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Thermal expansion of silver iodide-silver molybdate glasses at low temperatures

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Ionic glasses obtained combining silver iodide and silver molybdate are characterized by quite low values of the glass transition temperature T_g around 320–350 K, by high values of the dc ionic conductivity even at room temperature and by a peculiar behavior of the mechanical response at ultrasonic frequencies. In fact, at temperatures well below their glass transition temperature, these glasses exhibit an intense peak of acoustic attenuation well described by two different and almost overlapping relaxational contributions. Considering also that negative thermal expansion has been reported for some molybdate crystalline compounds, we have investigated in this work the thermal expansion of two silver iodomolybdate glasses $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ for $x=0.25$ and $x=0.33$ in a wide temperature range (4.2–300 K) from cryogenic temperatures up to some 20 K below T_g using a precision capacitance dilatometer aiming to understand whether the expansivity shows some possible fingerprint corresponding to the above-mentioned mechanical response. Two different measuring methods, a quasiadiabatic and a continuous one, have been used for the thermal expansion measurements. The results are discussed in comparison with the information obtained from previous investigations based on the extended x-ray absorption fine structure (EXAFS) technique and with the behavior of other ionic glasses. © 2009 American Institute of Physics. [DOI: 10.1063/1.3139450]

I. INTRODUCTION

The addition of silver iodide to different glassy matrices, like for instance silver borate glasses or silver phosphate glasses, has been often exploited to obtain glassy materials with enhanced ionic conductivity.¹ An interesting case is that of silver molybdate-silver iodide glasses

$(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ is characterized by high ionic conductivity² comparable to that of ionic liquids at room temperature. The glass transition temperature T_g of these solid electrolytes is quite low in the 45–75 °C range³ and correspondingly also low values of the longitudinal elastic modulus have been reported.⁴ As in other ionic glasses, a mechanical relaxation occurs below T_g : The temperature dependent profile of acoustic attenuation at ultrasonic frequencies shows a peak while the sound velocity relaxes toward higher values at lower temperatures.^{4,5} This kind of secondary relaxation occurring entirely in the glassy state is usually associated with the activated hopping of mobile ions in the glass matrix.^{6,7} Nevertheless, for the $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ glasses, the peak in acoustic attenuation results from two different and almost overlapping relaxational contributions.⁸

This unusual feature has been ascribed to the possible existence of two different kinds of local environments at microscopic level for silver ions in the glassy matrix, which would induce different mobilities of such cations. This hypothesis is supported by a previous investigation based on the nuclear magnetic resonance (NMR) technique, according to which different I/O ratios are dynamically experienced by the Ag^+ ions in the silver iodide-silver molybdate glasses.³ On the other hand, the occurrence of negative thermal expansion has been reported for a large family of molybdate compounds.^{9,10} Moreover, it has been observed that the average I–Ag distance measured by extended x-ray absorption fine structure (EXAFS) on the same $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ glasses decreases as the temperature increases from low temperatures (25 K) up to T_g .¹¹

In the present work, we want to shed light on those issues by trying to answer the following questions: (i) Is the observed unusual mechanical response related to possible features of the temperature-dependent thermal expansion coefficient? (ii) Do silver iodomolybdate glasses show a negative thermal expansion? (iii) Do different compositions of glasses have a significant influence on the expansivity? With such an aim, we have measured the thermal expansion coefficient of $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ glasses with different composition ($x=0.25;0.33$) between 4.2 K and temperatures

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slightly below the glass transition temperature $T_g \approx 50^\circ\text{C}$ using a precision capacitance dilatometer. Two different measurement methods offering distinct advantages have been used for this investigation: A typical quasiadiabatic method¹² and a continuous method based on an approach previously adopted for calorimetric measurements on glass-forming liquids.^{13,14}

II. EXPERIMENTAL

A. Materials

Samples of silver molybdate-silver iodide glasses ($\text{AgI}_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ (with $x=0.25$ and $x=0.33$) were prepared using the melt-quenching technique. Stoichiometric mixtures of AgI (99% pure, Aldrich) and Ag_2MoO_4 (prepared by precipitation from aqueous solutions of AgNO_3 and Na_2MoO_4) were melted at 600°C for 2 h in sintered alumina crucibles and then quenched down to room temperature in brass moulds with appropriate shape. Powder x-ray-diffraction patterns ruled out the possible presence of crystalline phases. The samples were cut as rectangular prisms with polished bases flat and parallel. The length of the different made samples was in the range of 15–23 mm.

The system ($\text{AgI}_{1-x}(\text{Ag}_2\text{MoO}_4)_x$) produces glasses in the range $0.2 < x < 0.4$.^{15,16} Outside this region, a glassy phase of composition near $0.66 \text{ AgI}-0.33 \text{ Ag}_2\text{MoO}_4$ (2:1) is always formed, which is accompanied by crystalline $\beta\text{-AgI}$ or Ag_2MoO_4 .³ The glass transition temperature for both glasses with $x=0.25$ and $x=0.33$ obtained by differential scanning calorimetry measurements is $T_g \sim 50 \pm 4^\circ\text{C}$.^{3,15,16} The samples were usually kept in a dry darkened container at about 4°C before the measurements.

Contrary to AgI-doped silver-borate and silver-phosphate glasses, where the binary matrices $\text{Ag}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{Ag}_2\text{O}-\text{P}_2\text{O}_5$ form continuous random networks, AgI-doped silver-molybdate glasses are depolymerized systems, where the oxyanions, mainly represented by $(\text{MoO}_4)^{2-}$ tetrahedra, do not form networks. According to Mustarelli *et al.*,^{16,17} the addition of AgI to the modified glassy matrix $\text{Ag}_2\text{O}-\text{MoO}_3$ causes a progressive increase in the silver ions in mixed coordination state I–Ag–O, and there is evidence that the mobile Ag^+ cations responsible for ionic conductivity are those which share bonds with both iodine and oxygen atoms. In this situation, the presence of oxyiodide structures would allow the formation of flexible O–Ag–I “bridges” between molecular MoO_4^{2-} ions dispersed in the glass matrix.^{18,19}

On the basis of NMR and EXAFS investigations the average number of I^- ions around Ag^+ was estimated as two for $x=0.33$.³ For $x=0.25$ composition, the number of silver ions which are surrounded almost only by iodine ions is increased, but still this does not allow the formation of $\beta\text{-AgI}$ crystalline domains that are instead revealed by x-ray diffraction experiments on samples with $x \leq 0.2$

B. Measurement setup

A three-terminal capacitance dilatometer was used to measure the linear thermal expansion coefficient of the glass samples. The measurement cell was based on the design de-

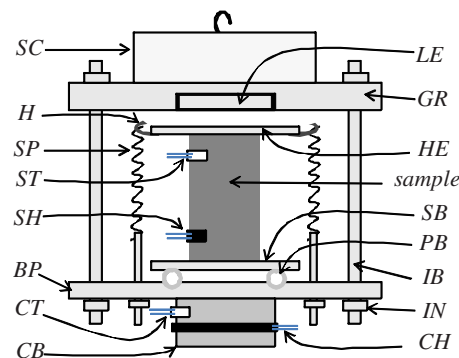


FIG. 1. (Color online) Schematic representation of the measurement cell for capacitive dilatometry. All the structural parts of the cell are made of Invar. The capacitor consists of two disk shaped electrodes: The high voltage one, HE, on top of the sample and the low voltage one, LE, surrounded by a guard ring GR. Electrode HE is kept pressed against the sample by springs SP connecting the insulated hooks H and the bolts in the base plate BP of the cell. The sample is placed on a disk base SB which rests on three Pyrex balls PB located on the base plate. Parallelism of the capacitor is achieved by adjusting the three supporting bolts IB using the nuts IN. One thermometer ST and one heater SH are attached to the sample. Another thermometer CT and another heater CH are attached to a copper block connected to the base plate of the cell. This copper block is used as a thermal reservoir to the measurement cell. A shielding cover SC made of brass is placed on top of the sensing electrode and it is used to hang the cell from the inset.

veloped in earlier work.^{20,21} The experimental cell was attached inside a high-vacuum chamber, inserted within a double-walled glass cryostat, using either nitrogen or helium as cryogenic liquids. A scheme of the experimental cell is shown in Figure 1. HE is the high-potential electrode of three-terminal parallel-plate capacitor whose low potential electrode is LE and its guard ring GR. The high-potential electrode rests on the upper face of the sample and is held against it by three springs SP whose tension can be adjusted by means of nuts. The lower face of the sample was laid on a thin Invar disk SB, separated from the thicker base plate BP, also made of Invar, at the bottom of the cell by three small balls of Pyrex (PB). The distance between the upper flat base of BP and the LE-GR assembly was fixed by means of three Invar bars. It should be noted that the samples investigated in the present work are electrically conducting, so those three balls of Pyrex placed as resting points onto the base plate BP played also the role of electrically and thermally isolating the sample from the rest of the cell. Parallelism was checked in the following way:²⁰ a small paper sheet is introduced between plates HE and LE a fixed amount from one side, the capacitance increases accordingly due to the high dielectric constant of the paper. If the sheet is introduced in some other point and the plates are not parallel, the capacitance change will be accordingly different. The screws are then adjusted until the parallelism is better than 1% of the capacitor gap. A silicon diode thermometer was thermally connected to the sample and another one was attached to a copper block connected to the base plate of the cell. Two heaters, one for the sample and another one for the cell, were used. The temperatures of the sample and the structure of the cell could therefore be controlled independently above that of the cryogenic liquid when the chamber was kept in high vacuum. The temperature of the cell was controlled and set by a LakeShore 321 temperature controller. The electric ca-

capacitance of the parallel-plate system was measured by a precision capacitance bridge AH 2005A (Handeen-Hagerling) with a resolution of the order of 10^{-7} pF.

C. Methods

The capacitance C of the three-terminal parallel-plate capacitor is given by $C = \epsilon_0 A / d$, where A is the area of the capacitor plates and d is their separation. According to the cell geometry, a variation in the sample length in ΔL will change the plate separation by $-\Delta d$, leading to the corresponding change in the capacitance ΔC . Therefore, changes in the length of the sample as a function of temperature are detected through the corresponding changes in the capacity of the three-terminal parallel-plate capacitor by

$$\Delta L = -\Delta d = \epsilon_0 A \frac{\Delta C}{C^2}. \quad (1)$$

Using the capacitance dilatometer in combination with a high precision capacitance bridge a resolution of 10^{-10} m on the absolute length changes was achieved. From the definition of the linear thermal expansion coefficient α , according to Eq. (1), it follows that

$$\alpha \equiv \frac{1}{L} \frac{\Delta L}{\Delta T} = \frac{\epsilon_0 A}{L} \frac{1}{C^2} \frac{\Delta C}{\Delta T}. \quad (2)$$

Moreover, if L_0 is the sample length and C_0 is the capacitance at a reference temperature T_0 , the fractional change in length achieved at a temperature T would be given by

$$\frac{\Delta L}{L_0} = \frac{L(T) - L_0}{L_0} = \frac{\epsilon_0 A}{L_0} \frac{C(T) - C_0}{C_0^2}, \quad (3)$$

assuming that the condition $C(T) - C_0 \ll C_0$ is satisfied, as it is in the present case. The values of α and $\Delta L/L_0$ were obtained experimentally using two different methods described below: The quasiadiabatic method and the continuous method.

1. Quasiadiabatic method

In all our measurements, the capacitance of the dilatometric cell as well as the temperature of both the cell frame and the sample are recorded continuously as a function of the elapsed time. In the quasiadiabatic method the cell frame is kept at a selected fixed temperature while the sample temperature is increased above that of the cell by discrete amounts (usually 1–3%) by using the heater directly attached on the sample in high vacuum conditions. A typical sequence of capacitance and temperature steps as a function of time during a quasiadiabatic measurement run¹² is shown in Fig. 2. Once the new equilibrium temperature is reached by the sample, the corresponding equilibrium value of the electric capacitance of the cell is used to calculate the linear thermal expansion coefficient α of the sample and the fractional length change $\Delta L/L_0$ according to Eqs. (2) and (3). After a few steps, in order to avoid large differences between the cell temperature and the sample temperature, the temperature of the dilatometric cell frame is set to a new equilibrium value (see Fig. 2).

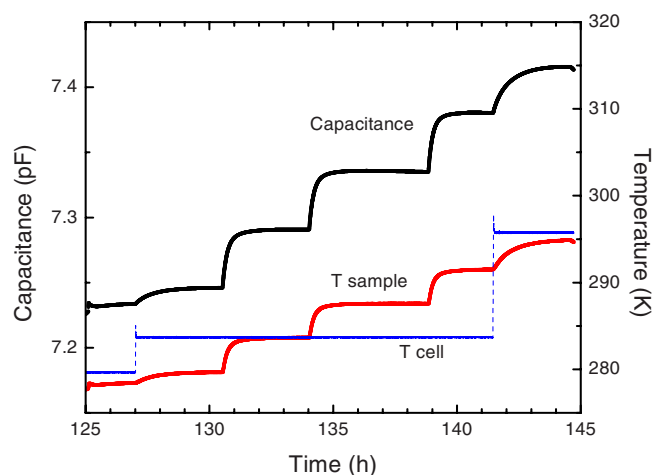


FIG. 2. (Color online) Capacitance of the dilatometric cell (left Y-axis) measured as a function of the elapsed time during an experiment performed with the quasiadiabatic method and corresponding measured temperatures (right Y-axis) of the sample and of the cell structure.

2. Continuous method

In this case, the whole system composed of the structure of the dilatometric cell plus the sample is cooled or heated at very slow rates, so that for purposes of the present experiments, the cell can be considered continuously in thermal equilibrium with the sample. This thermal equilibrium is facilitated by using a small pressure of He gas (2 mbar) in the chamber containing the dilatometric cell. The typical behavior of the capacitance C of the dilatometric cell as a function of temperature detected experimentally is shown in Fig. 3. The experimental $C(T)$ data, which are fitted to a suitable polynomial function, are used to calculate the thermal expansion coefficient according to Eq. (2).

Nonetheless, for an accurate calculation of the thermal expansion coefficient of the sample when using this method, the apparent expansivity computed from the capacitance

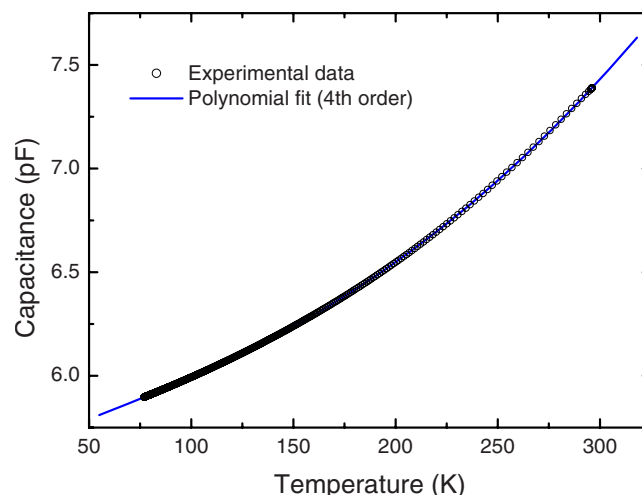


FIG. 3. (Color online) Experimental values of the capacitance of the parallel-plate condenser (open symbols) as a function of temperature during a dilatometric measurement on the $(\text{AgI})_{0.67}(\text{Ag}_2\text{MoO}_4)_{0.33}$ glass carried out with the continuous method between 300 and 77 K (continuous cooling). The solid line corresponds to the fourth order polynomial providing the best fit to the experimental data that is used to calculate the thermal expansion coefficient.

changes with temperature must be corrected considering the following contributions: (i) the length of the Invar bars that support the cell L_b (elements IB in Fig. 1) that work oppositely to sample expansion; (ii) the thickness of the Invar disks in direct contact with the sample L_d (elements SB and LE in Fig. 1) that partially cancel out the previous contribution; and (iii) the radius of the inserted Pyrex balls L_p (elements PB in Fig. 1).

Therefore, at a given temperature, the actual expansion of the sample ΔL_s is related to the variation in the gap of the capacitor Δd obtained from the measurement of ΔC by

$$\Delta L_s = -\Delta d - \Delta L_d - \Delta L_p + \Delta L_b. \quad (4)$$

It is now straightforward to find that the real expansion coefficient of the sample can be obtained from the expression

$$\alpha_{\text{sample}} = \frac{\Delta L_s}{L_s \Delta T} = \alpha_{\text{app}} - \alpha_{\text{Invar}} \frac{L_d}{L_s} - \alpha_{\text{Pyrex}} \frac{L_p}{L_s} + \alpha_{\text{Invar}} \frac{L_b}{L_s}, \quad (5)$$

where

$$\alpha_{\text{app}} = \frac{-\Delta d}{L_s \Delta T} = \frac{\varepsilon_0 A}{L_s \Delta T} \frac{\Delta C}{C^2}$$

is the apparent expansion coefficient determined without corrections.

The values of the linear thermal expansion for Pyrex and Invar between 300 and 4.2 K needed to calculate the actual thermal expansion of the sample α_{sample} through Eq. (5) are obtained from previous literature data.^{20,22} Several measurement runs using the continuous method were carried out for both studied samples at different cooling/heating rates, usually around 0.5 K/min, although rates as high as 5 K/min were occasionally tried. Best performance was obtained at moderate cooling rates that guarantee a good thermal equilibrium between the sample and the surrounding frame.

Let us finally point out that the former quasiadiabatic method does not require these corrections with the possible exception of the above-mentioned contribution (ii). However, given the small thickness of those Invar disks compared to the sample length and especially the very low thermal expansion of Invar at low temperatures, this effect can be neglected in the present case.

III. RESULTS

The values of linear thermal expansion coefficient α measured for the silver iodide-silver molybdate glasses $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ with $x=0.25$ and $x=0.33$ are shown in Fig. 4 as a function of temperature. Symbols refer to the values obtained with the quasiadiabatic measurement method,¹² whereas solid curves correspond to the values obtained using the continuous method. Good agreement is found between the experimental data obtained using the two different methods. The continuous method is less time expensive than the adiabatic one when the temperature-dependent behavior of thermal expansion has to be explored on a large temperature range, and it is more sensitive to fast changes or transitions. On the other hand, the adiabatic method allows a very good reproducibility and better accu-

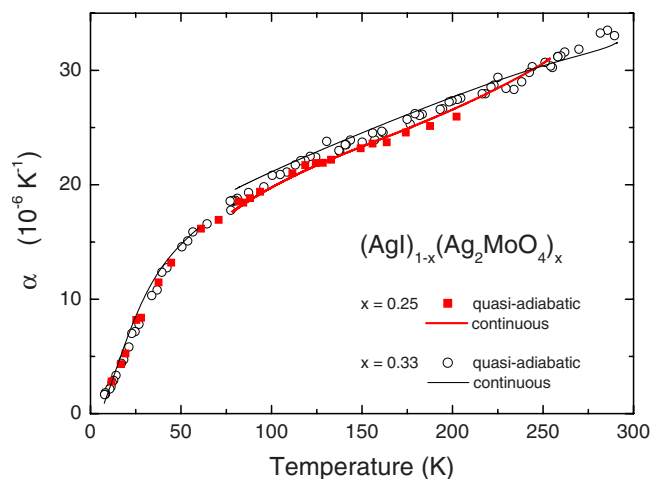


FIG. 4. (Color online) Linear thermal expansion coefficient of the two studied glasses between 5 and 300 K obtained using both the quasiadiabatic method (symbols) and the continuous method (solid lines).

racy, devoid of the possible influence of the cooling/heating rates on the results obtained with the continuous method. A comparison between the temperature-dependent behavior of the thermal expansion coefficient for two different compositions $x=0.25$ and $x=0.33$ is shown in Fig. 4. A close similarity can be observed in the low temperature region below 80 K, while the curve pertaining to the $x=0.25$ glass tends to cross over the $x=0.33$ line around 240 K and seems to increase more rapidly toward room temperature. This feature is compatible with the result of a previous investigation,² providing an average value of $\alpha=3.6 \times 10^{-5} \text{ K}^{-1}$ in the temperature range of 250–300 K for $x=0.25$ silver iodomolybdate glass. The fact that the thermal expansivity of $x=0.25$ glass has to be larger than that of the $x=0.33$ glass close to room temperature is also confirmed by the temperature-dependent behavior of the fractional length changes $\Delta L/L$ for two different glasses, as shown in Fig. 5. The comparison

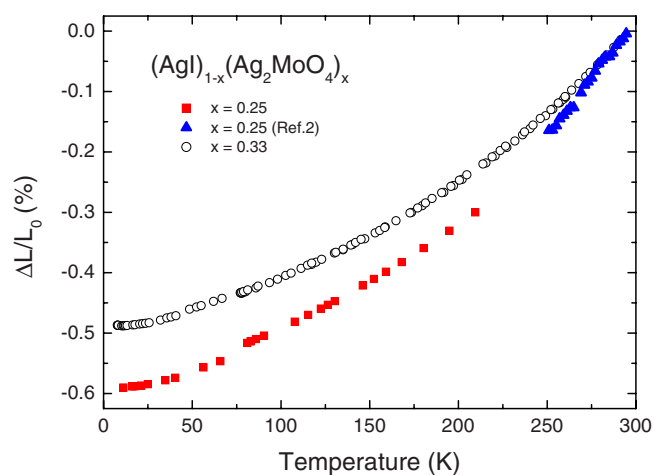


FIG. 5. (Color online) Plot of the fractional linear thermal expansion coefficient $\Delta L/L$ of the silver iodide-silver molybdate glasses $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ with $x=0.33$ (circles) and $x=0.25$ (squares) measured as a function of the temperature between 5 and 300 K. Earlier published results (Ref. 2) on $x=0.25$ glass in the 250–300 K temperature range are reported for comparison (triangles).

with expansivity data on $x=0.25$ glass from previous literature² is also provided in the same figure.

IV. DISCUSSION

Although thermal expansion data are often represented in terms of $\Delta L/L$ as in Fig. 5, the alternative representation in terms of the linear thermal expansion coefficient α will be better chosen for further data analysis and discussion. In fact, α is related (in the framework of the quasiharmonic approximation^{23–26}) to the specific heat through the Grüneisen relation^{27–29}

$$\alpha = \frac{1}{3} \frac{\gamma C_V}{V B_T} = \frac{1}{3} \frac{\gamma C_P}{V B}, \quad (6)$$

where V is the volume, B_T is the isothermal bulk modulus, B is the adiabatic bulk modulus, and C_V , C_P are the heat capacities at constant volume and pressure, respectively. The quantity γ is a thermal Grüneisen parameter, a widely used measure of the vibrational anharmonicity. It represents the weighted average of all the individual mode Grüneisen parameters $\gamma_i = -\partial(\ln \omega_i) / \partial(\ln V)$, which express the volume (or strain) dependence of the normal mode frequency ω_i associated with long-wavelength vibrational acoustic modes.^{23,24} To a first approximation the temperature dependence of the average Grüneisen parameter γ and of the bulk modulus could be neglected, so that the behavior of the thermal expansion coefficient α should essentially reflect the temperature dependence of the specific heat.²⁷ This would imply $\alpha \propto T^3$ at very low temperatures and $\alpha \sim \text{constant}$ at sufficiently high temperatures ($T \gg \Theta_D$, where Θ_D is the Debye temperature of the material). In particular, on the basis of the Debye model the heat capacity is given by

$$C_V = 9Nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (7)$$

where N is the number of atoms and $x_D = \Theta_D/T$. Therefore, using Eqs. (6) and (7), the temperature dependence of linear thermal expansion coefficient α should agree with the following equation:

$$\alpha(T) = A \left(\frac{T}{\Theta_D} \right)^3 \int_0^{x_D} \frac{x^4 e^x}{(e^x - 1)^2} dx, \quad (8)$$

with $A = (N/V) 3 \gamma k_B / B_T$.

From the measured elastic properties reported by Saunders *et al.*²³ for the glass with $x=0.25$, its Debye temperature is $\Theta_D=94.6$ K. In Fig. 6, we show this quasiharmonic prediction (with a prefactor $A=4 \times 10^{-5} \text{ K}^{-1}$ that would give an average value of the Grüneisen parameter $\gamma=0.4$). Although the agreement with experimental data is reasonable at intermediate temperatures, both glasses exhibit deviations from this ideal behavior both in low and high temperature regions. In fact, a linear additive contribution has to be considered together with the cubic term for very low temperatures.^{27,30} In metals the additional linear term is due to an electronic contribution to heat capacity. However in glasses the concentration of mobile electrons can be negligible, thus the linear term in the heat capacity should be

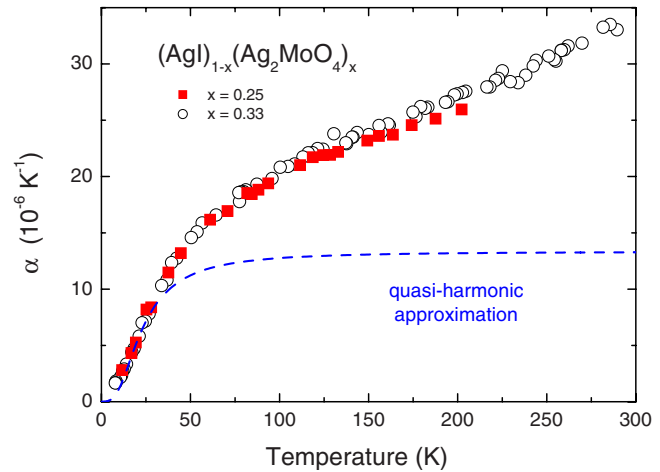


FIG. 6. (Color online) Experimental values of the linear thermal expansion coefficient α for the two silver iodide-silver molybdate glasses $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ with $x=0.25$ (squares) and $x=0.33$ (circles). The observed behavior appears compatible with that expected on the basis of the quasiharmonic approximation calculated from the elastic Debye temperature $\Theta_D=94.6$ K (dotted line), although deviations can be observed both at low and high temperatures.

ascribed to low-frequency vibrational modes not included in the Debye model. A phenomenological model based on the concept of excitations of two-level systems is often considered in order to account for the behavior observed experimentally.^{27,30} However, unlike the specific heat or the thermal conductivity, the linear thermal expansion $\alpha(T)$ does not exhibit a universal behavior.³¹ The Grüneisen parameter γ associated with these excitations (dominant below 1 or 2 K) may be large or small, positive or negative, being remarkable large and negative for tetrahedral glasses.³¹

In our case, the linear thermal expansion coefficient at low temperatures can be well described indeed by

$$\alpha(T) = aT + bT^3 \quad (9)$$

with $a = (2.0 \pm 0.1) \times 10^{-7} \text{ K}^{-2}$ and $b = (1.5 \pm 0.2) \times 10^{-10} \text{ K}^{-4}$ for $T < 25$ K, as can be seen in Fig. 7, for both

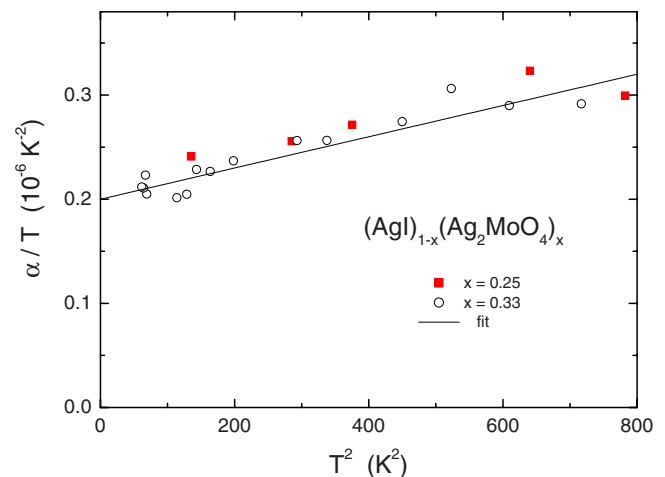


FIG. 7. (Color online) Low temperature data of the linear thermal expansion coefficient plotted as α/T vs T^2 for the two silver iodide-silver molybdate glasses $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ with $x=0.25$ and $x=0.33$. An overall linear fit to all shown data gives $\alpha(T) = aT + bT^3$ with $a = (2.0 \pm 0.1) \times 10^{-7} \text{ K}^{-2}$ and $b = (1.5 \pm 0.2) \times 10^{-10} \text{ K}^{-4}$.

$x=0.25$ and $x=0.33$ glasses that exhibit the same thermal expansion coefficient at low temperatures within the experimental error. This linear coefficient α is two orders of magnitude larger than those found in other glasses.³¹ Nonetheless, thermal-expansion data well below 5 K would be needed to properly determine a linear contribution ascribed to two-level excitations.

On the other hand, while a plateau region for the thermal expansion coefficient would be expected at high temperatures, instead of a real plateau a region characterized by a monotonic increase in the thermal expansion coefficient can be observed in different materials above $T \approx \theta_D$ because of anharmonic contributions²⁷ and/or variations in the Grüneisen parameter with temperature.²⁷ This feature also occurs for the present data (see Fig. 6): Above 50 K the experimental values progressively exceed those estimated using the quasiharmonic approximation. Moreover the macroscopic thermal expansion coefficient might also include additional contributions due to degrees of freedom related to the mobile ions in analogy to the role of vacancies in crystals.

The occurrence of negative values of the thermal expansion coefficient in some temperature ranges has been reported for different molybdate crystals⁹ as well as for different ionic glasses such as silver phosphate glasses^{23,32} and rare earth metaphosphate glasses.²⁴ Notwithstanding this, the thermal expansion coefficient of the silver iodide-silver molybdate glasses is positive in the whole temperature range investigated in this work from 5 K up to room temperature, which is close to the glass transition temperature for these materials. In particular, the comparison with the case of rare earth metaphosphate glasses appears instructive because these glasses exhibit a plateau of thermal expansion close to and above the Debye temperature. On the contrary the behavior of silver iodomolybdate glasses suggests that anharmonic contributions should play a relevant role. This feature is probably enhanced in these glasses because of the fact that the glass transition occurs at relatively low temperatures. The absolute values of thermal expansion are larger than those observed in other oxide glasses (phosphates,^{23,24} borates,³³ and silicates³⁴) in the same temperature region. The high thermal expansion coefficient of the iodomolybdate glass samples compared with the rather low value for quartz would explain the great difficulty experienced in maintaining the bonds between the quartz transducers and the glass samples down to low temperatures in ultrasonic mechanical measurements.^{2,4}

In spite of the slightly different local structure,^{3,19} the two silver iodide-silver molybdate glasses investigated, $x=0.25$ and $x=0.33$, show a closely similar behavior with differences occurring only in the high temperature part of the experimental spectra, close to and below room temperature, i.e., in the vicinity of their glass transition temperature. At room temperature the expansivity of $x=0.25$ glass should definitively overcome that of $x=0.33$ glass. The $x=0.25$ glass also exhibits lower values of sound velocity,⁴ lower activation energy, and higher conductivity prefactor.³⁵ Because of the higher AgI content and of the higher I/O ratio in $x=0.25$ glass the number of Ag^+ ions which are mobile¹⁷ and

only weakly linked to their nearest neighboring counterions is higher than in the $x=0.33$ glass. This suggests a higher fraction of softer bonding, and then a larger number of degrees of freedom, contributing to the increase in heat capacity and thermal expansivity, especially at temperatures close to the calorimetric glass transition. This picture is in agreement with the results of recent EXAFS investigations on the same glasses as a function of temperature^{11,36} that showed a progressive transfer of Ag ions from a first shell Ag–I–Ag distribution toward a position characterized by a much longer I–Ag distance, where I–Ag–O mixed coordinations are more probable. According to a general behavior common to many fast ion conducting glasses,³⁷ the lower activation energy for ion conduction of the $x=0.25$ glass would correspond to a longer I–Ag average distance, i.e., to a higher probability for Ag^+ ions to move toward the mixed environment where the ion diffusion is more favored.³

It should be recalled that the relaxational effects observed by mechanical measurements at megahertz frequencies⁸ have been explained considering the superposition of two different relaxational contributions, likely arising from the existence of two different kinds of local environment that mobile ions dynamically experience. However 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 (around 150–250 K) in which the mechanical relaxations occur in the same glasses. Therefore it seems that the microscopic mechanism responsible for the peculiar pattern of the ultrasonic attenuation as a function of temperature does not give rise to thermal expansion anomalies. Moreover, while the mechanical loss profile of the two compositions investigated is different, the behavior of the thermal expansion coefficient is quite similar for two glasses.

V. CONCLUSIONS

The temperature dependent behavior of the thermal expansion coefficient of the silver iodide-silver molybdate glasses $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ with $x=0.25$ and $x=0.33$ was studied in the temperature range between 5 and 300 K using a homemade precision capacitance dilatometer with two different measurement methods: A quasiadiabatic method and a continuous one. To the aim of characterizing faster the behavior of the thermal expansion coefficient in a wide temperature range the continuous method represents a more convenient approach, while the quasiadiabatic method provides higher reproducibility. Although the occurrence of negative values of the thermal expansion was reported in previous literature for molybdate crystals and silver based ionic glasses, $(\text{AgI})_{1-x}(\text{Ag}_2\text{MoO}_4)_x$ glasses only show positive values of α in the whole temperature range from 5 K up to nearly the glass transition region. The results do not show features that could be related to the unusual behavior of the ultrasonic attenuation in the same glasses previously shown.⁸ In the framework of the quasiharmonic approximation, the thermal response of the glass investigated is comparable with the temperature dependent behavior estimated assuming the validity of the Debye model of the heat capacity with an

independently obtained Debye temperature $\Theta_D=94.6$ K. In order to account for the low temperature behavior, a linear (and positive) temperature dependence of the thermal expansivity has to be considered in addition to the cubic term related to the quasiharmonic approximation. On the other hand, anharmonic effects play a relevant role above 100 K, preventing the observation of a plateau of thermal expansion as a function of temperature. This situation might be related to the fact that the glass transition temperature of the iodomolybdate glasses occurs at relatively low temperatures. The behavior of two compositions $x=0.25$ and $x=0.33$ corresponding to molar ratios (3:1) and (2:1), respectively, does not show significant differences below 100 K, while at higher temperatures the thermal expansion coefficient of the “softer” glass $x=0.25$ crosses over that of $x=0.33$ and tends to achieve a higher value around 300 K. This latter feature might arise from the consequences of the higher AgI content on the structure and on the mechanism of ionic mobility.

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¹J. Swenson and L. Börjesson, *Phys. Rev. Lett.* **77**, 3569 (1996).

²D. P. Almond, G. K. Duncan, and A. R. West, *J. Non-Cryst. Solids* **74**, 285 (1985).

³P. Mustarelli, C. Tomasi, E. Quartarone, A. Magistris, M. Cutroni, and A. Mandanici, *Phys. Rev. B* **58**, 9054 (1998).

⁴M. Cutroni, A. Mandanici, M. Federico *et al.* (unpublished).

⁵M. Cutroni, M. Federico, A. Mandanici, P. Mustarelli, and C. Tomasi, *Solid State Ionics* **113–115**, 677 (1998).

⁶K. L. Ngai and R. W. Rendell, *Phys. Rev. B* **38**, 9987 (1988).

⁷G. Carini, M. Cutroni, M. Federico, G. Galli, and G. Tripodo, *Phys. Rev. B* **30**, 7219 (1984).

⁸M. Cutroni, A. Mandanici, and E. Bruno, *Phys. Chem. Chem. Phys.* **4**, 4539 (2002).

⁹J. S. O. Evans, T. A. Mary, and A. W. Sleight, *J. Solid State Chem.* **133**,

580 (1997).

¹⁰G. D. Barrera, J. A. O. Bruno, T. H. K. Barron, and N. L. Allan, *J. Phys.: Condens. Matter* **17**, R217 (2005).

¹¹A. Sanson, F. Rocca, G. Dalba, P. Fornasini, and R. Grisenti, *New J. Phys.* **9**, 88 (2007).

¹²A. Raimondo, A. Mandanici, M. A. Ramos, J. G. Rodrigo, C. Armellini, M. Cutroni, and S. Vieira, *Philos. Mag.* **88**, 3973 (2008).

¹³E. Perez-Enciso and M. A. Ramos, *Thermochim. Acta* **461**, 50 (2007).

¹⁴A. Mandanici, M. Cutroni, A. Triolo, V. Rodriguez-Mora, and M. A. Ramos, *J. Chem. Phys.* **125**, 054514 (2006).

¹⁵C. Tomasi, P. Mustarelli, and A. Magistris, *J. Solid State Chem.* **140**, 91 (1998).

¹⁶P. Mustarelli, C. Tomasi, A. Magistris, and M. Cutroni, *J. Non-Cryst. Solids* **232–234**, 532 (1998).

¹⁷P. Mustarelli, C. Tomasi, and A. Magistris, *J. Phys. Chem. B* **109**, 17417 (2005).

¹⁸J. Swenson, R. L. McGreevy, L. Börjesson, J. D. Wicks, and W. S. Howells, *J. Phys.: Condens. Matter* **8**, 3545 (1996).

¹⁹J. Swenson, R. L. McGreevy, L. Börjesson, and J. D. Wicks, *Solid State Ionics* **105**, 55 (1998).

²⁰R. Villar, M. Hortal, and S. Vieira, *Rev. Sci. Instrum.* **51**, 27 (1980).

²¹E. S. Piñango, M. Hortal, S. Vieira, and R. Villar, *J. Phys. C* **20**, 1 (1987).

²²T. H. K. Barron and G. K. White, *Heat Capacity and Thermal Expansion at Low Temperatures* (Springer, New York, 1998).

²³G. A. Saunders, R. D. Metcalfe, M. Cutroni, M. Federico, and A. Piccolo, *Phys. Rev. B* **53**, 5287 (1996).

²⁴G. A. Saunders, T. Brennan, M. Acet, M. Cankurtaran, H. B. Senin, H. A. Sidek, and M. Federico, *J. Non-Cryst. Solids* **282**, 291 (2001).

²⁵T. N. Claytor and R. J. Sladek, *Phys. Rev. B* **18**, 5842 (1978).

²⁶J. A. Garber and A. V. Granato, *Phys. Rev. B* **11**, 3990 (1975).

²⁷S. R. Elliott, *The Physics and Chemistry of Solids* (Wiley, New York, 2000), p. 276.

²⁸N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Saunders, Philadelphia, 1976).

²⁹C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 2005).

³⁰R. O. Pohl, in *Amorphous Solids. Low-Temperature Properties*, edited by W. A. Phillips (Springer-Verlag, Berlin, 1981), p. 27.

³¹D. A. Ackerman, A. C. Anderson, E. J. Cotts, J. N. Dobbs, W. M. MacDonald, and F. J. Walker, *Phys. Rev. B* **29**, 966 (1984).

³²R. Bogue and R. J. Sladek, *Phys. Rev. B* **42**, 5280 (1990).

³³V. P. Klyuev and B. Z. Pevzner, *Glass Phys. Chem.* **28**, 207 (2002).

³⁴R. D. Greenough, P. Dentschuk, and S. B. Palmer, *J. Mater. Sci.* **16**, 599 (1981).

³⁵A. Mandanici, A. Raimondo, M. Cutroni, M. Federico, C. Armellini, and F. Rocca, (unpublished).

³⁶A. Sanson, F. Rocca, P. Fornasini, G. Dalba, R. Grisenti, and A. Mandanici, *Philos. Mag.* **87**, 769 (2007).

³⁷A. Sanson, F. Rocca, C. Armellini, G. Dalba, P. Fornasini, and R. Grisenti, *Phys. Rev. Lett.* **101**, 155901 (2008).