Journal of Non-Crystalline Solids 401 (2014) 254–257

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/ locate/ jnoncrysol

Ionic conductivity, electric modulus and mechanical relaxations in silver iodide–silver molybdate glasses

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ARTICLE INFO

Article history:
Received 24 September 2013
Received in revised form 25 November 2013
Available online 9 January 2014

Keywords:
Ionic conductivity;
Molybdate glasses;
Ionic glasses;
Relaxation

ABSTRACT

Silver iodide–silver molybdate glasses, $(AgI)_x(Ag_2MoO_4)_{1-x}$, with $x = 0.75$ and $x = 0.67$, exhibit high ionic conductivity, comparable to that of some ionic liquids at room temperature, and low values of the calorimetric glass transition temperature. The behaviour of the attenuation of acoustic waves as a function of temperature in silver iodomolybdate glasses below T_g is peculiar, arising from two different and almost overlapping relaxational contributions. In this work we investigate the frequency dependent conductivity and the dielectric properties of silver iodide–silver molybdate glasses in the mHz–GHz frequency range at temperatures between 300 K and 70 K, aiming in particular to ascertain whether a correlation can be found between the features of the dielectric response and the anomalous mechanical response of these fast ion conducting glasses.

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1. Introduction

The search for materials featuring high ionic conductivity and suitable mechanical properties to be used as solid electrolytes in batteries and devices plays a fundamental role in connection with the current effort on exploiting renewable energies. High values of ionic conductivity have been observed in oxide glasses, such as phosphate and borate glasses, obtained by adding silver iodide as dopant salt to the glass matrix. In fact, ionic conductivity increases on increasing the content of silver iodide until the limit of the glass-formation range is exceeded [1–3]. This typically happens for molar fractions, x, of the dopant higher than 0.6 in silver phosphate glasses $(AgI)_x(AgPO_3)_{1-x}$ and in silver diborate glasses $(AgI)_x(Ag_2O - 2B_2O_3)_{1-x}$. However, a higher AgI content, up to $x = 0.75$, and higher conductivity can be achieved in silver iodide–silver molybdate glasses $(AgI)_x(Ag_2MoO_4)_{1-x}$ [4]. While in the case of AgI-doped silver-borate glasses and silver-phosphate glasses the undoped binary matrices $Ag_2O - B_2O_3$ and $Ag_2O - P_2O_5$ already form network glasses, the $(AgI)_x(Ag_2MoO_4)_{1-x}$ system gives glasses only in a narrow range, $0.6 < x < 0.8$ [5,6]. This feature has been understood by modelling the structure using the reverse Monte Carlo method on neutron and X-ray diffraction data [7]. Accurate X-ray absorption (XAS) measurements [8,9] confirm that tetrahedral molecular ions $(MoO_4)^{2-}$ are almost randomly distributed in the material and cross-linked by –O–Ag–O– bridges. As a consequence of AgI doping, the formation of –O–Ag–I–Ag–O– links is favoured, giving more flexibility and less orientational order, so that a glass can be formed. If the AgI content is too low, the orientational correlations lead to crystallization of Ag_2MoO_4, whereas if the AgI content is too high, there are not enough –O–Ag–O– bridges to constitute a network, therefore crystalline AgI domains are obtained. Compared to silver phosphate glasses and silver borate glasses, silver iodide–silver molybdate glasses are characterized by low values of the glass transition temperature ($Tg \simeq 50$ °C) and of the sound velocity, and high values of the ultrasonic attenuation [10] and of the linear thermal expansion coefficient [11]. Moreover, on the basis of a previous solid state NMR investigation, the existence of two populations of silver cations having different mobilities has been proposed [5]. This evidence has been confirmed by XAS measurements as a function of temperature [12,13]. Along with this feature, a peculiar behaviour of the acoustic attenuation at ultrasonic frequencies has attracted our attention on the dynamical properties of this family of glasses. In fact, as in other ionic glasses a peak of ultrasonic absorption measured as a function of temperature occurs below T_g. This peak is usually associated with the hopping motion of mobile cations in the material [14–17], but in the case of silver-iodomolybdate glasses the attenuation profile arises from the superposition of two different relaxational contributions, with different activation energy [10,18]. Since strong analogies have been pointed out between the mechanical relaxation processes and the electric response (in terms of complex electric modulus) of some ionic glasses [14,19], in the present

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http://dx.doi.org/10.1016/j.jnoncrysol.2013.12.025

work we have studied comparatively the electric and the mechanical properties of $(AgI)_x(Ag_2MoO_4)_{1-x}$ glasses in order to gain further insight on the origin of their peculiar dynamical response.

2. Experimental

Glass samples of $(AgI)_x(Ag_2MoO_4)_{1-x}$ with x = 0.75 and x = 0.67 were obtained by the melt quenching technique as described in ref. [11]. The glass transition temperatures of the glasses investigated, determined by differential scanning calorimetry, were 46.8°C and 45.1°C, respectively [5,6].

Broadband dielectric measurements were performed using a homemade experimental setup based on a condenser cell being part of a coaxial transmission line [14]. This method was used in order to obtain the values of real and imaginary permittivity in the frequency range 100 mHz–3 GHz as a function of temperature in the range 300 K–70 K. From the complex permittivity, the frequency dependent conductivity and the complex electric modulus, $M^* = 1/\varepsilon^*$, were calculated. Mechanical measurements were performed previously, as described in references [10,18].

3. Results

The frequency dependent conductivity of the silver iodide–silver molybdate glasses investigated has the typical behaviour of ionic conducting materials (Fig. 1). The plateau region in the low frequency part of the spectra corresponds to the dc conductivity value, whereas the onset of a dispersive region can be observed at higher frequencies. The slope of the conductivity vs. frequency in the log–log plot increases up to a value nearly equal to one, suggesting that a single power law could not describe the frequency dependence of the conductivity in the entire frequency range investigated [20].

The dc conductivity of the $(AgI)_x(Ag_2MoO_4)_{1-x}$ glasses varies as a function of temperature (see Fig. 2) according to the Arrhenius equation

$$\sigma_{dc}T = A\exp\left(-\frac{E_\sigma}{k_B T}\right) \quad (1)$$

with activation energy $E_\sigma = 0.245 \pm 0.003$eV, for x = 0.75, and $E_\sigma = 0.255 \pm 0.009$eV for x = 0.67. The glass with higher AgI content exhibits higher dc conductivity at all temperatures. The values of E_σ are comparable with the values reported in previous literature about iodomolybdate glasses having the same or closely similar composition [21–24].

The behaviour of the complex electric modulus (real part and imaginary part) as a function of frequency is shown in Fig. 3 for the $(AgI)_{0.75}(Ag_2MoO_4)_{0.25}$ glass at selected temperatures.

The relaxation pattern is shifted towards higher frequencies as the temperature is increased, in agreement with a thermally activated

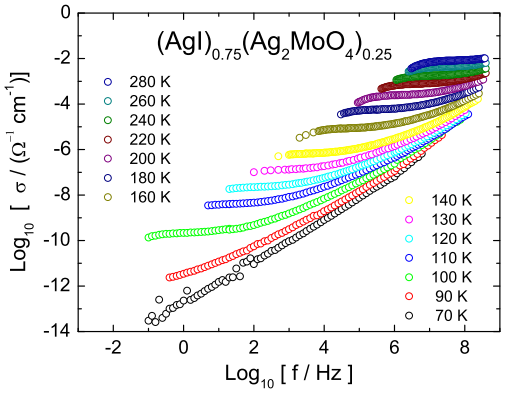

Fig. 1. Frequency dependent conductivity (real part) of silver iodide–silver molybdate glasses, $(AgI)_{0.75}(Ag_2MoO_4)_{0.25}$ at selected temperatures below T_g.

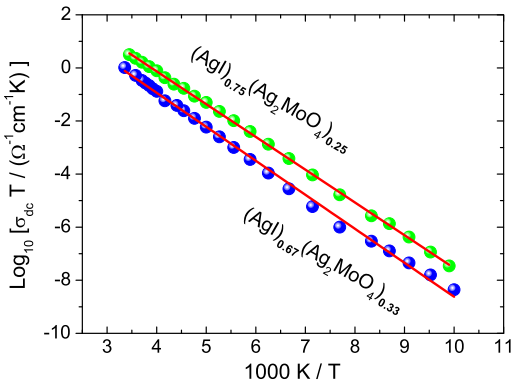

Fig. 2. Temperature dependence of the dc conductivity, σ_{dc}, for silver iodide–silver molybdate glasses, $(AgI)_x(Ag_2MoO_4)_{1-x}$, with x = 0.75 and x = 0.67. Straight lines correspond to the best fit of the Arrhenius Eq. (1) to the experimental data.

behaviour. The shape of the electrical relaxation does not depend on the temperature, and does not vary with composition. In fact, if the modulus values are scaled for the maximum amplitude and the frequencies are scaled for the frequency at which the maximum occurs [25], all the spectra, also corresponding to different glasses, collapse on a common master curve (see Fig. 4).

The relaxation peak of M″ can be described [26] using a phenomenological Kohlrausch–Williams–Watts (KWW) function,

$$\Phi(t) = \exp\left[-(t/\tau_{KWW})^{\beta_{KWW}}\right] \quad (2)$$

with stretching exponent $\beta_{KWW} = 0.52$[1]. As shown in Fig. 4, the function underestimates the experimental values of M " in the high frequency region of the spectra, suggesting the existence of some additional contribution, responsible for the excess loss. The high frequency part of the spectra might reflect the smooth transition from a correlated hopping motion to a Nearly Constant Loss regime [27,28]. In ionic glasses this behaviour could arise from localized motion of the ions [29–31] or from relaxation of the glass network [32].

In order to compare the present new data on the electrical response with those previously obtained [10] on the mechanical response of the $(AgI)_x(Ag_2MoO_4)_{1-x}$ glasses, we have chosen to consider the electric modulus together with the analogous variable for mechanical measurements, the mechanical modulus [33–35]. To this aim, the values of

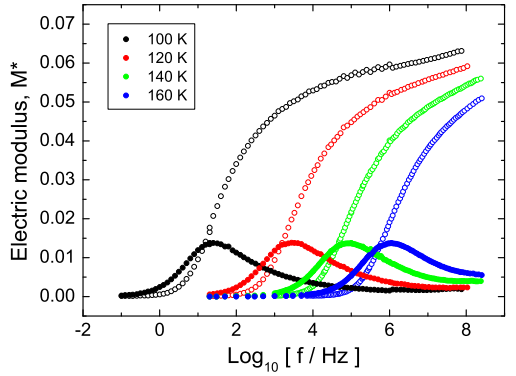

Fig. 3. Frequency dependent electric modulus (real part, open symbols, and imaginary part, full symbols) of silver iodide–silver molybdate glass, $(AgI)_{0.75}(Ag_2MoO_4)_{0.25}$ at selected temperatures.

[1] Aiming to achieve better agreement between the KWW function and the experimental data in the high frequency side of the peak, lower values of the β_{KWW} parameter would be obtained, comparable to the values reported in ref. [22]. Nevertheless, the function would fail in reproducing the behaviour of the experimental data in the peak region near the maximum.

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