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Journal:	*Philosophical Magazine & Philosophical Magazine Letters*
Manuscript ID:	TPHM-08-May-0180.R1
Journal Selection:	Philosophical Magazine
Date Submitted by the Author:	26-Jun-2008
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Keywords:	amorphous solids, dilatometry, fast ion conductors, glass, inorganic glasses, ionic conductors, mechanical properties, thermal expansion
Keywords (user supplied):	molybdate glasses, silver iodide

Philosophical Magazine,
Vol. XX, No. XX, Day Month Year, xxx-xxx

Experimental study of the thermal expansion of $(AgI)_{0.67}(Ag_2MoO_4)_{0.33}$ ionic glass from 5 K to 300 K

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(*Submitted 21 May 2008. Revised version submitted 27 June 2008*)

The thermal expansion of the ionically conducting silver iodide – silver molybdate glass $(AgI)_{0.67}(Ag_2MoO_4)_{0.33}$ has been investigated from low temperatures up to about the glass transition region using a capacitance dilatometer with a quasi-adiabatic method. The results do not show any anomalous behaviour in a temperature range where the existence of relaxation processes with peculiar features was previously revealed using mechanical spectroscopy, but rather a monotonic increase of positive values of the thermal expansion coefficient.

1. Introduction

The knowledge of the physical properties of solid electrolytes plays an important role in relation with the development of new solutions for energy storage and conversion. Among the oxide glasses studied as solid state ionic conductors, the class of silver molybdates with high content of silver iodide has received attention because of the high ionic conductivity [1,2], comparable to that of ionic liquids at room temperature. The $(AgI)_{1-x}(Ag_2MoO_4)_x$ system exhibits a narrow glass formation range, $0.2 < x < 0.4$ [3,4]. Outside this range vitreous-ceramic materials are obtained in which the glassy phase corresponding to the molar ratio 2:1 (i.e. to the composition $x = 0.33$) coexists with crystalline units of the species in excess. As in other ionic glasses, a mechanical relaxation associated with the dynamics of mobile ions occurs in the silver iodomolybdate glasses well below their calorimetric glass transition temperature, T_g [5,6]. In fact a relaxation of the sound velocity at ultrasonic frequency is observed, producing a sigmoidal-like increase of the speed of sound as the temperature is decreased. Moreover the coefficient of acoustic attenuation exhibits a peak as a function of temperature in the same temperature range in which the sudden change of the sound velocity occurs. The mechanical loss peak in $(AgI)_{1-x}(Ag_2MoO_4)_x$ glasses is however peculiar because it seems clearly arising from the superposition of two different, almost overlapping, relaxational contributions. The origin of this behaviour is probably related to the existence of different kinds of local environment for silver ions, that would lead to Ag^+ populations of different mobilities [3,6]. In fact the addition of Ag_2MoO_4 to AgI causes the formation of oxy-iodide structures, –O–Ag–I– , so

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that some –O–Ag–I–Ag–O– bridges can form between the MoO_4^{2-} molecular ions, instead of the –O–Ag–O– structures [3,7,8]. Recently, also EXAFS measurements have been devoted to study the thermal dependence of the molybdenum and iodine local environment in molybdate glasses [9,10,11]. However the link between these details of the microscopic configuration and the unusual properties of the observed sub-T_g macroscopic mechanical relaxation still needs to be clarified. Furthermore, it is not known if some anomaly of the thermal expansivity, as those reported for molybdate crystals [12] and for some ionically conducting oxide glasses [13,14], could occur in correspondence with the relevant features of the mechanical response. On the other hand, the knowledge of the thermal expansion coefficient of solid state electrolytes as a function of the temperature is fundamental for practical purposes, related to the construction and use of electrical and electronic devices for operation in hard environmental conditions (aerospace applications, cryogenic systems). On this basis, in the present work the linear thermal expansion coefficient of the $(AgI)_{0.67}(Ag_2MoO_4)_{0.33}$ glass has been studied with a quasi-adiabatic method, using a capacitance dilatometer in combination with a high precision capacitance bridge, achieving a resolution of 10^{-10} m on the absolute length changes in the temperature range between 300 K and 5 K. The results allowed to characterize the thermal response of the material from low temperatures up to about the glass transition region and provided useful information for the comparison with the relevant features previously revealed by different techniques.

2. Experimental section

2.1 Samples. Samples of the $(AgI)_{0.67}(Ag_2MoO_4)_{0.33}$ glass were obtained by quenching of a melt containing AgI and Ag_2MoO_4 in stoichiometric proportions. The mixture of purified reagents was melted at 600°C for 2 h in alumina crucibles and then quenched in brass moulds. A test to detect the possible existence of crystalline patterns was carried out using the x-rays-diffraction technique on a powdered sample. The glass transition temperature of the material, determined by differential scanning calorimetry, is 50 °C [3,4]. Considering also that T_g is not far above room temperature, the samples were kept in a dry dark container at about 4 °C in order to slow down the possible structural relaxation. The samples for thermal expansion measurements were cut as rectangular prisms, ~ 23 mm long, with flat and parallel bases, carefully polished.

2.2 Measurement setup. The measurement cell, realized as in refs. 15 and 16, consists of a parallel-plate empty capacitor with guard ring electrode. The lower capacitor plate rests on the upper base of the sample and is held against it by suitable springs. In this way, changes of the sample length L are simply related to changes of the distance d between the capacitor plates, being $\Delta L = -\Delta d$. Little spacers made of 0.2 mm thick Pyrex glass were placed between the lower electrode and the upper end of the sample with the aim of providing electrical insulation of the electrode from the ground potential. Three Pyrex spheres were allocated between the metallic plate on which the lower end of the sample rests, and the basis of the cell framework. The electric capacity of the parallel-plate capacitor was measured by a precision capacitance bridge, AH2500A (Andeen-Hagerling). A silicon diode for the measurement of the temperature and a small-size resistor, to be used as heater, were attached to a side wall of the sample. Another silicon diode and a heater were pasted on the framework of the dilatometric cell, made of Invar. A LakeShore 321 temperature controller was used to keep the cell framework at a selected temperature, that could be higher than that of the surrounding copper container. The setup was inserted in an

outer copper container that allowed to create an intermediate volume between the cell and the external liquid helium reservoir. High vacuum, or a little controlled pressure of Helium gas, could be established in that intermediate chamber.

2.3 Basic relations. Changes in the length of the sample as a function of temperature were detected through the corresponding changes of the capacity of the three-terminal parallel-plate capacitor. If A is the area of the capacitor plates, the capacity C is given by $C = \varepsilon_0 A / d$, from which

$$d = \varepsilon_0 A / C \tag{1}$$

From this relation it follows that $\ln(d) = \ln(\varepsilon_0 A) - \ln(C)$, and $\Delta d/d = -\Delta C/C$. Thus a high sensitivity of the method for detecting small fractional changes of the distance d between the electrodes can be achieved if the capacity can be measured with high resolution. Exploiting equation (1), one has

$$\Delta d = -\varepsilon_0 A \frac{\Delta C}{C^2} \tag{2}.$$

Therefore,

$$\Delta L = \varepsilon_0 A \frac{\Delta C}{C^2} \tag{3}$$

From the definition of the linear thermal expansion coefficient, α, according to eq. (3) it follows that

$$\alpha \equiv \frac{1}{L}\frac{\Delta L}{\Delta T} = \frac{\varepsilon_0 A}{L}\frac{1}{C^2}\frac{\Delta C}{\Delta T} \tag{4}$$

The values of α were obtained experimentally using a quasi-adiabatic method described in the following text.

2.4 Quasi-adiabatic method. The temperature of the measurement cell was kept constant while the sample temperature was increased by a discrete amount. The size of the temperature step was chosen depending on the sample expansivity and on the temperature range, so that temperature steps were about 1-3 %. The capacitance of the dilatometric cell, as well as the temperature of the cell and the temperature of the sample, were recorded continuously as a function of the elapsed time, as shown in figure 1. After a few temperature steps of the sample temperature, the temperature of the dilatometric cell was increased as well, in order to avoid large differences between the cell temperature and the sample temperature. The thermal expansion coefficient can be directly obtained from eq. (4), using the corresponding equilibrium values for temperature and capacitance changes.

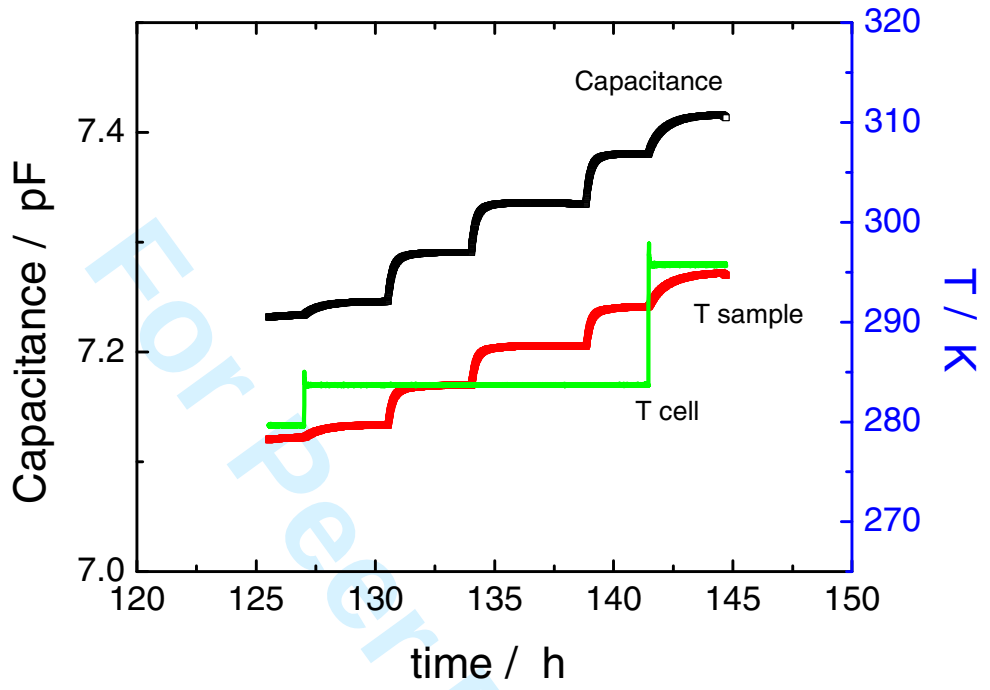

Figure 1. (Color online) Plot of the relevant quantities measured during a typical thermal expansion experiment with the quasi-adiabatic method: capacitance of the parallel-plate capacitor, temperature of the measurement cell and temperature of the $(AgI)_{0.67}(Ag_2MoO_4)_{0.33}$ glass sample as a function of time.

3. Results and discussion

The values of linear thermal expansion coefficient α for the silver iodide – silver molybdate glass $(AgI)_{1-x}(Ag_2MoO_4)_x$, with x = 0.33, are shown in figure 2 as a function of temperature between 300 K and 5 K. The thermal expansion coefficient of the molybdate glass is positive in the whole temperature range investigated in this work, notwithstanding evidence of negative thermal expansion has been provided for different molybdate crystals [12] as well as for different ionic glasses, such as silver phosphate glasses [13,14], and rare earth metaphosphate glasses [17]. As can be seen in figure 2, the slope of the thermal expansion coefficient is higher in the low temperature range, 5 K – 50 K, than at higher temperatures: a 'knee' occurs around 70 K. The temperature dependent behaviour of thermal expansion, including the occurrence of such evident change of the slope, is similar to that usually observed in glasses and crystals [17]. It approximately follows the behaviour of the specific heat [18] and is governed essentially by the Debye-like phonon contributions. The absolute values of thermal expansion are larger than those observed in other oxide glasses (phosphates [14,17], borates [19], silicates [20]) in the same temperature region. Aiming to establish a comparison with the unusual properties of the mechanical response at ultrasonic frequencies [5,6], it should be pointed out that the results of the present investigation rule out the existence of anomalous features (such as possible

negative values) of the thermal expansion coefficient in the temperature range in which the mechanical relaxations occur in the same glass. On this basis we expect that the peculiar pattern of the ultrasonic attenuation as a function of temperature is definitively not associated with thermal expansion anomalies. Additional information on the thermal expansivity of silver iodide – silver molybdate compounds within the glass formation region and the comparison with the results obtained using a different measurement method will be reported elsewhere [21].

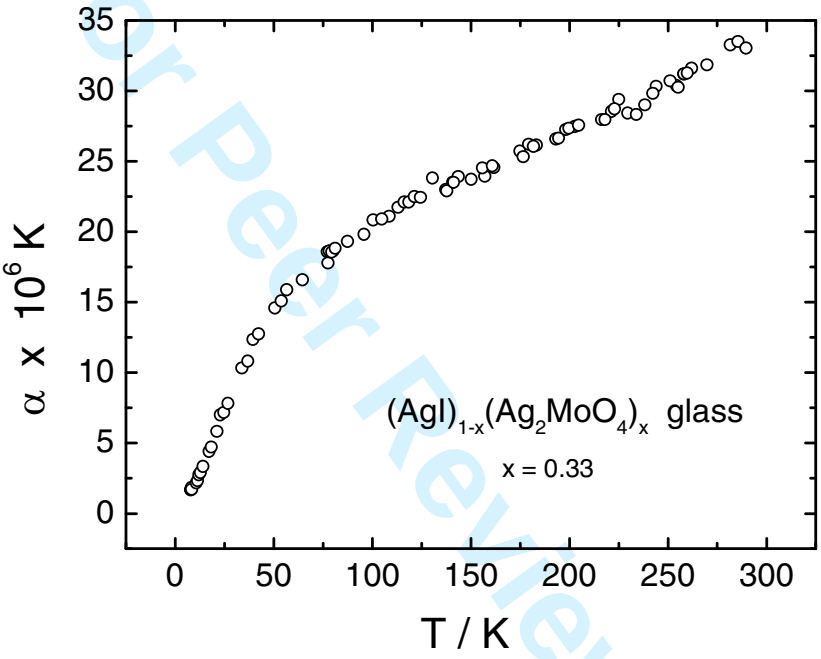

Figure 2. Experimental values of thermal expansion coefficient for the $(AgI)_{0.67}(Ag_2MoO_4)_{0.33}$ glass between 5 K and 300 K obtained using the quasi-adiabatic measurement method.

4. Conclusions

The macroscopic linear thermal expansion coefficient of the silver iodide / silver molybdate glass $(AgI)_{1-x}(Ag_2MoO_4)_x$, x = 0.33, was obtained by means of a capacitance dilatometric cell, using a quasi-adiabatic method, in the temperature range between 5 K and 300 K. The results do not show any anomalous behaviour that could be related to the peculiar pattern of the ultrasonic attenuation in the same glass, revealed by previous investigations. Only positive values of the thermal expansion coefficient have been detected in the whole temperature range, while on the contrary the existence of negative thermal expansion was reported in the literature in the case of molybdate crystals and silver based ionic glasses.

Acknowledgments

This work was partially supported by the Spanish Ministery of Education and Science within project FIS2006-01117. The authors thank gratefully Andres Buendia for his help with the experimental equipment and Dr. Francesco Rocca for fruitful discussion.

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