mass of interlocking and touching doped TiO_2 needles precipitates from the glass. The degree of contact initially increases with heat-treatment time. However, the point is reached when a second non-conducting phase will eventually start to increase the resistivity of the sample.

Further work is in progress to establish both the optimum level of TiO_2 in the glass and also the ratio of TiO_2 to Nb_2O_5 for obtaining the desired crystallization characteristics and electrical properties.

5. Conclusions

Partial crystallization of a calcium aluminosilicate glass containing both TiO_2 and Nb_2O_5 has shown that

1. precipitation of doped TiO_2 crystals produces a semiconducting glass–ceramic;
2. phase separation prior to crystallization produces a finer dispersion of TiO_2 needles than a glass which has not been phase separated;
3. the conductivity is related to the length of the heat treatment and the size of the TiO_2 needles; and
4. prolonged heat treatment produces a second crystalline phase which impairs the electrical conductivity.

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