Concentration dependence of Raman scattering in superionic glasses $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$

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We have studied low-frequency Raman scattering in $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$ superionic glasses as a function of AgI content. In particular, we found evidence for a quasielastic contribution. Such scattering has been interpreted as being due to relaxation modes originating from the jumping of silver ions in the available sites of the local network of AgI units. The intensity I_L of the quasielastic scattering (of Lorentzian shape, centered at zero frequency) has been correlated with the number of silver ions participating in the conduction. The variation of I_L as a function of silver iodide concentration is exponential, implying cooperative effects. This is shown also by conductivity measurements.

I. INTRODUCTION

During the past decade there has been considerable interest in the dynamics of superionic conductors, particularly of fast-ion-conducting glasses. Among such glasses the family of silver borate glasses $(AgI)_x(Ag_2O \cdot n B_2O_3)_{1-x}$ has been extensively studied from both a physical and a technological point of view.[1-4] The ease of varying the relative concentrations of the three chemical components in a wide glass-forming range enabled us to investigate the influence of AgI both in modifying the structure of the glass matrix $(Ag_2O \cdot n B_2O_3)$ and in increasing the ionic conduction.

Silver iodide is one of the most studied crystalline superionic conductors. At 147 °C it goes through a first-order phase transition and its ionic conductivity increases suddenly. At first it seemed easy to directly correlate the presence of AgI in the glass matrix with the fast-ion properties of the resulting glasses. However, it must be noted that the ionic conductivity of borate glasses not only changes with increasing AgI content, but is also strongly related to the silver oxide content. For example, at $x = 0.2$ the room-temperature dc conductivity increases by 5 orders of magnitude when n changes from 4 to 1.[1]

Recent measurements by extended x-ray-absorption fine-structure spectroscopy (EXAFS) and x-ray-absorption near-edge structure technique (XANES) on various silver borate glasses provided useful information about the local structure of Ag and I atoms.[5,6] In particular, the k edge of silver showed two well-defined bond lengths: the measured distances are 2.2 Å for the Ag—O bond and 2.7 Å for Ag—I. Moreover, the progressive insertion of AgI does not modify the Ag—O coordination, with two oxygen atoms nearest neighbors of the silver atoms of the binary matrix. The first shell of coordination of iodine in the ternary glasses is very similar to that of AgI. On the other hand, the second-shell I—I bond is not present in the Fourier-transformed EXAFS signal; this indicates a great disorder of the I—I distances in the hypothesized tetrahedra,

which hinders their connection or arrangement in microdomains.

The structural information is not sufficient for a complete and unambiguous interpretation of the high conductivity of these glasses. In particular, we must clarify two points: how many Ag^+ ions participate in the conduction for different compositions and temperatures, and whether or not there are two different local bonds for the silver ions (one with the oxygens of the glass matrix and one with the iodines), resulting in two distinct jump processes.

In this work we present light scattering measurements in the family of superionic glasses $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$ at several AgI contents $(0.45 < x < 0.75)$.

In previous works[7,8] on $(AgI)_x(Ag_2O \cdot n B_2O_3)_{1-x}$ with $n = 3,4$, we have interpreted the Raman spectra as being mainly due to AgI, which is expected to contribute heavily to the vibrationally induced electronic-polarizability modulation. By comparing the Raman scattering of these glasses to that of silver iodide, we have hypothesized that the AgI tends to reproduce, at the local level, connected tetrahedra; such connection would favor the conductivity of Ag^+ ions and would allow them to travel through some "diffusion paths," due to the presence of many available sites in the distorted units of AgI.

Optical-absorption measurements[9] seem to support this hypothesis; measurements of Brillouin scattering[10] and of small-angle neutron scattering[11] on similar AgI-containing phosphate glasses also indicate that our hypothesis is reasonable.

In the very-low-frequency region of Raman spectra, a new quasielastic contribution to the scattering process appears, which could be due to local relaxation modes associated with the hopping of the mobile ions between equivalent sites in the glass. This scattering has been shown to increase with increasing AgI content. Its temperature dependence (easily measurable only for high AgI and Ag_2O content) suggests that the highly mobile ions are thermally activated, as in ionic crystals.[12]

The aim of this work is to test our previous interpretation of very-low-frequency scattering at various AgI concentrations and to correlate the intensity of the scattering with conductivity and transport measurements.

II. EXPERIMENTAL RESULTS

The samples were prepared in our laboratory; the glasses present the same glass transition temperature T_g, density, and composition reliability as those obtained previously by other workers.[1]

The Raman spectra were measured by a standard system consisting of a krypton laser, a Jobin-Yvon double monochromator with holographic gratings, and a photon-counting system, connected to a computer for data storage and handling. We obtained high-resolution spectra from 2 to 400 cm^{-1}; the best instrumental resolution was 0.8 cm^{-1}.

The light scattering of the relaxation modes is totally depolarized, that is, it contributes only to the off-diagonal elements of the polarizability tensor. In order to select only these elements, the HV 90° scattering geometry was used.

Since the samples are of dark-red color, we used the 6471-Å krypton line at low power (30 mW). In any case the system absorbed the radiation, and the Raman intensity depends on the absorption coefficient and consequently on the effective scattering volume. To minimize this latter variation the laser light was nearly parallel to the surface of samples. In order to correct the intensity of Raman measurements, we performed optical-absorption measurements using the same procedure as used in the previous work.[12] This correction does not significantly alter the variation of intensity with AgI content.

The Raman spectra are superimposed on a luminescence background, which was fitted by a polynomial
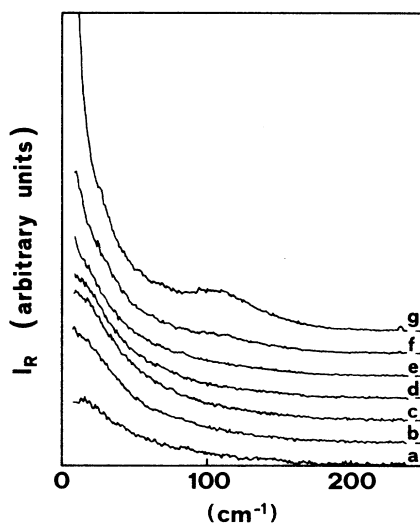

FIG. 1. Experimental HV Raman spectra as a function of AgI content x: $a = 0.45$, $b = 0.50$, $c = 0.55$, $d = 0.60$, $e = 0.65$, $f = 0.70$, $g = 0.75$. Room temperature. The resolution is 2 cm^{-1}.
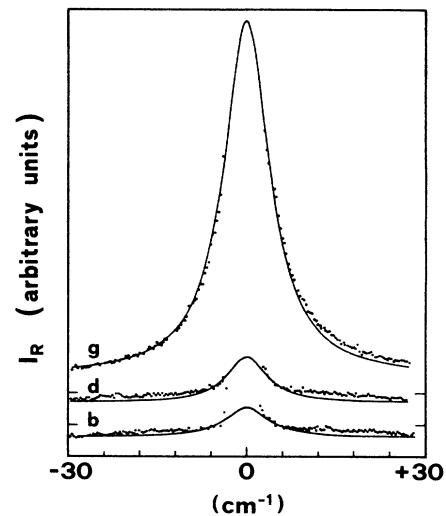

FIG. 2. Typical best fits of the quasielastic Lorentzian contribution. For the symbols see Fig. 1. The HWHM is 4.7 ± 0.6 cm^{-1}.

curve and then subtracted from the experimental points.

In Fig. 1 we report experimental HV Raman spectra at several x values. At low concentration, we can see a bump centered at about 20 cm^{-1} and a long tail extending up to 200 cm^{-1}. As x increases, the low-frequency light scattering overwhelms the bump; at $x = 0.65$ we can see a second bump centered at 110 cm^{-1}. At $x = 0.75$ a strong quasielastic scattering and a peak at 110 cm^{-1} are evident.

In Fig. 2 we report the variation of the low-frequency scattering with increasing AgI content; we note a strong intensity increase, which becomes dramatic at $x = 0.75$. We fitted such quasielastic scattering by means of a Lorentzian and a constant background, as shown in Fig. 2. The fit was performed in the same range for each AgI concentration: from -7 to -3 cm^{-1} (anti-Stokes part) and from $+3$ to $+7$ cm^{-1} (Stokes part). The reliability factor is better than 5% for all the best fits. The half width at half maximum (HWHM) is 4.7 ± 0.6 cm^{-1}, nearly constant for all the samples within our experimental accuracy.

III. DISCUSSION

In superionic conductors we have the coexistence of a set of mobile ions with a "rigid" lattice. The low-frequency fluctuations of these systems can reveal a strong coupling of the diffusive excitations with the "phonon" modes; the diffusive motion would produce a depolarized quasielastic scattering[13-16] of Lorentzian shape (or, more precisely, a superposition of several Lorentzians centered at zero-frequency shift).

Our previous measurements on $(AgI)_x(Ag_2O \cdot nB_2O_3)_{1-x}$ glasses showed that the scattering is mainly due to the silver iodide; in the low-frequency region, the Raman spectrum of binary glasses $(Ag_2O \cdot nB_2O_3)$ has relatively low intensity, and its contribution to the spec-

trum may be neglected. Thus the scattering in the range $0-30$ cm^{-1} may be attributed to acoustic modes mainly connected with the AgI local network. Upon this scattering is superimposed the quasielastic scattering due to the mobile Ag$^+$ ions.

In an extensive work,[17] Zeyher studied the hydro-dynamics of superionic conductors, particularly of α-AgI. He stated that the Lorentzian of 3.8 cm^{-1} HWHM experimentally found in α-AgI cannot be explained according to a hydrodynamic theory. He suggested that this component might be due to local relaxation modes associated with the hopping of the mobile ions between equivalent sites in the primitive cell.

On the basis of this hypothesis we have interpreted the low-frequency light scattering in the system $(AgI)_x(Ag_2O \cdot B_2O_3)_{1-x}$. The behavior of the zero-centered Lorentzian contribution as a function of temperature was accurately studied in our previous work[12] on $(AgI)_{0.65}(Ag_2O \cdot B_2O_3)_{0.35}$. The room-temperature variation of the integrated intensity of the Lorentzian, I_L, as a function of the AgI concentration is reported in Fig. 3. It is exponential up to $x = 0.70$ (we will consider the concentration $x = 0.75$ later); the intensity increases about 3.3 times.

Let us note that the conductivity behavior in the same range of AgI content is also exponential: the conductivity increases about 30 times. This difference may be due to the fact that our experiment is not *directly* connected to the motion of silver ions. For this reason (as we pointed out before), our results are not sensitive to this motion, but rather to the variation of the polarizability of the $(AgI)_n$ units due to silver jumps. However, the fact that I_L does not change linearly with the AgI content implies cooperative effects, since the Raman intensity, in contrast, is nearly constant.

The behavior of the glass with $x = 0.75$ is different. As a matter of fact, the shape of the Raman spectrum is very similar to that of α-AgI; we can reasonably claim that the influence of AgI in the Raman spectrum dominates the other components of the ternary glass. The integrated reduced Raman intensity and the Lorentzian intensity (see Fig. 3) are very different from those of the other concentrations, whereas the width remains constant within our experimental accuracy.

A possible explanation of these three observations is that the connectivity of AgI clusters increases dramatically at $x = 0.75$; in this way the coherence of the Raman scattering would strongly increase, and the integrated intensity, too. In the same way, we can explain the Lorentzian intensity: the tetrahedrally connected units make the jump between the available sites easier.

In conclusion, our analysis implies that within the $(AgI)_x(Ag_2O \cdot nB_2O_3)_{1-x}$ glasses an "amorphous phase"
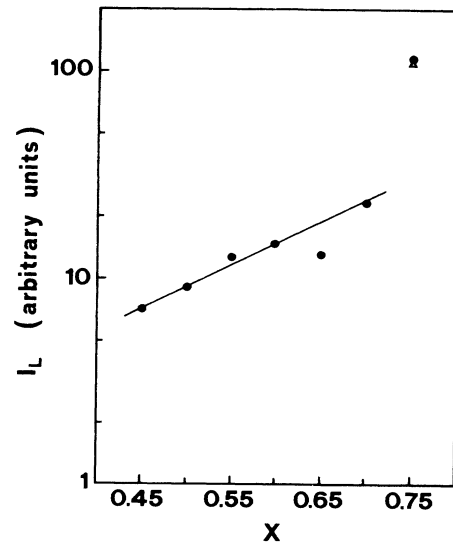

FIG. 3. Integrated intensity of the Lorentzian contribution at several AgI concentrations. The intensity of the Lorentzian at $x = 0.75$ deviates from the exponential behavior, increasing about 1 order of magnitude with respect to the intensity at $x = 0.70$.

of silver iodide is present. Such a phase, of course, is totally disordered with regard to the angles of the tetrahedra; a partial order due to the presence of fixed ions (iodine), as in α-AgI, does not exist. We want to stress that this hypothesis does not imply the formation of crystalline microdomains within the glass matrix; rather, we are in the presence of a distorted configuration due to the interaction with the atoms of the binary matrix, particularly with the oxygen atoms.

EXAFS measurements in these glasses, which are in progress, should provide a good test of these conclusions. Light scattering studies in the concentration range $0.70 < x < 0.75$ would also be interesting, particularly if the behavior of our samples in this range could be indicative of some sort of percolative transition. Such measurements are also in progress.

ACKNOWLEDGMENTS

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