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Anelastic spectroscopy in potassium aluminum metaphosphate glasses

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Abstract

Anelastic spectroscopy (internal friction and the dynamic modulus) was measured by means of a torsion pendulum at 3–12 Hz, in the range of 100–300 K, for a KAP metaphosphate glass. Two thermally activated internal friction peaks appeared at ~190 and ~250 K. These peaks were attributed to the behavior of potassium ions (high temperature) and to hydrogen (low temperature). Dynamic modulus showed a gradual decrease with increasing temperature in the range studied for all compositions.

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1. Introduction

Phosphate glasses, especially alkali metaphosphate, have a low melting temperature and a special thermal expansion coefficient compared to most silicate glasses. These properties, and some optical characteristics, make these glasses a potential option for a variety of technological applications, such as sealing materials, high-power lasers, medical uses, dosimetric uses and solid-state electrolytes [1–3]. However, the development of devices based on phosphate glasses is often limited by their relatively poor chemical durability. Several investigations have shown that the addition of aluminum oxide improves the chemical durability of phosphate glasses [1,4].

Anelastic spectroscopy measurements are an important tool in the study of materials. This measurement determines precisely the frequency of jumps of an atomic species, regardless of the model or of the possible different types of jumps. In fact, the type of jump is selectively determined. A peak in the spectrum of the elastic energy loss, as a function of temperature, appears in the temperature range in which a particular type of atomic jump occurs at a rate of 2π times the frequency of sample vibration [5,6]. The temperature trajectory of the elastic energy absorption spectrum allows for the determination of the occurring relaxation process [7].

In this paper, internal friction and the dynamic modulus of metaphosphate glasses were investigated by a torsional vibration method for KAP50 glass.

2. Experimental details

In conventional low-frequency internal friction measurements, the sample is placed in order to present vibrations at a fixed frequency, and the temperature of the sample is changed so that mechanical relaxation can be observed. An inverted torsion pendulum composed of a thin plate sample is used, and an initial vibration is induced in the sample by dc magnetic excitation at a constant frequency. The phase difference, δ, between the external force and the induced deformation of the sample is measured in order to determine the internal friction (Q^{-1}) of the sample [5]. This method is used when the internal state of the sample can be altered, as in the case of temperature changes.

The anelastic relaxation (internal friction) measurements were carried out in an inverted torsion pendulum, operating at a frequency range between 3 and 12 Hz, strain

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amplitude less than 10^{-4} and temperature range between 100 and 300 K [8]. This technique allows the measurement of the dynamic modulus (related to the oscillating frequency) and the internal friction (the elastic energy loss, Q^{-1}) as a temperature function. The internal friction is determined by the free decay method [5]:

$$Q^{-1} = \tan\delta = \frac{1}{N}\ln\frac{A_o}{A_N}, \tag{1}$$

where N is the number of oscillating cycles, and during which the amplitude decreases from A_o to A_N.

From the measurements of oscillating frequency f, the dynamic shear modulus G can be obtained from the ratio [5]:

$$f = \frac{1}{2\pi}\sqrt{\frac{\pi G b^4}{32 l I}}, \tag{2}$$

where b and l refer to the thickness and length of the sample and I refers to the inertia of the rotating equipment.

In the internal friction measurements, an anelastic relaxation phenomenon gives rise to an internal friction peak and a modulus defect. The peak height and the amplitude of the modulus defect are related to the concentration of relaxing entities and the peak position is determined by their mobility. For pure Debye relaxation, the peak height is half of the modulus defect [5].

Potassium aluminophosphate (KAP) glasses in the metaphosphate compositions $x\mathrm{KPO_3} - (100 - x)\mathrm{Al(PO_3)_3}$, in which $x = 10$, 30, 50 (mol%), were prepared by melting an appropriate mixture of analytical grade precursors, KH_2PO_4 (KDP) crystals and $Al(PO_3)_3$, in an open platinum crucible heated in an electric furnace. The glass of compositions $x = 50$ mol% will be hereinafter referred to as KAP50. The mixtures were heated from 1000 °C to 1250–1450 °C, depending on the composition, at a heating rate of approximately 15 °C/min in air atmosphere. The melts were stirred from time to time and were held at the fusion temperature for 35 min. Each melt was then cast into a graphite mold to form glass cylinders and was annealed at 450 °C for 15 h. A slight chemical attack from the platinum crucibles was found, but the glass samples proved to be free of Pt inclusions when analyzed by optical microscopy. The KAP50 samples used were thin plates of dimensions: $30 \times 3 \times 1$ mm^3.

Differential thermal analysis (DTA) measurements (2910 TA instruments, platinum crucible) were carried out on undoped glass ground in an agate mortar and screened to a particle size of 90–180 μm in order to determine the range of thermal stability of the glass against devitrification. The data were obtained in a synthetic air atmosphere at a gas flux of 80 ml/min.

3. Results

The DTA curves of the KAP glasses were obtained at a heating rate of 3 °C/min and the characteristic temperatures are shown in Table 1. The improvement in the $Al(PO_3)_3$ quantity in the glass produced an increase in the glass transition temperature (T_g), since Al^{3+} ions increase the bonding strength between phosphate chains [4]. The parameter $\Delta T = T_x - T_g$, which is widely used as a quantitative scale for assessing the resistance of glass against devitrification, was higher than 100 °C, indicating that the glasses present good thermal stability. No traces of water adsorption on the glass surfaces were observed after several days of exposure to environmental humidity.

An anelastic relaxation spectrum for KAP sample is shown in Fig. 1, measured at the approximate frequency of 12 Hz. Two relaxation peaks at ~190 and 250 K can be observed. The dynamic modulus decreases slightly with temperature, at least in this measured temperature range.

In order to verify if the anelastic relaxation processes observed in the KAP glass are thermally activated, the internal friction was measured with another two frequencies and the results are also shown in Fig. 1, in which it can be observed that the peaks move to the high temperature zone when the frequency is increased: i.e., the observed relaxation processes are thermally activated.

The linear response of non-crystalline solids under mechanical stress has been extensively investigated by means of mechanical spectroscopy (internal friction measurements). Such a technique allows for the determination of the evolution of the dynamic shear modulus G versus temperature at a fixed frequency (temperature scan). These measurements clearly demonstrate the presence of mechanical relaxation processes, manifested by a decrease in the dynamic modulus, associated with a maximum value in internal friction.

Table 1
Thermal properties of the KAP metaphosphate glasses indicated by the DTA curves

Sample (mol%)	T_g (°C)	T_{x1} (°C)	T_{x2} (°C)	$\Delta T = T_{x1} - T_g$ (°C)
$x = 10$	594	860	908	156
$x = 30$	528	719	740	191
$x = 50$	467	609	670	142

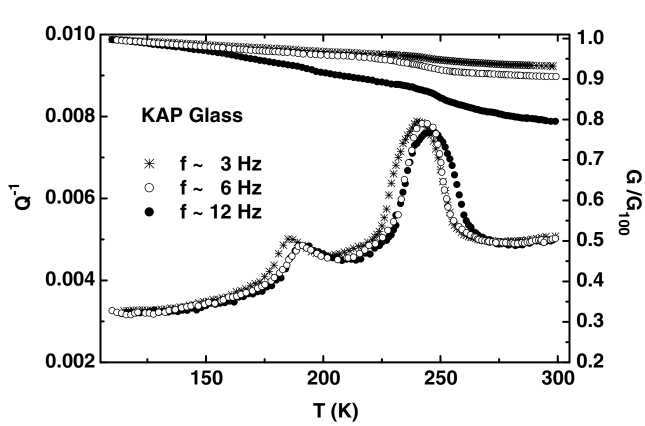

Fig. 1. Internal friction and dynamic modulus as a function of temperature for KAP glasses measured at three different frequencies.