Electronic conduction in basalt glass and glass–ceramics – correlation with magnetite crystallization

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The d.c. conductivity measurements have been made in a wide range of temperature on a basalt glass heat-treated at different temperatures to form magnetite particles. Small polaron hopping mechanism is operative in the as-annealed glass between Fe^{2+} and Fe^{3+} ions in the isolated state. This mechanism is operative in the heat-treated samples between these ions in the magnetite grains. The d.c. conductivity at 473 K and the activation energy show significant changes around 700° C, when magnetite forms in the basalt glass, which has been correlated with the magnetic data on these samples. TSPC and TSDC data are interesting, but the data analysis is complicated by the possible occurrence of Verwey transition in the small particles of magnetite. Preliminary a.c. conductivity data support the small polaron hopping mechanism.

1. Introduction

The electronic conductivity of semiconducting oxide glasses containing transition metal (TM) ions has been studied extensively (see Bandyopadhyay et al. [1] for references). However, very little work has been reported on such glasses, which have been crystallized to form magnetic crystals dispersed in the glass matrix [2]. The magnetic properties of these types of glasses are also very interesting, particularly when the crystalline phase is magnetite [3–5].

The magnetic properties of a basalt glass, heat-treated at different temperatures, have been studied in detail by Mössbauer and ESR spectroscopy [3, 4], and also by magnetization measurements between 4 and 800 K as a function of a wide range of magnetic field ($H = 0$ to 60 kG) [5]. The main crystalline phase is magnetite. The nucleation and crystallization behavior of this basalt glass has also been studied by small-angle neutron scattering (SANS) [6, 7].

Because, in a basalt glass containing about 13% Fe_2O_3, the iron ions in different redox states are dispersed in the glass matrix, the charge transfer can take place between Fe^{2+} and Fe^{3+} ions, as normally interpreted for TM ion glasses [8, 9]. On heat-treatment, with the formation of the magnetite phase, the charge transfer can also take place between Fe^{2+} and Fe^{3+} ions within the magnetite crystals. The activation energy in such a situation is expected to show some changes with the progress of crystallization of mag-

netite, because of the difference in the nature of the sites in a glass and a crystal.

As no work has been reported on oxide glasses containing magnetite crystals, it was thought interesting to study the electronic conductivity of basalt glass as a function of crystallization of magnetite. Therefore, the electrical studies are complimentary to those of magnetic and crystallization properties of basalt glass and glass-ceramics.

2. Experimental details

The basalt glass was supplied by Corning Glass Works (USA) for the present investigation. Its composition was (wt %) 52.0 SiO_2, 14.1 Al_2O_3, 12.8 Fe_2O_3, 9.3 CaO, 6.4 MgO, 3.2 Na_2O, 1.2 K_2O and 1.0 TiO_2. The preparation procedure has already been described [3, 4]. The glass was annealed at 525° C, and the glass transition temperature was estimated to be 635° C by dilatometry.

The samples were heat-treated at 600, 650, 700, 800 and 900° C, for a fixed time of 8 h. Some samples were also heat-treated at 700° C for 2, 4, 8, 16 and 32 h to study the electronic conductivity as a function of time. The three-terminal electrical measurements were made on disc-shaped samples of 1 cm diameter and 2 to 3 mm thick, with gold electrodes evaporated on to the flat surfaces, made through polishing by the normal procedure.

The d.c. conductivity measurements were made

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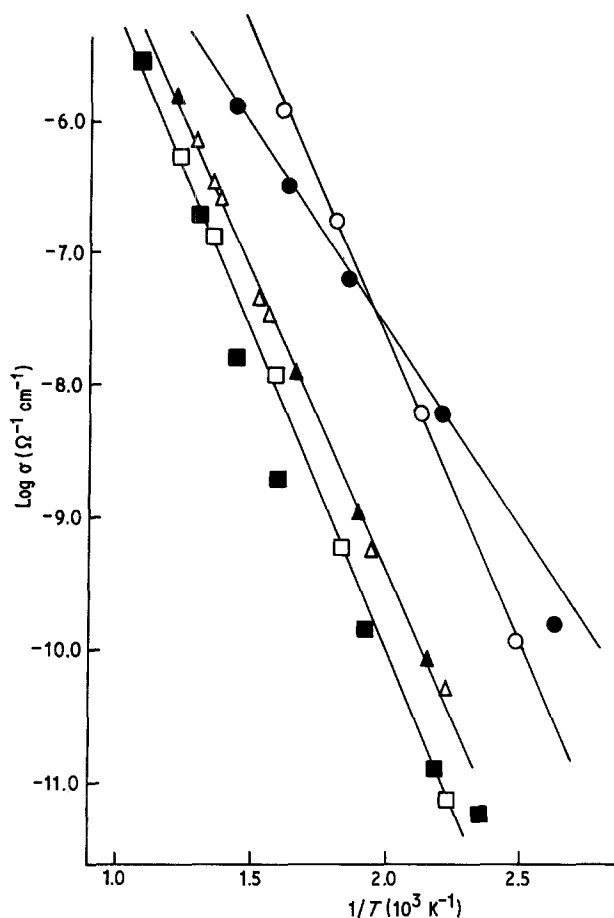‡Present address: College of Ceramic Technology, 73, A.C. Banerjee Lane, Calcutta 700 010, India.

Figure 1 The d.c. conductivity plotted against temperature for the basalt glass heat treated at different temperatures. ($\triangle$) As-annealed, and ($\blacktriangle$) 600°C, ($\blacksquare$) 650°C, ($\square$) 700°C, ($\bigcirc$) 800°C, ($\bullet$) 900°C, for 8 h.
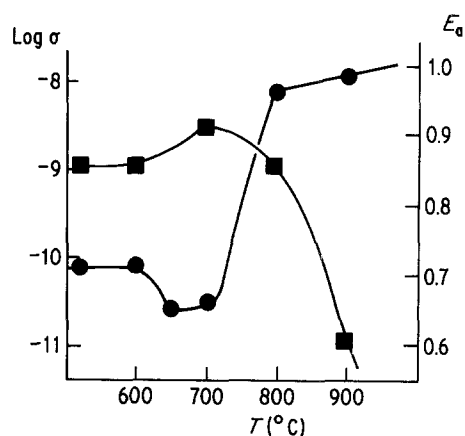

Figure 2 The ($\bullet$) d.c. conductivity, σ, at 473 K and ($\blacksquare$) activation energy, E_a, plotted against heat-treatment temperature.

between 373 and 1000 K using a standard electrometer. The conductivity measurements were also made down to 77 K in some cases. The a.c. conductivity measurements were made as a function of frequency only at room temperature.

3. Results and Discussion

Although $\log \sigma T$ against $1/T$ plots are normally shown to elucidate the small polaron hopping conduction [1], $\log \sigma$ against $1/T$ plots are presented here, as has been done by various other workers [10]. Such plots are shown in Fig. 1 in the temperature range 373 to 1000 K. There is some scatter in the experimental results, but the plots generally give straight lines. No appreciable time-dependent effects were observed during the conductivity measurements, indicating that the conduction is mainly electronic. The activation energy (E_a), calculated from the slopes of these straight lines, varies from 0.88 eV for the as-annealed glass to 0.60 eV for the glass heat-treated at 900°C; E_a for the 700°C sample was found to be 0.93 eV.

It should be noted that $2BaO-3B_2O_3$ glasses containing about 10% Fe_2O_3 showed an activation energy of 0.93 eV [8, 9]. Therefore, the present results could be considered to be consistent with the small polaron hopping between isolated Fe^{2+} and Fe^{3+} ions within the glass matrix for the as-annealed glass.

The samples heat-treated at 700°C for 2 to 32 h do

not show any significant changes in the d.c. conductivity. Therefore, these data are not reported here. However, an abrupt change in the conductivity and activation energy is observed as a function of heat treatment at higher temperatures. The results are shown in Fig. 2, in which $\log \sigma$ at 473 K (i.e. 200°C) and E_a are plotted against the heat-treatment temperature. It is noted that the abrupt changes in both the conductivity and the activation energy take place around 700°C. These changes could be related to the formation of magnetite crystals in the basalt glass.

The Mössbauer parameters (for Fe^{3+}) like isomer shift and quadrupole splitting showed significant changes around 700°C [3, 4]. The minimum quadrupole splitting and the maximum isomer shift observed around 700°C were related to the "improved" symmetry of the magnetite lattice. This was ascribed to the rapid crystallization of magnetite around 700°C. After 700°C, it was also found that the magnetite structure was "disturbed" by other cations (e.g. Ca^{2+}, Mg^{2+}), thereby reducing the symmetry of the magnetite crystals [3].

It should be noted that, while the magnetite crystals are "superparamagnetic" in nature in the samples heat treated at 650 and 700°C, the presence of both "ferrimagnetic" and "superparamagnetic" magnetite crystals were detected in the samples heat-treated at 800 and 900°C, even in the room-temperature Mössbauer spectra. At 4 K, all the spectra except that of the as-annealed glass showed six-line magnetic hyperfine structure due to the "bulk" magnetite below the blocking temperature [3, 4].

The values of saturation magnetization (M_s) at ~ 270 K were also found to show a significant change around 700°C. M_s remained constant between the as-annealed glass and the 600°C sample, then it increased rapidly up to 700°C, after which the increase was less rapid [3–5]. This was ascribed to a cation redistribution process, associated with increasing number and volume of the magnetite crystals [3, 4]. It is plausible to mention that M_s at 300 K increases by about 75% in the case of pure magnetite in the particle size range 20 to 75 nm [11]. But, in the present case, M_s increases by 50% between 650 and 900°C corresponding to a particle size between 4.5 and 7 nm, as estimated by XRD and TEM. This shows the
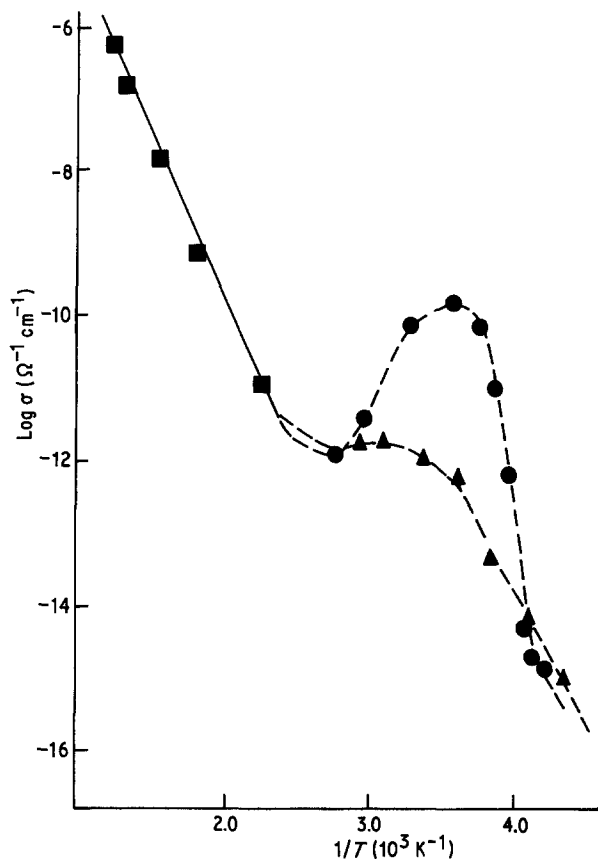
Figure 3 TSPC curves at two different cooling rates for the sample heat treated at 700°C (8 h). (●) 1 K min⁻¹, (▲) 0.35 K min⁻¹.
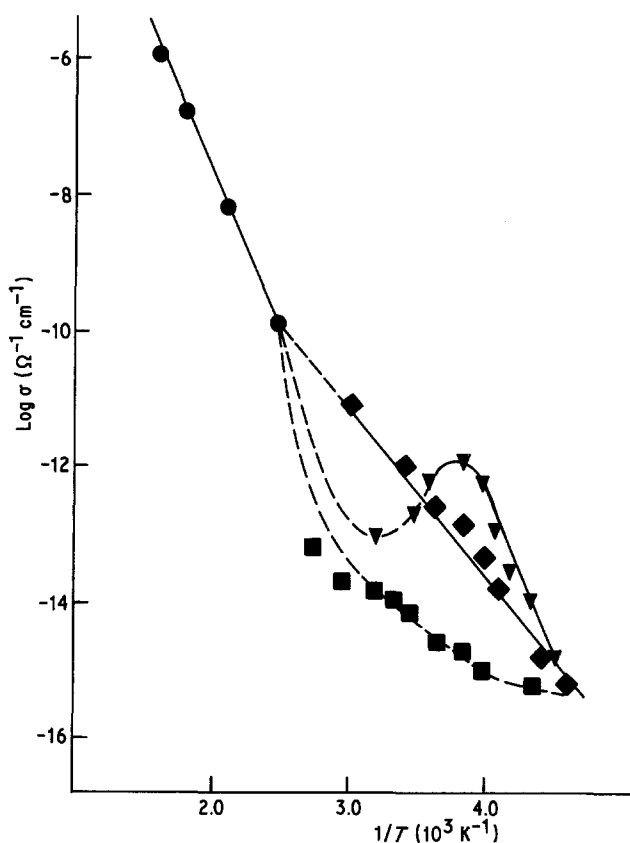

Figure 4 TSPC and TSDC curves at a cooling rate of 1 K min⁻¹ for the sample heat treated at 800°C (8 h). (◆) Cooling, 2 K min⁻¹, (▼) TSPC, 1 K min⁻¹, (■) TSDC, 1 K min⁻¹.

remarkable behaviour of small superparamagnetic magnetite crystals embedded in a glassy matrix.

Finally, it should be remarked that ESR spectra of Fe^{3+} ions showed both $g = 2.0$ and $g = 4.3$ resonances in the as-annealed glass and 600°C sample. The disappearance of $g = 4.3$ resonance for the samples heat-treated at higher temperatures was ascribed to the decrease of the number of isolated Fe^{3+} ions, which have started migrating into the formation of the magnetite crystals. The integrated intensity of $g = 2.0$ resonance was found to increase substantially from about 700°C, due to the proximity of the Fe^{3+} ions, which also indicates that there is a progress in the crystallization of magnetite towards higher temperatures of heat treatment [3, 4].

All the magnetic data, discussed above, show consistency with the electronic conductivity data as a function of heat-treatment temperature (as shown in Fig. 2), i.e. with the progress of crystallization of magnetite.

A structural interpretation can be given to the d.c. conductivity data in correlation with the magnetic data as follows. Below 700°C, the Fe^{2+} and Fe^{3+} ions are mainly in isolated octahedral sites in the glass matrix, and the conduction is via electron (or small polaron) hopping between these ions. The initial nucleation of magnetite in the region 600 to 650°C removes some of the Fe^{3+} ions from the glassy phase, and they are incorporated instead in the magnetite crystals, where they are mainly in tetrahedral coordination. Thus some of the Fe^{3+} ions are in different structural coordination and there are fewer "equivalent" Fe^{2+} and Fe^{3+} sites available for conduction.

However, as the crystallization proceeds with increasing heat-treatment temperature, more and more of the Fe^{2+} and Fe^{3+} sites are created in the magnetite phase, where the ratio of Fe^{2+} and Fe^{3+} ions in similar (octahedral) coordination is optimized and hence the conductivity will increase. The implication is that the easy conduction path is via magnetite crystals. It should be noted, therefore, that the maximum amount of magnetite available for precipitation from the basalt glass is about 2 mol %. However, the magnetite is a good n-type semiconductor with a very low activation energy (~ 0.015 eV), and even a relatively small volume fraction of a crystalline magnetite phase is probably sufficient to cause a substantial change in the conductivity. Furthermore, the increase in the conductivity is not due simply to a decrease in activation energy; the pre-exponential constant (i.e. the intercept of the straight lines in Fig. 1) also changes, which is particularly marked in the sample heat treated at 900°C. This is additional evidence of a change in conduction path.

The measurements of conductivity have also been made at low temperature (down to 77 K), and the results over the whole temperature range are shown in Fig. 3 for the sample heat-treated at 700°C and in Fig. 4 for the sample heat-treated at 800°C. In Fig. 3, the measurements between 77 K and room temperature were made by cooling the sample first *with* a field applied and taking readings as the temperature was raised at a constant rate, i.e. the experiment known as thermally stimulated polarization current (TSPC). The two curves in Fig. 3 correspond to heating rates of 1 and 0.35 K min⁻¹. The results in Fig. 4 also
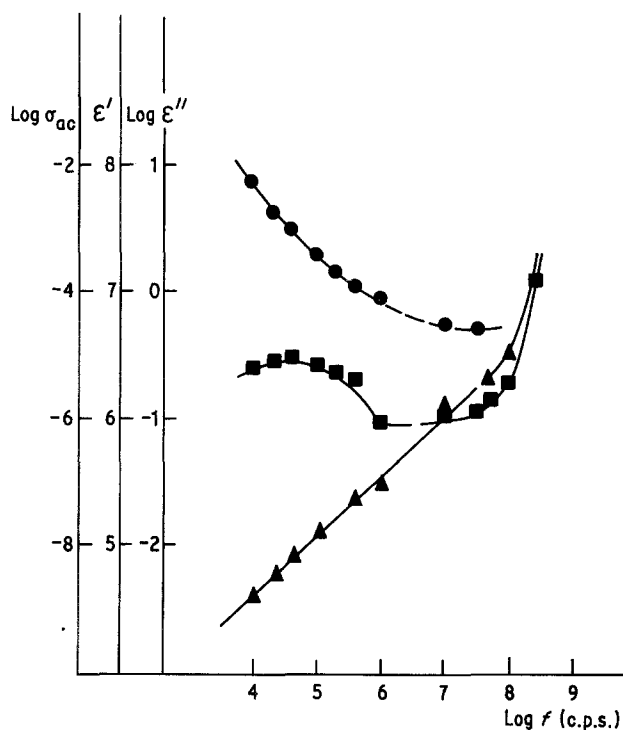
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Figure 5 The a.c. conductivity, dielectric constant and dielectric loss (at room temperature) plotted against frequency for the sample heat treated at 800° C (8 h). (▲) Log $\sigma_{a.c.}$, (■) log ε'', (●) ε'.

Figure 6 The dielectric constant (at 10^5 Hz) against heat-treatment temperature.

indicates the data obtained on cooling, which probably correspond to the "quasi-steady-state", and on reheating at 1 K min^{-1} *without* a field, i.e. the experiment known as thermally stimulated depolarization current (TSDC). Very similar results have been obtained with other samples.

The TSPC and TSDC data in Figs 3 and 4 are similar to those reported in other glasses and dielectrics [12, 13], and are normally related to the trapping and release of charge carriers (ions or electrons). The trapping parameters can be derived from the TSPC and TSDC curves. However, in the present case, the situation may be complicated by the possible occurrence of a Verwey transition in the magnetite phase within the glass matrix. The Verwey transition temperature (T_v) in bulk crystalline magnetite is 119 K [14], i.e. well below the observed peaks in Figs 3 and 4. But, according to Krupyanskii and Suzdalev [11], it should be noted that T_v is a function of crystallite size, and T_v is reported by these authors to be in the range 300 to 350 K in magnetite crystals of about 10 nm. Roggwiller and Kundig [15] have also shown that the Verwey transition is spread over a range of temperatures from 100 K to nearly 300 K in magnetite crystals with a mean size of about 14 nm. Therefore, further experiments are required to separate the possible contributions from non-steady-state thermally-stimulated effects and the Verwey transition in the magnetite crystals.

Typical results of dielectric measurements are illustrated in Figs 5 and 6. In Fig. 5, the a.c. conductivity (log $\sigma_{a.c.}$), the dielectric constant (ε') and the dielectric loss (log ε'') are plotted as a function of frequency for the sample heat treated at 800° C for 8 h; the measurements were only taken at room temperature. It is interesting to note that there are indications of a broad
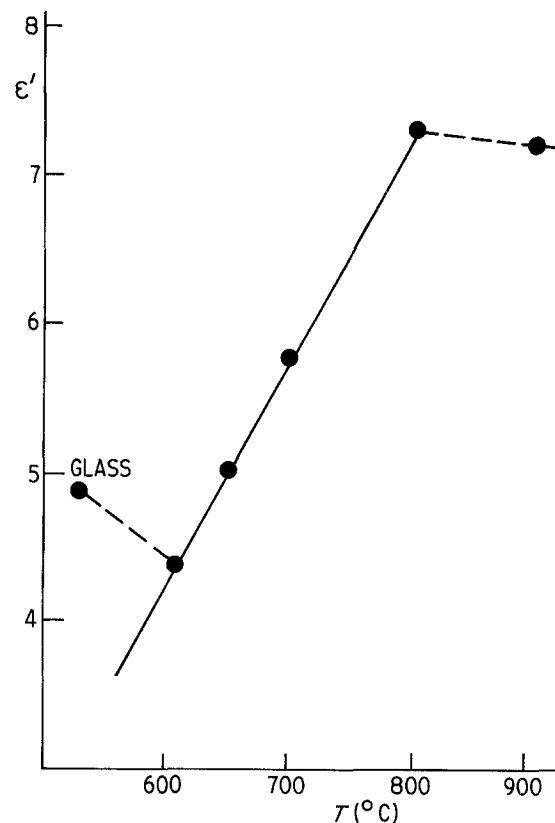
relaxation peak, typical of hopping conduction, centred at about 50 × 10^3 Hz. But more complete data, particularly as a function of temperature, are required for a detailed interpretation. In Fig. 6, the dielectric constant (ε') at 10^5 Hz is plotted as a function of the temperature of heat-treatment, and it is worth noting that the linear variation of ε' with T suggests that the volume fraction of the crystallizing phase (magnetite) is also a linear function of temperature of heat-treatment over the range 600 to 800° C.

4. Conclusion

The d.c. conductivity data are interpreted as being due to the small polaron hopping between the isolated Fe^{2+} and Fe^{3+} ions in the as-annealed glass. With increasing heat-treatment temperature, associated with the formation of magnetite, the hopping can take place between these ions in similar coordination in the magnetite crystals within the glass matrix. The abrupt change in both the conductivity and the activation energy can be correlated with the magnetic data in terms of magnetite formation and possible structural change with increasing heat-treatment temperature. The TSPC and TSDC data cannot be utilized to derive the trapping parameters because of the possible contribution of the Verwey transition. Preliminary a.c. conductivity and dielectric data also indicate that the conduction is by small polaron hopping, but detailed work is necessary to elucidate the relaxation behaviour.

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