

Inelastic light scattering in superionic glasses $(\text{AgI})_x(\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3)_{1-x}$

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Raman spectra in superionic glasses $(\text{AgI})_x(\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3)_{1-x}$ for various values of x ($0.1 \leq x \leq 0.55$) and for various n ($2 \leq n \leq 4$) are reported. For comparison we also studied spectra of binary glasses $\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3$. They provide light scattering experimental evidence of the network-modifier nature of the Ag_2O in borate matrix. The model of Martin and Brenig for the interpretation of the low-frequency Raman band in the glasses is applied to the series of our samples with increasing content of AgI: A phenomenological "correlation length" is obtained from the study of the low-frequency peak of the various glasses, by introducing the values of the transverse and longitudinal sound velocities, obtained by ultrasonic measurements. That kind of calculation confirms our hypothesis of the increase on the correlation length from 8 Å at $x=0$ to 12 Å at $x=0.55$.

INTRODUCTION

The phenomenon of high ionic conductivity in the glasses has involved a great interest in the past years. For the systems we present in this work, $(\text{AgI})_x(\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3)_{1-x}$, the main problem is to understand the role of AgI in the silver borate glasses in connection with the high ionic mobility shown from these systems.^{1,2} In the crystalline superionic conductors, the importance of the availability of many empty sites for the ionic mobility has been recognized, together with a low activation energy.³ However, the existence of the crystalline order, ensured by the sublattice of the fixed ions, seems to promote the diffusion of the mobile ions, providing some "connected" diffusion paths. As an example of this fact, we can note the behavior of ionic conductivity in AgI, which is lower in the melt than in the solid α phase near the melting point.⁴ The disorder of the superionic crystal is "substitutional" and can be represented by Ising-like models. The disorder of the liquids and similarly of the glasses is instead, "topological," i.e., in these systems it is not possible to define any preferred values of some vector giving translational invariance for a sufficiently long range.⁵

Thus it is very interesting to understand what happens to the random network of silver borate glasses when AgI is introduced. Many different techniques have been used to obtain some insight about that question: x-ray diffraction,¹ conductivity measurements,⁶ NMR,^{7,8} ultrasonic attenuation,⁹ etc. In this work we develop previous Raman measurements¹⁰ on binary $(\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3)$ and ternary $[(\text{AgI})_x(\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3)_{1-x}]$ glasses.

From the analysis of Raman spectra we make the hy-

pothesis that AgI keeps the short-range configuration of the crystal in the glass, based on tetrahedric units and does not considerably affect the glass network. Furthermore, the AgI units show some "connection" for lengths of some basic units and that correlation length increases with the concentration of AgI. We obtain this phenomenological parameter by applying the Martin-Brenig model¹¹ developed for the interpretation of low-frequency Raman scattering in other nonsuperionic glasses. The sound velocities we measure with independent methods enter into the calculation of correlation length from the peak of Raman scattering in the low-frequency range. On the basis of the model we give an estimation for the structural correlation range in studied glasses between 8 and 12 Å.

EXPERIMENTAL DETAILS

Raman data were obtained with a standard system, consisting of argon laser excitation, double-monochromator, and photon counting, followed by a multichannel analyzer storage. The laser radiation was defocalized, and its power was about 30 mW. The high quality of obtained spectra was due both to optical quality of the samples and to instrumental resolution of the Jobin-Yvon double monochromator with holographic gratings, which allowed us to obtain spectra from 3 cm^{-1} from the excitation line: The resolution was 1 cm^{-1} . We used two scattering geometries: the incident beam polarized and the scattered light analyzed both perpendicular to the scattering plane ($\perp\perp$) and the incident beam polarized parallel to and the scattered light analyzed perpendicular to the scattering plane ($\parallel\perp$). The Raman data were obtained from the ex-

perimental spectra by subtracting a luminescence background.¹¹ For low-temperature measurements the samples were placed in good contact with the cold finger of a variable temperature optical cryostat with temperature stability of ± 0.5 K. The velocity of 5-Mhz longitudinal and transverse sound waves were measured at room temperature, by the pulse-echo overlap method using the same apparatus described in Ref. 9.

The samples were made¹ by heating weighted quantities of reagent silver nitrate, silver iodide, and boron oxide; the powders contained 2% water. Thermogravimetric analysis indicated that when the samples were heated the weight decreased as expected for complete delivery of water (from B_2O_3) and nitrogen oxide (from $AgNO_3$). The melt samples were poured into stainless-steel molds at 300 K. The optical quality of glasses was excellent, homogeneous and transparent; the color varied from clear yellow to orange at the various AgI contents and at the various ratios $[Ag_2O]/[B_2O_3]$. The binary glasses were fairly hygroscopic and they tended to darken especially during laser light exposition: The latter phenomenon was avoided when the light power on the samples was below 100 mW. The ternary glasses do not present such effects.

RAMAN RESULTS

With the aim of studying the vibrational dynamics of ternary glass it is convenient to first know the dynamics of the binary ones. In Fig. 1 we report the $Ag_2O \cdot nB_2O_3$ Raman spectra at room temperature with $4 \leq n \leq 9$. For a better description and understanding of obtained results we can distinguish two spectral regions.

(1) The region below 200 cm^{-1} where, in all samples examined by us, a large band with a maximum in the region $18\text{--}28\text{ cm}^{-1}$ is evident.

(2) The region above 200 cm^{-1} : Besides 460-- and 650 cm^{-1} weak bands, two intense bands centered at 770 and 800 cm^{-1} are also present; the latter bands are totally polarized as is shown in Fig. 2.

First let us take into account this last region, which is interesting for structural investigations. In particular we

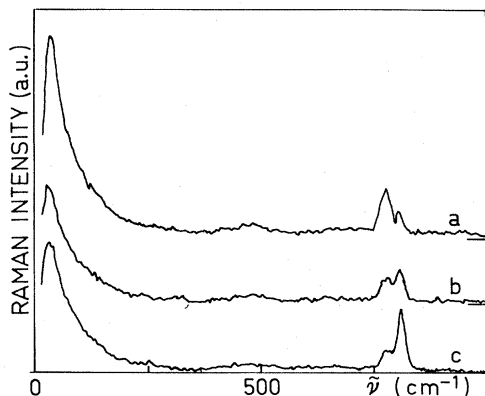


FIG. 1. Raman spectra of binary glasses $(Ag_2O)_y(B_2O_3)_{1-y}$ in the frequency range $0\text{--}1000\text{ cm}^{-1}$. Spectra *a*, *b*, and *c* correspond to $y = 0.20, 0.15,$ and 0.10 , respectively. All of the spectra are collected in the $\perp\perp$ polarization. Room-temperature luminescence background has been subtracted.

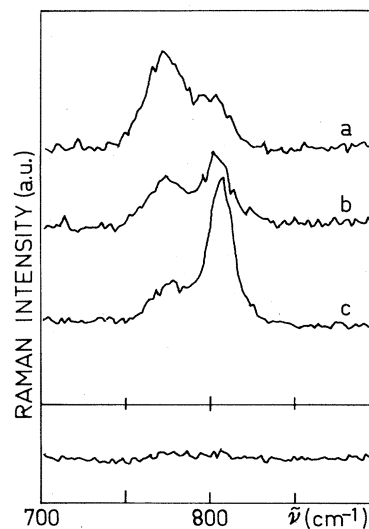


FIG. 2. Upper: Raman spectra in the $(700\text{--}900)\text{ cm}^{-1}$ frequency range; *a*, *b*, and *c* have the same correspondence of Fig. 1. The polarization is $\perp\perp$. Lower: Raman spectrum with $\parallel\perp$ polarization of the glass *a*; the *b* and *c* glasses give similar results. Note the total polarization of the two bands.

focus our attention on the two bands at 770 and 800 cm^{-1} because of their energy: It is well known that the Raman spectrum of B_2O_3 has only one very peaked band at about 800 cm^{-1} which is polarized¹² (not activated in infrared absorption). Such a frequency is characteristic of particular ring structures,¹³ and some authors have proposed the hypothesis that B_2O_3 glass is essentially made up of a random boroxol network with a high component of boroxol rings with six members. The 800 cm^{-1} band has been attributed to a symmetric breathing motion.^{13,14}

The Ag_2O in the borate glass promotes the breakdown of boroxol rings and the formation of BO_4 tetrahedric units. The experimental evidence for such a process is the increasing of a Raman band at 770 cm^{-1} together with a decrease of the band at 800 cm^{-1} . This phenomenon is already well known for the mixing of alkali oxides to B_2O_3 glass matrix;¹⁵ the rise of the 770 cm^{-1} Raman band with the increasing concentration of Ag_2O confirms the network-modifying nature of Ag_2O , similar in this behavior to alkali oxides.

However, let us note the difference in the ratio of the intensity of the two bands in the two types of glasses: In $Ag_2O\text{--}B_2O_3$ for concentration of 20% Ag_2O , the two peaks have a comparable intensity. By means of these considerations and in accordance with ir and internal friction measurements^{15,16} we think that for such a concentration, the number of BO_4 groups has not yet reached the saturation value. The introduction of silver iodide in glass matrix does not modify substantially the vibrational dynamics of binary glass in the region above 200 cm^{-1} (see for comparison Fig. 3 where the two Raman spectra are reported). The region under 200 cm^{-1} presents a great interest; in fact the band centered at 25 cm^{-1} is present in glasses of different nature, for instance B_2O_3 , SiO_2 , GeO_2 , and in almost all the borate glasses. Such a band is also

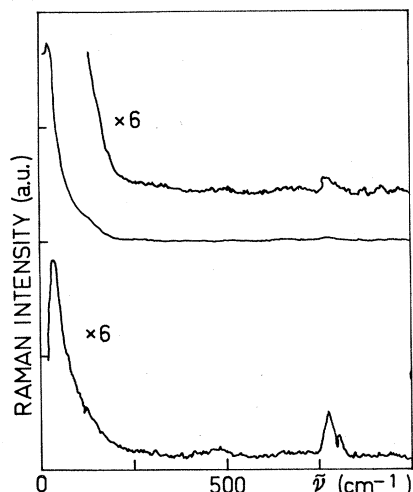


FIG. 3. Upper: Spectrum of ternary glass with $x=0.4$ and $n=4$. Lower: Spectrum of binary glass with $n=4$. Both the spectra have \perp polarization. The intensity of the upper spectrum is about 6 times greater than the lower one. All the bands above 200 cm^{-1} have the same energy in both the spectra.

present in $\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3$ and in the superionic $(\text{AgI})_x(\text{Ag}_2\text{O}\cdot n\text{B}_2\text{O}_3)_{1-x}$. It is present in materials which have in common only the glass nature and it is still the subject of study by different authors.

At the same time (see Fig. 4) we can note large modifications showing that the low-frequency region of spectrum is strongly influenced by the presence of AgI. The Raman results in this region of spectrum may be summarized in three points.

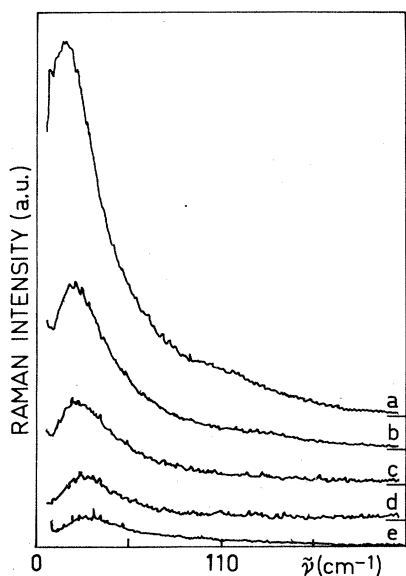


FIG. 4. Spectra in the low-frequency region at various x : a: $x=0.55$; b: $x=0.30$; c: $x=0.20$; d: $x=0.10$; e: $x=0$. Note the different spectral shape between the binary and ternary glasses (the ternary glasses have the low-frequency band more and more peaked with increasing x), the great increase of the low-frequency band, and the appearance of the band at about 110 cm^{-1} .

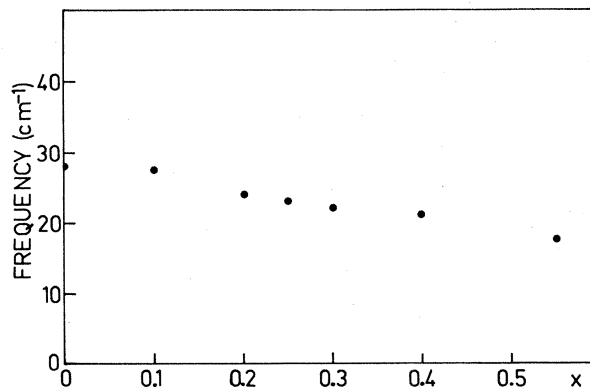


FIG. 5. Peak frequency of the band around 25 cm^{-1} vs increasing AgI content.

(1) The intensity of Raman scattering increases by increasing the AgI concentration: from $x=0$ to 0.5 . However, a great change in Raman intensity occurs between $x=0$ and 0.1 .

(2) A new band centered at about 110 cm^{-1} appears, and it increases with the AgI concentration: It seems roughly proportional to AgI content, but a quantitative evaluation is difficult at this stage.

(3) The peak frequency of the band centered at about 28 cm^{-1} linearly shifts (see Fig. 5) towards a low frequency by increasing the AgI concentration (see Fig. 6); At this point we can sum up that we have identical results when we change the $[\text{Ag}_2\text{O}]/[\text{B}_2\text{O}_3]$ ratio ($n=2,3$), and finally the shape of bands has not been modified by varying the temperature as has been noted in Fig. 7 where the Raman spectra taken at $\sim 35\text{ K}$ and room temperature are reported while the intensity obeys the Bose-Einstein population factor (Fig. 7). Our measurements have been repeated several times, on the same samples and by changing the sample series, obtaining the same results: These facts underline the reproducibility of Raman scattering behavior in our samples.

ANALYSIS OF RAMAN DATA

An inspection of Raman spectra in the low-frequency region of binary and ternary alloys proposes again a question that seems typical of the "glassy state." In fact, an

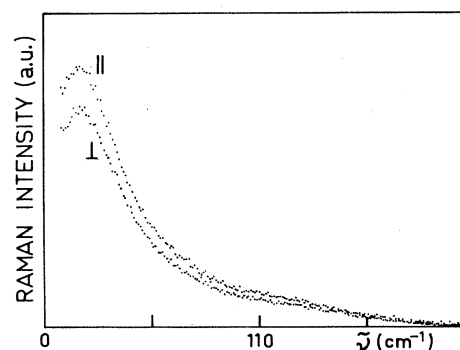


FIG. 6. Low-frequency spectra of $(\text{AgI})_{0.55}(\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3)_{0.45}$ in the parallel and perpendicular polarizations.

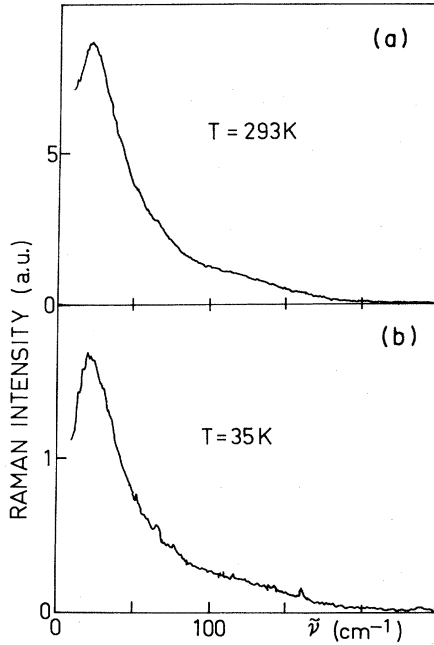


FIG. 7. Raman spectra of $(\text{AgI})_{0.4}(\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3)_{0.6}$ at different temperatures: (a) 293 K; (b) 35 K.

intense low-frequency band at $\sim 25 \text{ cm}^{-1}$ shown from dielectric and chalcogenide glasses^{16,17} is present in all the investigated concentrations (see Fig. 4).

Now many hypotheses have been debated about the nature of low-frequency Raman scattering in the glasses. The model of Martin and Brenig¹¹ applied by Nemanich to some chalcogenide glasses and alloys,¹⁶ attributes the low-frequency peak of the glasses to structural disorder of the amorphous material affecting the Raman coupling constant. An interesting consequence of this model is the direct relation between the maximum frequency of this peak and the structural correlation range (SCR) of the glass.

Following the notation of Nemanich we can write the experimental Raman intensity:

$$I_{\beta\alpha\gamma\delta} \propto C_{\beta\alpha\gamma\delta}(\omega) G(\omega) \frac{1}{\omega} [n(\omega, T) + 1], \quad (1)$$

where the $G(\omega)$ is the vibrational density of states, assumed to be $G(\omega) = \omega^2$, in the Debye approximation, and $n(\omega, T) + 1$ is the Bose-Einstein factor. The more interesting term, however, is the Raman coupling coefficient $C_{\beta\alpha\gamma\delta}(\omega)$. In solids having electrical and mechanical disorder the ω dependence of C is expressed by the following formula:

$$C_{\beta\alpha\gamma\delta}(\omega) \propto x^2 [g_t(x) E_{\beta\alpha\gamma\delta}^t + g_l(x) E_{\beta\alpha\gamma\delta}^l], \quad (2)$$

where the variable x is linear in ω :

$$x = 2\pi c \omega \delta / v_l. \quad (3)$$

v_l is the longitudinal sound velocity, and σ is the structural correlation length.

The terms E^t and E^l , respectively, contain the transverse and longitudinal fluctuations of the elastic and elasto-optic constants, weighted by the Gaussian functions

$g_t(x)$ and $g_l(x)$,

$$g_l(x) = \exp(-x^2), \quad (4a)$$

$$g_t(x) = \left[\frac{v_l}{v_t} \right]^5 \exp \left[-x^2 \left[\frac{v_l}{v_t} \right]^2 \right]. \quad (4b)$$

Combining the previous equations we obtain this ω dependence for the Raman coupling constant in the $\parallel\perp$ scattering

$$C_{\parallel\perp}(\omega) A \omega^2 \left[3 \left[\frac{v_l}{v_t} \right]^5 \exp \left[-\frac{(2\pi c \omega)^2 \sigma^2}{v_t^2} \right] + 2 \exp \left[-\frac{(2\pi c \omega)^2 \sigma^2}{v_l^2} \right] \right], \quad (5)$$

where in the constant A the value of the elastic constant fluctuations is contained.

The experimental $C_{\parallel\perp}(\omega)$ to be compared with the formula (5) can be obtained by dividing the experimental $I_{\parallel\perp}(\omega)$ intensity by the Bose-Einstein factor and the frequency ω (of course in the Debye approximation, assuming the acoustical density of states is proportional to ω^2). Since v_t and v_l can be obtained from other measurements only the parameters A and σ are unknown. For the Raman coupling constant in the $\perp\perp$ scattering the theoretical dependence is

$$C_{\perp\perp}(\omega) = A \omega^2 \left[2 \left[\frac{v_l}{v_t} \right]^5 \exp \left[-\frac{(2\pi c \omega)^2 \sigma^2}{v_t^2} \right] + (15V + \frac{2}{3}) \exp \left[-\frac{(2\pi c \omega)^2 \sigma^2}{v_l^2} \right] \right], \quad (6)$$

where

$$V = \frac{\delta C_t^2 + \lambda C_l^2}{\delta C_t^2 + \lambda C_l^2}$$

is the ratio between the mean-square spatial fluctuation for longitudinal and transversal elastic and elasto-optic constants.

The parameter V can be obtained from the depolarization ratio:

$$\rho(\omega) = \frac{I_{\perp}}{I_{\parallel}} = \left[\frac{4}{3} + \frac{10}{\frac{2}{3} + g_t/g_l} \left[\frac{\delta C_t^2 + \lambda C_l^2}{\delta C_t^2 + \lambda C_l^2} \right] \right]^{-1}$$

Thus we can deduce a value of the SCR by fitting the theoretical $c(\omega)$ from Eq. (5) or (6) to the experimental values.

In Fig. 8 typical best fits of Eqs. (5) and (6) are reported (solid line) and experimental data (solid circles) normalized by the factor $\omega[n(\omega, T) + 1]$ for one binary and one ternary glass. The agreement between the theoretical curve and the experimental points is also confirmed by similar results, obtained in the other concentrations: Only in the glass with higher content of AgI were small deviations observed. It is to be noted that we were able to obtain a good fit for $\Delta\omega \geq 8 \text{ cm}^{-1}$, since in the lower-

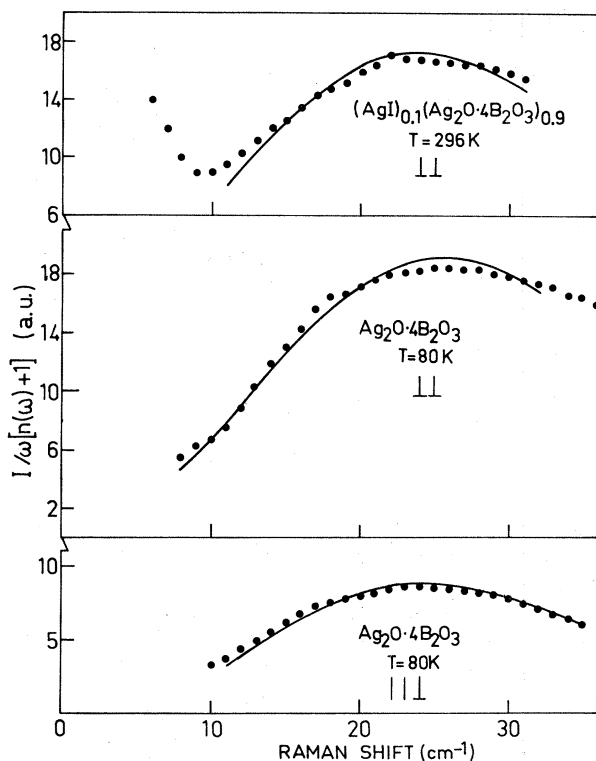


FIG. 8. Theoretical fit (solid lines) of $I/\omega[n(\omega)+1]$ (solid circles) by Eqs. (5) and (6).

frequency region an incompletely rejected straight light, and also the scattering events, were present, due to another kind of phenomena typical of the disordered systems: the so-called "light scattering excess."¹⁸ The corresponding results for the correlation length in the binary and ternary glasses are reported in Table I with the one obtained by maximizing the $C(\omega)$ function. In the latter case the SCR was obtained from the relation

$$\sigma = \bar{v}/2\pi c\omega_{\max}$$

\bar{v} being the average sound velocity and ω_{\max} the frequency of experimental maximum. The two series of results are very similar in magnitude and also in behavior with AgI and Ag_2O contents. In all the calculations we have used the 5-MHz sound velocity values, also reported in Table I,

by assuming that in the explored temperature range the influence of the dispersion, connected to the inelastic effects due to Ag^+ mobile ions in the glassy matrix, is groundless in binary and ternary glasses with low AgI contents and is negligible at high AgI concentration.¹⁹

Now the main result of the SCR data is the gradual increase with AgI content, which could be interpreted as a lowering of the "disorder degree" of the glassy matrix. This hypothesis also follows from the impossibility of obtaining glassy materials for $n > 2$ and $x > 0.6$, respectively, in the binary and ternary alloys.^{15,2} In our systems both a structural-like disorder and an electric disorder exist. We make the hypothesis that our results concern a local order modification from a structural point of view. In particular, in the ternary alloys the AgI could originate a cooperative structural arrangement whose dimensions increase with its content in order to reproduce the structure and the vibrational dynamics of crystalline AgI. This hypothesis seems to be confirmed by the close similarity of the low-frequency Raman spectrum with that of crystalline AgI.^{10,20,21} In fact it is to be noted that the addition of AgI does not substantially change the vibrational spectrum of silver borate glasses in the high-frequency region ($770\text{--}800\text{ cm}^{-1}$) but only introduces a strong additional scattering in the low-frequency region ($\Delta\omega < 200\text{ cm}^{-1}$), provoking also the gradual appearance of a $\sim 110\text{ cm}^{-1}$ band, typical of crystalline silver iodide. In this respect, also, if other measurements are not available in order to ensure the accuracy of the absolute value of our SCR data, we can try, equally, to obtain a quantitative check of our structural hypothesis. In fact, if we consider the volume occupied by a single AgI unit we find 20 \AA^3 compared to a correlation volume of about 2000 \AA^3 ; hence 100 AgI_n units may enter in such a correlation volume.

CONCLUSION

NMR spectroscopy and ultrasonic attenuation measurements have raised several questions concerning local order of such ternary glasses. For instance, some authors have suggested that AgI is mainly coordinated by BO_4^- groups and that whether Ag^+ is one of AgI or Ag_2O is unimportant; other authors² propose a different picture which is based upon the distinction between "immobile" cations and "mobile" ones and hence upon a clear distinction between the "different" Ag^+ .

TABLE I. Values of 5-MHz sound velocities and of structural correlation range in silver-halide-silver-borate glasses.

	v_l (cm sec ⁻¹)	v_t (cm sec ⁻¹)	$\bar{v}/\pi c\omega$	2σ (Å) Curve fitting
$\text{Ag}_2\text{O}\cdot 9\text{B}_2\text{O}_3$	2.06×10^5	3.92×10^5	8.9	8.3
$\text{Ag}_2\text{O}\cdot 6\text{B}_2\text{O}_3$	2.17	4.05	9.4	8.5
$\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3$	2.26	4.25	9.8	8.7
$(\text{AgI})_{0.1}(\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3)_{0.9}$	2.24	4.17	10.5	10.0
$(\text{AgI})_{0.2}(\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3)_{0.8}$	2.20	4.06	10.7	10.6
$(\text{AgI})_{0.3}(\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3)_{0.7}$	2.05	3.87	10.8	10.8
$(\text{AgI})_{0.4}(\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3)_{0.6}$	1.93	3.64	11.2	11.3
$(\text{AgI})_{0.55}(\text{Ag}_2\text{O}\cdot 4\text{B}_2\text{O}_3)_{0.45}$	1.81 ^a	3.42 ^a	12.2	11.6

^aExtrapolated values.

The Raman spectroscopy suggests that the "solved" AgI tends to reproduce on the local level connected tetrahedra in interstitial sites of the matrix host: The connection favors the Ag^+ conductivity; in fact, the speculated structure allows traveling of Ag^+ ions along the "diffusion path" due to the presence of the available positions in the distorted sublattice of AgI. Our reply is tentatively more similar to the one suggested in Ref. 2, which is based upon the distinction between immobile cations and mobile ones. However, a more complete set of mea-

surements is necessary, in particular extended x-ray absorption fine structure measurements are being carried out: Such measurements would give useful and direct information about local structure of Ag^+ ions.

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