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Internal friction in Bi–Sr–Ca–Cu–O glasses

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Abstract

The results of internal friction and d.c. conductivity measurements in Bi_2O_3–CaO–SrO–CuO glasses and partially crystallized glasses are reported. Furthermore, a comparison between the internal friction spectra of superconducting ceramics and those of copper phosphate glasses has been done.

The internal friction measurements were performed by means of low frequency vibrating reed and torsion pendulum methods. A mechanical loss peak observed at 150 K (at 200 Hz) in crystallized glass and bismuth superconducting ceramics can be correlated with the mechanism of the d.c. conductivity in crystallized glass. The comparable value of the relaxation parameters suggests the same mechanism to be responsible for both processes. In the glassy state the internal friction peak observed at about 275 K corresponds to the mechanism of small polaron hopping between copper ions in different valency states (Cu^I–Cu^{II}).

The copper phosphate glass exhibits a mixed electronic–ionic behaviour. The large internal friction peak in the high temperature region can be related to Cu^I ion and proton migration in the glass matrix.

1. Introduction

The properties of Bi_2O_3–CaO–SrO–CuO glass may attract attention when the characteristics of high T_c superconducting ceramics are considered. It has been well confirmed that the crystallization of this glass yields to the formation of superconducting phases [1]. Very little is known about the structure of Bi–Cu glass. This system does not contain a typical glass former. It is presumed that the Bi_2O_3 and CuO oxides play an important role in the forming of glass [2].

Recently Ghosh and Chakravorty [3] have published some experimental results on the electrical properties of the precursor glasses in the high T_c superconducting system Bi–Sr–Ca–Cu–O. The mechanism of the d.c. conductivity can be described as electron or hole hopping between copper ions of different valency states (Cu^I–Cu^{II}). They interpreted the obtained data in terms of the theory of small polaron hopping.

It has been found that a close relationship between electrical conductivity parameters and internal friction peak characteristics exists in glasses containing vanadium or iron oxides [4, 5]. The aim of this paper is to find such a correlation in the glassy and partly crystallized precursors of superconducting high T_c bismuth ceramics.

2. Experimental details

The samples of Bi_2O_3–CaO–SrO–CuO glasses were prepared from reagent grade bismuth oxide, strontium carbonate, calcium carbonate and copper oxide. The chemicals were mixed in the Bi:Sr:Ca:Cu ratio 4:3:3:4. The samples were melted in alumina crucibles at three temperatures, 1150, 1250 and 1350 °C, and then quenched by pressing the cast liquid between two steel plates.

The Cu^I and total Cu contents were determined by the method described by Zheng *et al.* [6].

In the low temperature range (from 20 to 250 K) the internal friction measurements were performed by the vibrating reed technique. The frequency excited was about 200 Hz. The samples had the shape of a thin plate (30 mm × 5 mm × 0.3 mm). The amplitude of oscillations was about 10 μm, which corresponds to a strain amplitude of 5×10^{-6}. In the high temperature range the internal friction measurements were performed on fibre samples (15–30 mm in length) by a torsion pendulum method at frequencies from 10 to 30 Hz. The temperature was raised from 170 to 550 K at a heating rate of 1 K min^{-1}.

3. Results and discussion

A representative phosphate glass containing copper exhibits a very low conductivity with a high activation

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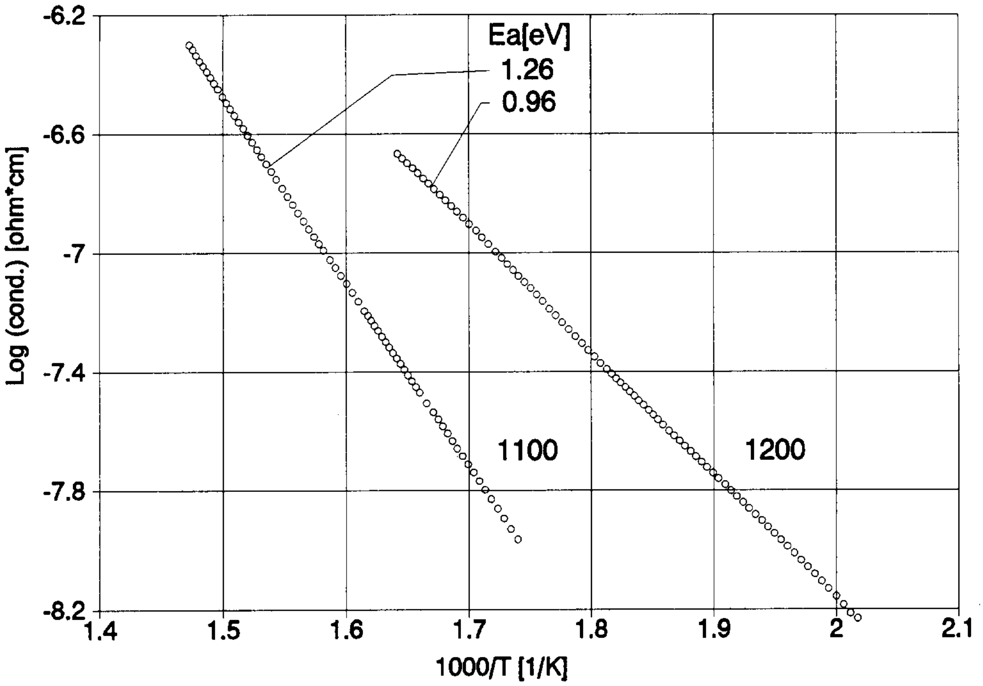

Fig. 1. Log (conductivity) *vs.* 1000/*T* for two samples of 50P_2O_5–50CuO glass melted at 1100 and 1200 °C respectively.

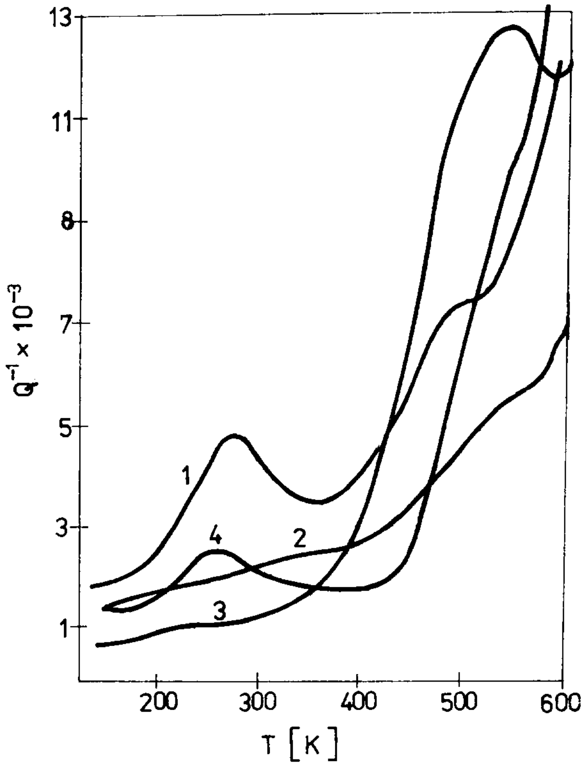

Fig. 2. Internal friction spectra of various glasses: 1, 50P_2O_5–50FeO; 2, 50P_2O_5–50CaO; 3, 50P_2O_5–50CuO; 4, $Bi_4Sr_3Ca_3Cu_4O_x$.

energy (greater than 1 eV) and is usually of poor chemical durability [7]. Copper ions in glass melted above 1100 °C coexist in two valence states, Cu^I and Cu^{II}. However, phosphate glasses melted in a neutral atmosphere contain only a small amount of Cu^I ions. Usually the ratio $c = Cu^I/Cu_{total}$ is rather small (around 0.1) and does not depend on the total amount of copper oxide in the glass, unless a reducing agent is introduced during melting [7].

It is confirmed that copper phosphate glass exhibits a mixed electronic–ionic behaviour because copper(I) ions can act as ionic diffusion elements [8]. The high value of the activation energy (about 1 eV) of the d.c. conductivity (Fig. 1) is indicative of the domination of ionic diffusion in the conduction process. It corresponds to a large internal friction peak existing in the high temperature (about 550 K) region (Fig. 2). The relaxation parameters of this peak are an activation energy of 1.1 eV and a relaxation time $\tau_0 = 10^{-15}$ s. The maximal friction amplitude is much higher than usually observed in other phosphate glasses [4, 5, 9]. Van Ass and Stevels [9] have proposed that this process is a result of proton migration, it is very likely that in copper phosphate glass the migration of Cu^I ions coexists with that of protons. We have observed no peak which could be a result of electronic hopping between Cu^I and Cu^{II} ions. This is in contrast with the behaviour of iron or vanadium phosphate glasses [10] and probably results from the small ratio $c = Cu^I/Cu_{tot}$ (we found 0.017 and 0.085 respectively for glasses melted at 1100 and 1200 °C). The latter implies that the number of polarons is also small and hence the polaron-induced peak is not visible in internal friction spectra.

In contrast with the phosphate glasses, the Bi–Sr–Ca–Cu–O glass (Fig. 3) exhibits a typical elec-

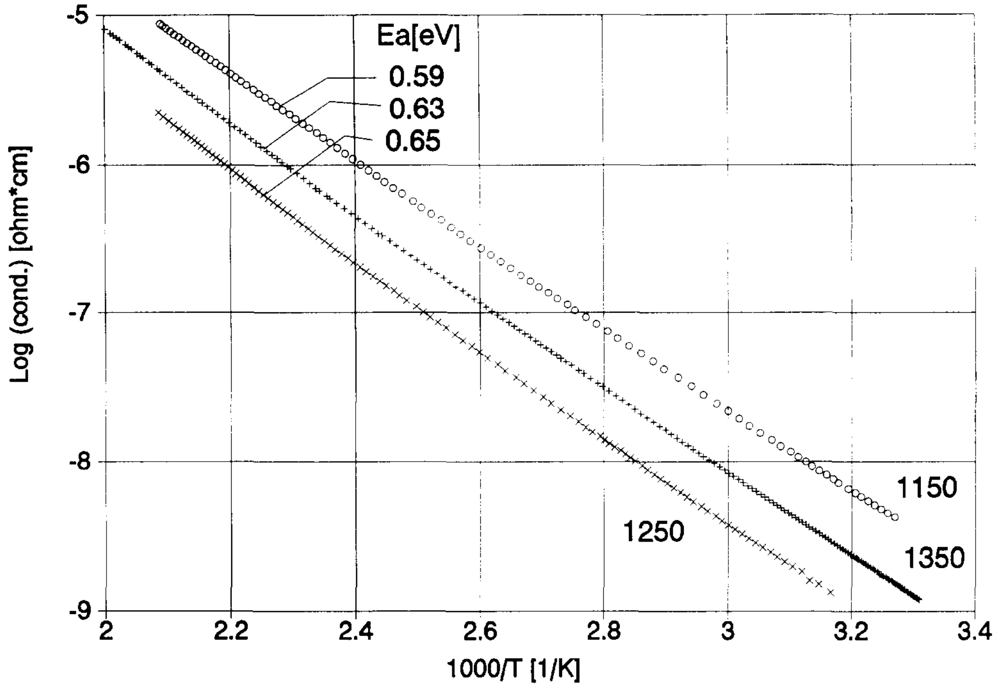

Fig. 3. Log (conductivity) *vs.* 1000/*T* for $Bi_4Sr_3Ca_3Cu_4O_x$ samples melted at various temperatures.

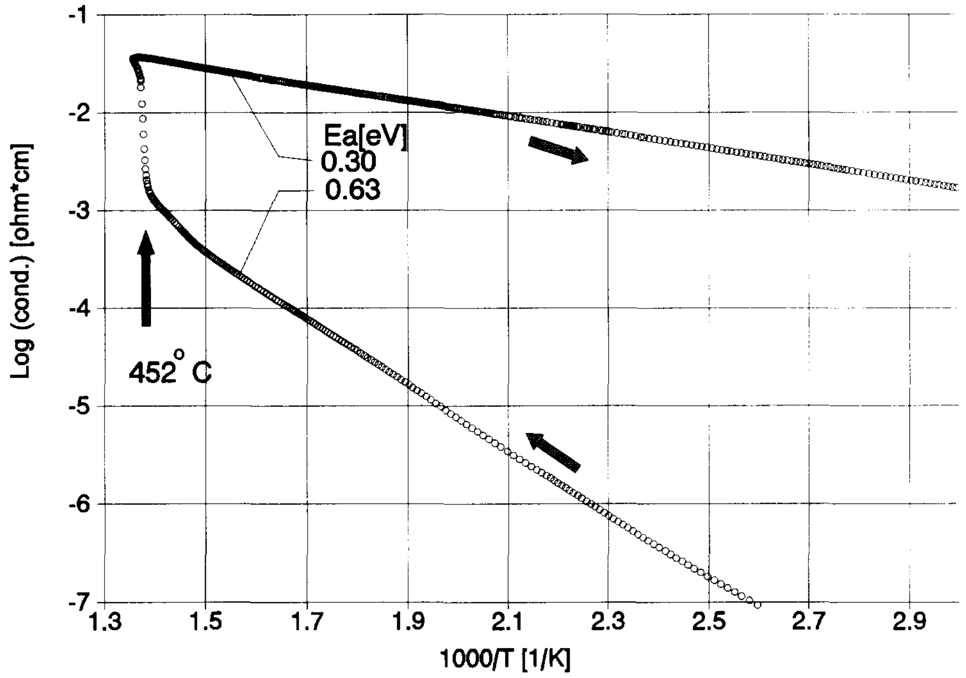

Fig. 4. Change in conductivity of $Bi_4Sr_3Ca_3Cu_4O_x$ glass during crystallization.

tronic d.c. behaviour. For this system it is easy to produce glasses with a high concentration of copper(I) ions. Depending on the melting condition, it is possible to obtain glasses with the ratio $c = 0.4–0.98$ [6, 11]. The activation energy of the d.c. conductivity is much lower (0.59–0.65 eV) and is comparable with that of phosphate glass containing a high amount of iron [12]. In Bi–Sr–Ca–Cu–O glass the electron transfer takes place between Cu^I and Cu^{II}. As shown by Ghosh and Chakravorty [3], the results of the d.c. conductivity are consistent with a model of phonon-assisted hopping of small polarons in the non-adiabatic regime. In the internal friction spectrum (Fig. 2) obtained by the torsion pendulum method we have observed a low temperature peak of corresponding activation energy which may result from electron or hole hopping between transition metal ions of different valency states.

Figure 4 shows the change in conductivity of $Bi_4Sr_3Ca_3Cu_4O_x$ glass during crystallization. The crystallization occurs at 452 °C, which agrees fairly well with differential thermal analysis (DTA) results. The transition is displayed in Fig. 4 by a sharp increase in conductivity. After crystallization a quite different d.c. behaviour is observed upon decreasing the temperature again. The conductivity is several orders of magnitude higher than in the glassy state and the activation energy is significantly lower (about 0.30 eV). It is well known [13] that the first phase which forms during the crys-

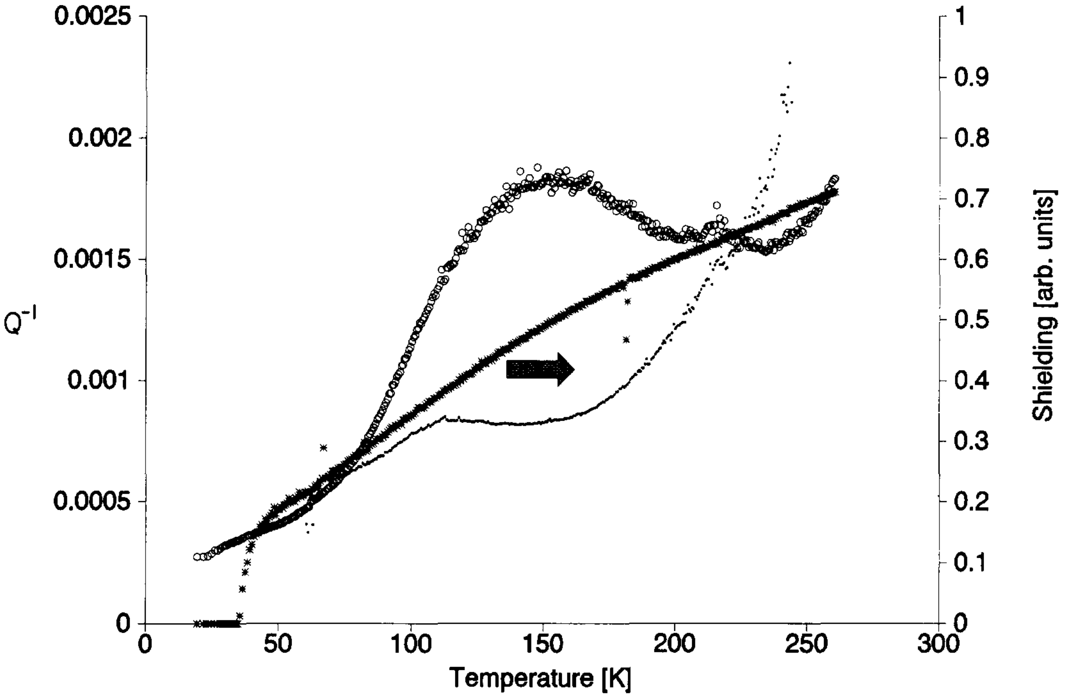

Fig. 5. Internal friction spectra of virgin (●) and partially crystallized (○) $Bi_4Sr_3Ca_3Cu_4O_x$ samples. The shielding effect of a crystallized sample is also shown (∗).

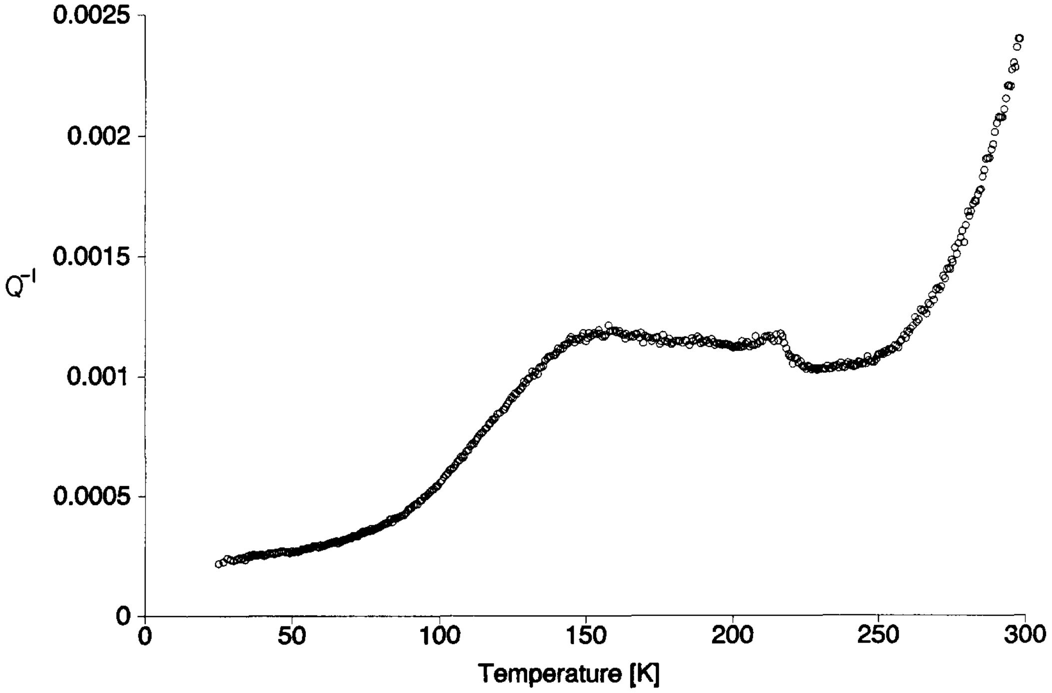

Fig. 6. Internal friction spectrum of a superconducting 2:2:1:2 bismuth ceramic.

tallization of Bi-based glass is the $Bi_2Sr_2CuO_6$ compound.

Because partially crystallized Bi–Cu glass is a good semiconducting material, it is interesting to investigate the correlation between d.c. conductivity and internal friction. It may give some evidence to determine the origin of the internal friction peaks that have been found in superconducting bismuth ceramics in the low temperature region.

Figure 5 shows the internal friction spectrum obtained by the vibrating reed technique in partly crystallized $Bi_4Sr_3Ca_3Cu_4O_x$ glass, which exhibits a superconducting transition (visible in the shielding effect curve) at a temperature of about 20 K, most probably due to the $Bi_2Sr_2CuO_6$ phase. The internal friction relaxation peak at 150 k has also been observed in the superconducting ceramics (Fig. 6) [14] of the bismuth family. Its activation energy is estimated as 0.30 eV (the relaxation time τ_0 is of the order of 10^{-12}), which corresponds closely to the activation energy of the d.c. conductivity. In virgin glass this peak is very weak or not visible at all (see Fig. 5). The similarity of the activation energies suggests that the same mechanism associated with the charge transfer is responsible for both processes.

The change in the activation energy during crystallization indicates a different mechanism of charge transport that appears in non-homogeneous, partially crystallized glass. We suppose that this mechanism may be due to the formation of metallic crystallites of the 2201 phase and that the conduction is due to electron transfer between these crystallites. A similar behaviour has been observed in lead silicate glasses after partial reduction in hydrogen. It is confirmed that the conduction in these glasses is due to tunnelling of the electrons between lead crystallites [15]. We have also observed a similar change in conductivity in partially crystallized V_2O_5–GeO_2 glass, where the crystalline phase is semiconducting V_2O_5 [16].

4. Conclusions

Bi–Sr–Ca–Cu–O glass exhibits a typical electronic d.c. behaviour. In the glassy state the peak in the internal friction observed at about 275 K corresponds to the mechanism of small polaron hopping between copper ions in different valency states (Cu^I–Cu^{II}). The crystallization is observed as a sharp jump in conductivity just at the temperature which is expected from DTA results. The mechanical loss peak observed at 150 K in crystallized glass and superconducting bismuth ceramics can be correlated with the mechanism of the d.c. conductivity. The similar value of the activation energies suggests that both phenomena can be attributed to the same mechanism associated with the charge transfer between granules of the metallic phase.

Copper phosphate glass exhibits a mixed electronic–ionic behaviour. The large internal friction peak in the high temperature range is related to Cu^I ion and proton migration in the glass matrix.

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