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Raman and Brillouin scattering in superionic glasses

P. BENASSI and A. FONTANA

Dipartimento di Fisica, Università degli studi di Trento, 38050 Povo (Trento), Italy

In this paper we report some experimental results obtained from Raman and Brillouin light scattering measurements on two different families of disordered systems: the $(AgI)_x(Ag_2O_nB_2O_3)_{1-x}$ and $(AgI)_x(AgPO_3)_{1-x}$ glasses.

Measurements were performed at several AgI concentrations covering the full glass-forming region and over a wide temperature range, from liquid helium to room temperature.

Increasing the silver iodide content, the behaviour of the Brillouin and Raman intensities together with the Raman spectral shape, suggest that the spectra of these glasses can be mainly interpreted as the superposition of that pure α -AgI and that of the host matrix.

Introduction

The superionic glasses $(AgI)_x(Ag_2O_nB_2O_3)_{1-x}$ and $(AgI)_x(AgPO_3)_{1-x}$ have been studied using several spectroscopic techniques in order to understand the structural and dynamical properties which determine the high mobility of the silver ions: by varying the relative concentrations of the components of the glassy matrices, Ag_2O , B_2O_3 , PO_4 and AgI, it has been possible to study their influence on the superionic properties.

First of all, it should be stressed that the addition of AgI to the borate and phosphate glasses increases the ionic conductivity of several orders of magnitude. A possible explanation (given on the basis of neutron scattering/1/, exafs/2/, and light scattering results/3/), is that at increasing AgI content distorted tetrahedra of AgI units become connected inside the host matrix, which form some diffusion paths for the silver ions.

We have studied the influence of the concentration of AgI on Raman and Brillouin spectra and in the following are summarized the main results obtained.

Results

The Raman spectrum can be divided into two frequency ranges from which different kinds of information can be extracted: the high frequency region, whose peaks and bands are related to the normal vibrational modes of molecular units (in our case roughly $|\omega| \geq 200 \text{ cm}^{-1}$), and the

low frequency region ($|\omega| < 200 \text{ cm}^{-1}$) related to the acoustic vibrational density of states. From Brillouin scattering we can obtain information about the hypersonic properties. We measured sound velocities, from liquid helium to room temperature, and at several AgI concentrations.

Fig. 1. Experimental Raman spectra for the superionic glasses $(\text{AgI})_x(\text{Ag}_2\text{O}_4\text{B}_2\text{O}_3)_{1-x}$. Upper, $x = 0.4$; lower, $x = 0$. Both spectra in VV polarization.

Fig. 2. Experimental Raman spectra for the superionic glasses $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$. The spectra are normalized to the intensity of the high frequency peak.

Fig. 3. Experimental HV Raman spectra at room temperature as a function of AgI content in $(\text{AgI})_x(\text{Ag}_2\text{O}_n\text{B}_2\text{O}_3)_{1-x}$, (a) $x = 0.45$, (b) $x = 0.50$, (c) $x = 0.55$, (d) $x = 0.60$, (e) $x = 0.65$, (f) $x = 0.70$, g = 0.75. The resolution is 2 cm^{-1} .

In figure 1 and 2 present Raman spectra of the silver borate glasses at two AgI concentrations, and of silver phosphate glasses at three AgI concentrations. As can be seen, increasing the AgI

content, the frequency shifts and the spectral shapes do not change significantly in the high frequency part of the spectrum. This is evident for the phosphate glasses thanks to the presence of intense peaks related to the eigenfrequencies of PO_4 units.

The Raman scattering below 200 cm^{-1} is strongly affected by the presence of silver iodide: see figure 3, where we show the low frequency spectra of $(AgI)_x(Ag_2OnB_2O_3)_{1-x}$ glasses at several AgI concentrations.

This scattering is mainly attributed/4/ to the presence of AgI, which strogly contributes to the modulation of the induced polarizability. The two main reasons for this idea are:

- 1- The spectral shape is very similar to that of pure α - AgI, see insert in Fig. 4
- 2- The intensity of the scattering increases linearly at increasing AgI content.

In the following, we can make the hypothesis that the full spectrum below 200 cm^{-1} can be regarded as a superposition of that of the glass matrix and that of α - AgI, the last one being the most intense. Then the experimental spectrum at for instance $(AgI)_x(AgPO_3)_{1-x}$, can be reconstructed using the following formula:

$$I(\omega) = aI_{(\omega)}^{AgPO_3} + bI_{(\omega)}^{\alpha-AgI} \quad (1)$$

Fig.4. Reconstruction of the room-temperature $x = 0.3$ experimental anisotropic spectrum performed using Eq. (1). Solid line, experimental data; dots, reconstruction. The inset shows the α - AgI (-) and $AgPO_3$ (0) spectra used to obtain reconstruction.

Fig.5. Ratio of the coefficient (b/a) used in the reconstruction of the experimental anisotropic spectra as a function of AgI content. The solid line is the function $x/(1-x)$.

The experimental spectrum obtained for the $x = 0.3$ glass is reported in figure 4 together with the result obtained using equation 1. We found such a model satisfactory for $\omega > 10\text{ cm}^{-1}$ for all AgI concentrations. At lower frequencies, quasi-elastic-scattering becomes predominant and here we found discrepancies which increase with the amount of dopant salt. In figure 5 where we report the b/a ratios obtained from such a superpositron procedure together with the expected curve $x/(1-x)$.

In figure 6 we show the room temperature longitudinal Brillouin doublet for the $(AgI)_x(AgPO_3)_{1-x}$ glass family at three different AgI concentrations. Since these glasses cause much stray-light, it was not possible to measure the transverse Brillouin doubled for all the AgI concentrations; hence we focus on the longitudinal sound velocity, see Fig. 7/5/. As we can see, the longitudinal sound velocity decreases when the AgI content is increased and linearly tends to that of the pure α - AgI.

In conclusion Raman and Brillouin measurements on $(AgI)_x(AgPO_3)_{1-x}$ and $(AgI)_x(Ag_2On$

$B_2O_3)_{1-x}$ are consistent with the hypothesis that these glasses are formed by two weakly interacting phases: a pure α - AgI - like phase and a $AgPO_3$ (or $Ag_2O \cdot B - 2O_3$) phase. The dimension of such clusters are an open question though if neutron diffraction/2,7/ and Raman measurements/3/ (this last performed on $(AgI)_x (Ag_2O \cdot B_2O_3)_{1-x}$) indicate that there are correlation lengths in these glasses of the order of about 10-30 Å.

Fig.6. Room-temperature longitudinal Brillouin doublet of $((AgI)_x(AgPO_3)_{1-x})$ glass family at three different AgI contents: $x = 0.0, 0.2, 0.4$. The inset shows the traverse modes measured in HV configuration at $x = 0.2$. The weak peaks at about 0.5 cm^{-1} are the spillover of the longitudinal peaks.

Fig.7. Room-temperature sound velocities as a function of AgI concentration (circles). Crosses and the α - AgI longitudinal sound velocity ($\diamond$) are from Ref. 6.

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