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Acoustic properties and diffusion in superionic glasses

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An ultrasonic study of the loss characteristics and sound velocity was carried out in AgI-Ag_2O-B_2O_3 glasses as a function of temperature and silver-compound concentration. From the behavior of the sound velocity in $(Ag_2O)_y(B_2O_3)_{1-y}$, the formation of fourfold-coordinated boron ions is suggested. This increases rapidly, as a function of y, until $y \simeq 0.25$; for larger y, a strong production of singly bonded oxygen ions (nonbridging oxygen ions) prevails, which weakens the glassy network. From the analysis of the attenuation peaks in terms of a relaxation-time Gaussian-type distribution, arising from the thermally activated relaxations of mobile silver ions, it is argued that there exists a similarity between the ion motion in a stress field and in an electric one. By way of this analogy and by combining the ultrasonic results with the dc conductivity data in $(AgI)_x[(Ag_2O)_y(B_2O_3)_{1-y}]_{1-x}$, the ion-jump distances are calculated. The behavior with AgI concentration is consistent with the structural hypothesis of the existence of silver ions differently bonded and mobile in the glassy matrix.

I. INTRODUCTION

During the last few years, the interest in superionic glasses increased not only because of their technological applications, but also because of the desire to understand how a disordered structure could assist the fast-ion dynamics. The various hypotheses concerning AgI-Ag_2O-B_2O_3 glassy systems can be roughly divided into two classes: the first one hypothesizes the existence of only one type of mobile silver ion,[1] and the other, which postulates more than one type of mobile silver ion.[2] However, no details are given concerning the ion-motion mechanism in either case. Acoustic[3] and Raman spectroscopy[4] measurements supported mostly the latter hypothesis, leading to the assumption of the building up of an AgI distorted sublattice, characterized by more-readily-diffusing Ag^+ ions.

In this paper we present an extensive analysis of ultrasound velocity and attenuation in "binary" (Ag_2O-B_2O_3) and "ternary" (AgI-Ag_2O-B_2O_3) alloys. In such a way we obtain useful information about the microscopic structure of these glasses. Moreover, by combining our data with the dc conductivity results, it was possible to estimate the Ag^+ ion-jump distances. In turn, the behavior of the jump distances, as a function of the AgI concentration, seems to confirm the existence of two distinct channels for the jumps. In such a sense one can speak of two types of mobile ions.

II. EXPERIMENTAL PROCEDURE

Samples of the system $(AgI)_x[(Ag_2O)_y(B_2O_3)_{1-y}]_{1-x}$, x and y being the molar fractions, were prepared in the binary ($x=0$, $0 \le y \le 0.33$) and ternary form ($0 \le x \le 0.7$, $0.25 \le y \le 0.5$) using the same procedure elsewhere described.[1,5] The analysis of the intensity of Mo K x rays as a function of the diffraction angle did not reveal crystalline peaks, but very broad bands, typical of glasses, in all the samples. The possible presence of a sizable amount of water, which would strongly influence the acoustic loss in borate glasses,[6] has been excluded by analyzing our samples with ir absorption. In order to prevent any possible contamination of glasses, they were carefully stored in a darkened dessicator.

The attenuation and sound-velocity measurements of longitudinal and shear waves were performed in the (5—45)-MHz frequency range, by a pulse-echo technique previously described.[3] Only for the ternary alloys with $y=0.5$, which showed the highest attenuation, was it necessary to use a double-transducer configuration.

In the samples that have a strong dispersion effect at room temperature, typically some glasses with $y=0.5$ and 0.3,[7] the values of sound velocity were taken by making the correct echoes overlap at temperatures outside the dispersion region and then by following the differential temperature shift of the central part of the echoes until room temperature.

The bonding agents between samples and transducer were Nonaq-Stopcock grease and cyanoacrylate resin, respectively, in the temperature ranges 80—300 K and 300—460 K. In the whole temperature range a stability better than 0.1 K was achieved by a home-made apparatus in which calibrated platinum sensors were used. All the attenuation data are corrected for an average diffraction loss λ/a^2 (db cm^{-1}), λ being the ultrasonic wavelength and a the transducer radius.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Sound velocity

In Figs. 1(a) and 1(b) we reported the 5-MHz longitudinal and transverse sound-velocity data in binary alloys, as

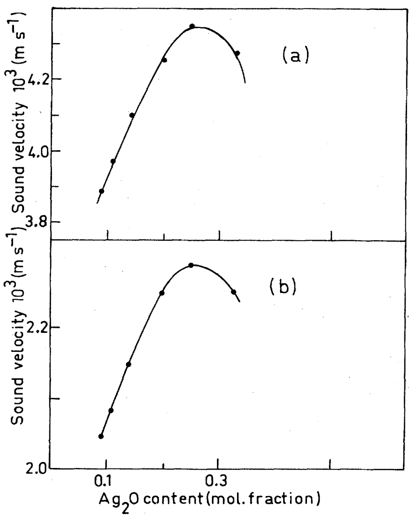

FIG. 1. Sound velocity in $(Ag_2O)_y(B_2O_3)_{1-y}$ at 295 K: (a) 5-MHz longitudinal waves; (b) 5-MHz transverse waves.

a function of Ag_2O concentration at 295 K. It is evident that the velocity greatly increases in the low-y region, reaching a maximum at $y \simeq 0.25$, and then decreases. A similar behavior, elsewhere found in sodium borate glasses,[8] suggests that the role of silver oxide in B_2O_3 is similar to that of alkali oxide. Such a conclusion, also supported by measurements of acoustic losses,[9] ir absorption,[9] and Raman scattering,[4] encourages us to discuss our results along the same lines.

The random network of B_2O_3 is essentially built up on planar triangles BO_3 (Ref. 8), and the addition of silver oxide (similar to the effect of Na_2O) would strengthen the structure by producing fourfold-coordinated borons, i.e., assisting the formation of BO_4 tetrahedric groups with consequent crosslinks between some planar units. The existence of such groups is directly shown by the analysis of the Raman bands at ~ 770 cm^{-1}.[4] The concentration of BO_4 groups (as well as the related stiffness) increases at a maximum formation rate up to a critical concentration of about 0.25 molar fraction. Further addition of Ag_2O weakens the network by producing essentially singly bonded oxygen ions (nonbridging oxygens), near which the metallic ions should be, ensuring the electric neutrality. In such a process some oxygen ions, that originally bridge between two structural units, are substituted by two oxygen ions, bonded only to a single unit.[10] It is to be noted that the existence of nonbridging oxygen ions is also confirmed by the appearance of a peak in the internal friction curves, for $y > 0.25$.[11] In Figs. 2(a) and 2(b) the sound-velocity behavior is shown as a function of AgI content in ternary alloys for various y.[12] In such a case the velocity decreases continuously with AgI concentration. Such a circumstance can be related to a progressive softening of the network, introduced by the new species. We will readdress this question with more detail to the microscopic explanation of this in the following sections.

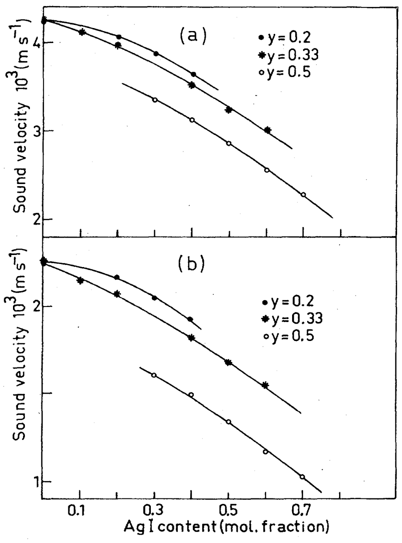

FIG. 2. Sound velocity in $(AgI)_x[(Ag_2O)_y(B_2O_3)_{1-y}]_{1-x}$ at 295 K: (a) 5-MHz longitudinal waves; (b) 5-MHz transverse waves.

B. Acoustic attenuation

In Fig. 3 we show the acoustic attenuation of longitudinal sound waves, as a function of T, in the ternary alloys with $y = 0.5$ and at various concentrations of AgI ($x \geq 0.3$). Lower concentrations are not considered, because decomposition problems arise in the preparation, or they do not vitrify at all ($x = 0$).

In our measurements the presence of a very high peak is evident, whose position shifts to lower temperatures and whose height increases with AgI content. Similar behavior was also revealed in the ternary alloy with $y = 0.33$.[3] The enormous value of the acoustic attenuation prevented the investigation of the shift of the peak temperature with the ultrasound frequency in the samples with $y = 0.5$, although such an analysis is possible in the ones with $y = 0.33$ and 0.20. Typical results are shown in Figs. 4(a) and 4(b), revealing an increasing peak temperature with the frequency, which indicates a thermally activated relaxation process.

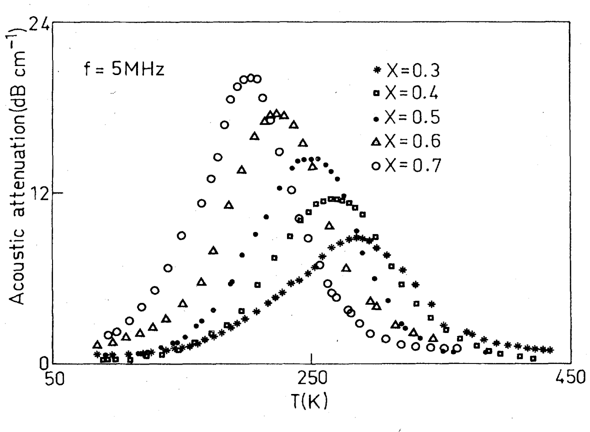

FIG. 3. Acoustic attenuation as a function of temperature in $(AgI)_x[(Ag_2O)_{0.5}(B_2O_3)_{0.5}]_{1-x}$.

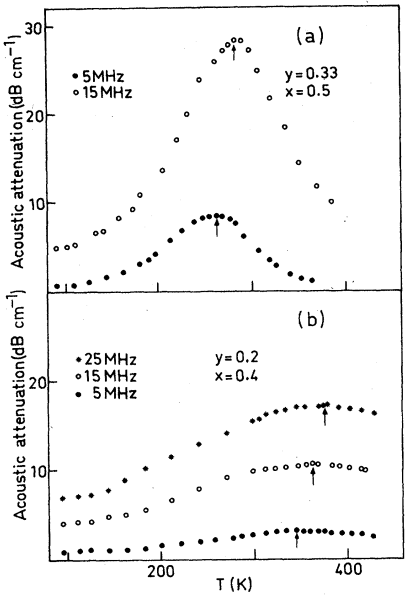

FIG. 4. Acoustic attenuation vs temperature at various frequencies in two different glasses. The shift of the peak temperature with the frequency is evident.

In Fig. 5 it is possible to observe that the increase of Ag_2O concentration, at a constant AgI content, has a double effect on the acoustic losses $Q^{-1}=\alpha\lambda/\pi$ (α being the acoustic loss in Np cm^{-1} and λ the wavelength of the ultrasound).

(i) A decrease of the peak temperature that in a thermally activated process can be connected to an energy activation decrease.

(ii) A strong increase of the maximum relaxation loss.

Considering that these glasses have about the same elastic characteristic (see Fig. 2), an analysis of the maximum relaxation loss can give information as to how it depends on the defect concentration. In the inset of Fig. 5 we show that such a quantity, obtained by subtracting a "flat background value" due to other dissipative processes, rises linearly with the total concentration of silver ions present in the alloys.

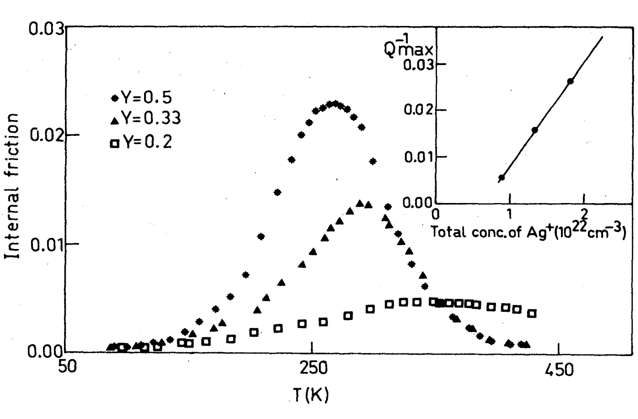

FIG. 5. Temperature behavior of the internal friction in $(AgI)_{0.4}[(Ag_2O)_y(B_2O_3)_{1-y}]_{0.6}$ glasses. In the inset is plotted the maximum relaxation loss as a function of the total concentration of silver ions (see text).

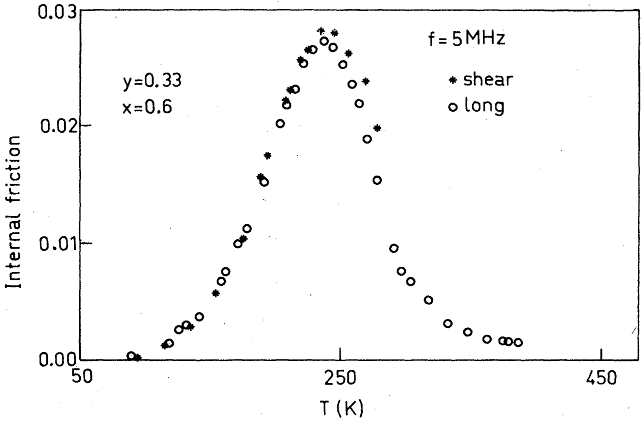

FIG. 6. Comparison of the relaxation loss of longitudinal and transverse waves in $(AgI)_{0.6}[(Ag_2O)_{0.33}(B_2O_3)_{0.67}]_{0.4}$.

The comparison between the relaxation losses, in transverse and longitudinal sound waves, emphasizes a close similarity (e.g., see Fig. 6): The magnitude of Q^{-1} for the shear loss is about the same as that for the longitudinal one. For the $y=0.5$ series such a comparison can be made only outside the main peak, because of the very high absorption as mentioned before. However, in the examined regions (i.e., on the right- and left-hand side of the peak), we found again the same magnitude both for longitudinal and shear waves.

In all the investigated samples of the present work, the behavior of α, as a function of ultrasound frequency, shows the f^2 and $f^{\sim 0.8}$ dependence, respectively, on the right- and left-hand side of the peak, already previously observed.[3] Our experimental results indicate that the observed anomalies can be connected with the thermally activated relaxation processes involving silver ions, weakly bonded to the glassy network (i.e., "network modifying ions"). The ultrasonic stress changes the microscopic environment of these ions at an angular frequency ω, modifying their equilibrium distributions between equivalent (or near-equivalent) positions available in the network. Actually, the new equilibrium distribution will be reached in a time τ (relaxation time), mainly determined by the jump frequencies. The maximum loss per cycle (the Q^{-1} maximum value) will be reached when $\omega\tau=1$. These dissipative processes are well described in terms of the anelasticity theory.[13] Elsewhere we pointed out,[3] however, that the same nature of the glassy state rules out a single relaxation time approach in these systems. In fact all the revealed relaxation peaks are much broader than a Debye peak, and this can be interpreted as arising from the existence of a distribution of relaxation times due to random deviations in the local arrangement of the system.

In the hypothesis that the relaxation losses are not too large, one can write for the acoustic attenuation, in the case of a distribution $f(\tau)$ of relaxation times:

$$\alpha=\frac{\Delta}{2v}\int\frac{\omega^2\tau}{1+\omega^2\tau^2}f(\tau)d\tau\ , \tag{1}$$

Δ being the relaxation strength, ω the ultrasonic angular frequency, and v the sound velocity. In our case, despite the very large attenuation found in some samples, the condition for the validity of Eq. (1) is always fulfilled. In fact, in many glasses the losses are of the order of $Q^{-1}\sim 10^{-3}$. We found values up to ten times larger, i.e., for the order of 10^{-2}, which is large enough to make an experimental investigation hard, but not so large as to invalidate Eq. (1).

The relaxation time is connected to the activation energy E for the process and to the frequency factor by an Arrhenius-type equation $\tau^{-1}=\tau_0^{-1}\exp(-E/k_BT)$. In order to apply such an equation to our experimental data, we assume a single value for τ_0. As a consequence, the τ distribution can be connected to a distribution of activation energies E, representing the heights of the barriers that the ions must surmount to go into the near allowed positions (many-well potential description). A useful form of Eq. (1), which takes into account only an E distribution can be derived by the microscopic theory of Jäckle *et al.*:[14]

$$\alpha=\frac{B^2}{4\pi\rho v^3k_BT}\int P(E)\frac{\omega^2\tau(E)}{1+\omega^2\tau^2(E)}dE\ . \tag{2}$$

In Eq. (2), B is an average deformation potential that expresses the coupling between the ultrasonic stress and the system, $P(E)$ is the E distribution function, T the absolute temperature, and the other parameters are defined as in Eq. (1).

It is quite reasonable, due to the inherent randomness of our system, to assume for $P(E)$ a Gaussian distribution, i.e.,

$$P(E)=\frac{N}{(2\pi)^{1/2}E_0}\exp\left[-\frac{(E-E_m)^2}{2E_0^2}\right]\ , \tag{3}$$

N being the total number of jumping particles per unit volume; E_m and E_0 are the most probable of the width of the distribution.

In order to find the value of τ_0, the following two-step procedure was used, in the least-squares fits of our results with a MINUIT CERN minimum search program.

(i) The use of a Gaussian distribution function implies that at the peak temperature, the product $\omega\tau_m$ is equal to 1, $\tau_m=\tau_0\exp(E_m/k_BT_{\text{peak}})$ being the most probable relaxation time. Such an equation can be solved for τ_0 and the obtained expression inserted in Eq. (2). This expression contains the values of ω and the T peak that can be easily and directly found from experimental data. Then a three-parameter best fit with the full set of experimental data would furnish the values of the remaining parameters E_m, E_0, and NB^2.

(ii) Taking into account some uncertainty in the evaluation of the T peak (especially in the broadest peaks), a further four-parameter best fit of experimental data was carried out, using E_m, E_0, NB^2, and τ_0 (as free parameters). In this case, however, the starting values of the parameters were those obtained in the first step and very narrow ranges of variability were allowed.

The values of the parameters obtained with this procedure are reported in Table I and a typical fit of the relaxation loss is shown by a continuous line in Fig. 7. The good quality of the theoretical approach is also confirmed by the fact that the values of the involved parameters, obtained from the fits of experimental data taken at different fixed frequencies, are practically coincident. The values of the average deformation potential B_l for longitudinal waves, are also inserted in Table I and are obtained from NB_l^2, assuming that all the silver ions in the glass are involved in the dissipative processes (and this is also supported by the results of Fig. 5).

Now the inspection of the behavior of the fit parameters, as a function of AgI and Ag_2O molar fractions, reveals that B and τ_0^{-1} do not show a definite dependence on the relative amount of the two species. The values, in fact, are distributed quite randomly around 0.4 eV and 10^{14} s^{-1} with very small deviations.

TABLE I. Values of the most probable activation energy E_m, frequency factor τ_0^{-1}, width of the E distribution E_0, and of the deformation potential in $(AgI)_x[(Ag_2O)_y(B_2O_3)_{1-y}]_{1-x}$.

x	E_m (ev/mol)	E_0 (eV/mol)	τ_0^{-1} (10^{14} s^{-1})	NB_l^2 (10^{21} $eV^2\,cm^{-3}$)	B_l (eV)
$y=0.5$					
0.3	0.385	0.057	1.39	3.98	0.47
0.4	0.346	0.05	0.75	3.90	0.47
0.5	0.335	0.047	1.33	3.24	0.44
0.6	0.30	0.045	1.67	2.44	0.38
0.7	0.251	0.033	0.46	1.58	0.31
$y=0.33$					
0.0	0.528	0.071	0.91	1.62	0.35
0.1	0.502	0.066	1.59	1.34	0.33
0.2	0.46	0.076	1.26	2.00	0.40
0.4	0.372	0.062	0.63	2.56	0.44
0.5	0.35	0.052	1.06	2.52	0.44
0.6	0.32	0.050	1.56	2.22	0.41
$y=0.2$					
0.4	0.48	0.11	1.64	1.30	0.38

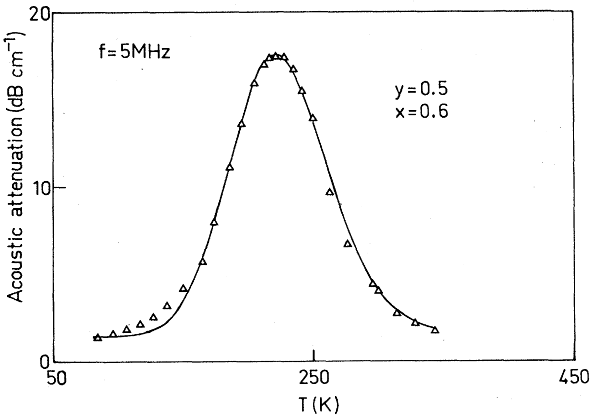

FIG. 7. Comparison between the experimental data (triangles) and the theoretical fit with a distribution of activation energies (continuous line).

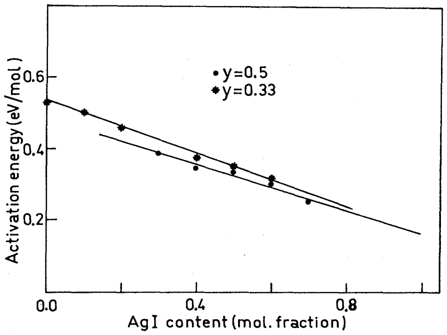

FIG. 8. Behavior of the most probable value of activation energy E_m as a function of AgI content in the glasses with $y=0.33$ and 0.5.

On the contrary, the values of E_0 and E_m decrease monotonically with AgI content. In particular the most probable activation energy E_m decreases linearly in the two series of glasses, but with different slopes (see Fig. 8), showing a clear trend to converge at high AgI concentration. Moreover a peculiar characteristic of these values is their close similarity (at most within a few percent) with the results derived from dc conductivity measurements.[1] Such a circumstance, once more, testifies that the same microscopic mechanism regulates the anelastic and electric behavior of these glasses, giving clear evidence concerning the origin of the relaxation losses.

The decrease of the parameter E_0, with increasing AgI content, indicates a tendency of the system towards a single relaxation time process. Such a circumstance can be connected with an increasing degree of order in the system. In fact, Raman measurements[4] support the idea that AgI tends to ordinate the random network of the glass on a distance scale that increases with the AgI content. Also the circumstance that at high AgI content the glass formation is prevented supports such a conclusion.

IV. THERMALLY ACTIVATED RELAXATION AND DIFFUSION PROCESSES

The close connection between the "acoustical" and "electrical" activation energies suggests that the same jump mechanism regulates the silver-ion dynamics in a dc electric field and in a stress field. The same analogy, also including the self-diffusion processes, was previously observed in silicate glasses for sodium ions.[10] In the diffusion process the jump distance d is involved and one can try to take advantage of the above-mentioned analogies to evaluate d.

In a random-walk process, the self-diffusion coefficient is connected to the jump distance d and to the mean residence time τ^* by the equation

$$D=\frac{d^2}{6\tau^*} \; . \tag{4}$$

Now if the same microscopic mechanism gives rise to diffusion and relaxation processes, the mean residence time τ^* is simply proportional to the relaxation time τ,[15] defined in the preceding section. The ratio between the two times depends, in fact, only on the geometry of the atom movements. The values of this ratio have been calculated for interstitials in bcc lattices and equal 1.5.[15]

Assuming that the jumps of silver ions occur in a large number of interstitial sites, available in the glassy network, and using the previous value for the ratio between τ^* and τ (Ref. 16) we can use the values (E_m and τ_0) of Table I, corresponding to the most probable relaxation time τ_m, in order to evaluate the corresponding τ^*.

Now, owing to the lack of diffusion data in the studied glasses, we can calculate the self-diffusion coefficient by the Nernst-Einstein equation:[16]

$$D=\frac{k_B T}{q}\mu \; , \tag{5}$$

q being the charge of the ions, k_B the Boltzmann constant, T the absolute temperature, and μ the drift mobility. This last term can be written as $\mu=\sigma/qN$, σ and N being the electrical conductivity and the number of ions per unit volume. Inserting in Eqs. (4) and (5) the room-temperature values of σ (Ref. 5) and τ_m and the total concentration of silver ions for N, we have obtained in the various glasses the values of d that are reported as a function of AgI content in Fig. 9.

It clearly results that the average jump distance increases linearly with AgI and it is essentially independent from the value of y, at most for $x \geq 0.3$. This behavior and that of the activation energies (see Fig. 8) seem to indicate the appearance of silver ions introduced by AgI that are characterized by jump distances and bond energies different from those of silver ions in Ag_2O-B_2O_3. These remarks suggest once more that the addition of AgI only slightly affects the random network of borate glass, which keeps, in fact, its vibrational dynamics unchanged.[4] Rather it seems to promote the formation of microdomains that at most remind one on a local scale of the crystalline AgI and, at high concentration of AgI, tend to give rise to some kind of distorted sublattice.

In this respect the increase of the average jump distance and the decrease of the activation energy with AgI can be

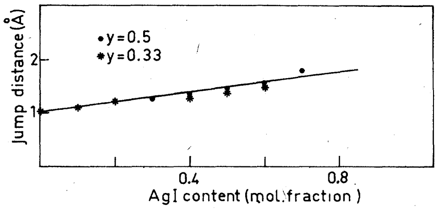

FIG. 9. Dependence of the average jump distance from the AgI content in the glasses with $y = 0.33$ and 0.5.

explained as arising from an appropriate overlap of the two different contributions of the silver ions, jumping in the sites available in the borate and iodide networks. The extreme values at $x = 0.0$ and 1.0 can be assumed as peculiar to the two ionic species.

The independence of d from the relative content of Ag_2O and B_2O_3 seems to give further confirmation to the expressed hypothesis: Reasonably, in fact, we presume that the distances between the sites in the borate network change not much for $y = 0.33$ and 0.5 and consequently the overlap with those typical of AgI must give about the same values. Along the same line, the detachment between the values of E_m in these glasses especially at low concentrations of AgI (see Fig. 8), derives from the large difference existing between the activation energies typical of borate networks in the two cases. This peculiarity is probably connected to the strong increase of the number of nonbridging oxygens in the region $y > 0.25$, as confirmed by velocity measurements, that give rise to more and more soft structures, that consequently warp more easily to permit the ion movements with a consequent decrease in the mean activation energy.

IV. CONCLUSIONS

The analysis of the acoustic properties of silver halide—silver borate glasses reveals anomalies that permit a possible insight into the microscopic structure of these systems. In Ag_2O-B_2O_3 glasses the behavior of sound velocity suggests a high formation rate of nonbridging oxygen atoms, which decreases the stiffness of the network, for an Ag_2O molar fraction higher than 0.25.

In AgI-Ag_2O-B_2O_3 the thermally activated jumps of silver ions between the interstices in the network are at the origin of the acoustic attenuation peaks. From the analogy of the jump mechanism in an electric field and in a stress field, it was possible to determine the jump distances, whose behavior with AgI supports the idea of the existence of two types of mobile ions. This statement is based on the presence of two different types of sites for the silver ions: those of the borate network and those of the iodide domains.

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