PHYSICAL REVIEW B VOLUME 47, NUMBER 21 1 JUNE 1993-I

Ultrasonic study of $(AgI)_x(Ag_4P_2O_7)_{1-x}$ glasses in the region of the glass-transition temperature

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(Received 29 December 1992)

Ultrasonic velocity and attenuation have been measured on the superionic-glass system $(AgI)_x(Ag_4P_2O_7)_{1-x}$, with $0.50 \le x \le 0.875$, from room temperature to 200 °C through the glass-transition temperatures. X-ray diffraction, differential scanning calorimetry, and density measurements were made, besides ultrasonics, to clarify the nature of the supercooled liquid, with or without dispersed crystallites. We observed velocity dispersion and a single attenuation peak for $0.5 \le x \le 0.75$ glasses, which decreased in location with increasing x in close correlation with the glass-transition temperature, and was assigned as due to relaxation of the supercooled liquid. For more AgI content, $0.80 \le x \le 0.875$, another attenuation peak(s) and velocity peak(s) were detected and were considered to be due to nucleation and/or crystallization of some unidentified crystal(s).

I. INTRODUCTION

Ultrasonic studies on AgI-based superionic glasses have been devoted, mainly, to clarifying the relaxation process of the silver ions at low temperatures. There has been a report about studies at higher temperatures, where the glass transition (and sometimes the crystallization afterwards) takes place.[1] The relative scarcity of reports, however, is partly due to a difficulty in maintaining sample shape and size when the sample changes from the glass to the supercooled liquid (SCL). Nevertheless, the acoustic approach to the latter phenomena may prove fruitful.

We measured the ultrasonic velocity, v, and attenuation, α through the glass-transition region for one of the superionic-glass systems, $(AgI)_x(Ag_4P_2O_7)_{1-x}$, with $0.50 \le x \le 0.875$. In a previous paper on the $x=0.75$ and 0.80 glasses,[2] we reported an observation of three steps in the velocity dispersion, caused by three different kinds of relaxation in the SCL. They were assigned, tentatively, as due to relaxations in the AgI-rich phase, in the $Ag_4P_2O_7$-rich phase, and in the AgI-$Ag_4P_2O_7$ mixed phase. It was claimed further that the mixed phase would be dominant in the SCL.

The structure of an AgI-oxysalt glass such as ours is believed to be composed of amorphous AgI microdomains, which are dispersed in, and interacting only weakly with, the oxysalt matrix.[3] This leads to an expectation of the presence of two phases, rather than three, in the glass. However, there is no evidence that these two phases survive even in the SCL, nor that AgI really constitutes microdomains, even if one accepts that the mobile silver ions are those that are attached to the iodine ions, rather than to the oxysalt. A recent neutron-diffraction study[4] suggests the opposite: that microdomains of the oxysalt would be dispersed in the disordered AgI matrix or AgI-oxysalt solid solution.

The purpose of this paper is to show, for various compositions, how v and α change with temperature when the sample changes from the solid to the SCL state.

II. EXPERIMENT

The samples were of the composition $(AgI)_x(Ag_4P_2O_7)_{1-x}$, with $0.50 \le x \le 0.875$. The mixture of AgI and $Ag_4P_2O_7$ was melted in vacuo or air at 450–500°C for six hours, and poured into an aluminum tube, 1 cm in length and 1 cm in inner-diameter. A sample-stuffed aluminum tube was then polished on both ends and covered with transducers using silicone grease as a bonding agent. This enabled us to maintain sample shape and size over the transition region. Since the expansion of an aluminum tube was 0.4% when the temperature was raised from room temperature to 200 °C, we neglected it.

Ultrasonic measurements were made with the dual-cell method.[5] The dual cells were immersed in a silicone oil bath and heated up to 200 °C at the rate of 22 deg/h. Piezoelectric transducers (PZT) were used for generation and detection of the 1 MHz longitudinal wave. They were activated by a Metrotec MP215 pulser, and the transmitting pulses were amplified by a MP106 receiver and displayed on a Philips PM3350A digital storage oscilloscope.

Since ultrasonic alone is insufficient for having satisfactory insight into the related phenomena, the differential scanning calorimetric (DSC) measurements were made at the same heating rate of 22 deg/h. The possible presence of the crystalline phases was checked by x-ray diffraction at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the DSC for ten samples of different compositions. The glass transition temperature, T_g, defined here as the temperature at the deflection and

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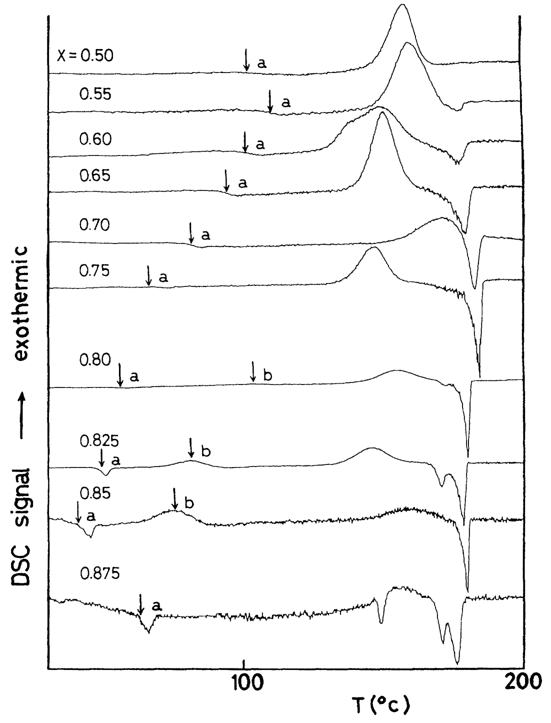

FIG. 1. DSC data for $(\mathrm{AgI})_x(\mathrm{Ag_4P_2O_7})_{1-x}$ glasses measured at the heating rate of 22 deg/h. The arrows marked "a" indicate glass transition temperature and those marked "b" indicate location of exothermic peak which we believe would give rise to the attenuation and/or velocity peak due to nucleation and/or crystallization of some unidentified crystal.

marked "a", steadily decreased with increasing x. Figure 2 illustrates T_g as a function of x, superposed on the equilibrium phase diagram.[6] X-ray diffraction (Fig. 3) showed only a halo for compositions of $x=0.50$ to 0.80, while the crystalline peaks, besides halo, for the $x \geq 0.825$ glasses which increased in intensity with x. The crystalline peaks were identified with phase IV, of the composition $\mathrm{Ag_{19}I_{15}P_2O_7}$. This was substantiated by the observation of the endothermic peak at 147 °C (due to decomposition of phase IV into α-AgI plus phase VII, of the composition $\mathrm{Ag_{16}I_{12}P_2O_7}$) for the $x=0.875$ glass.

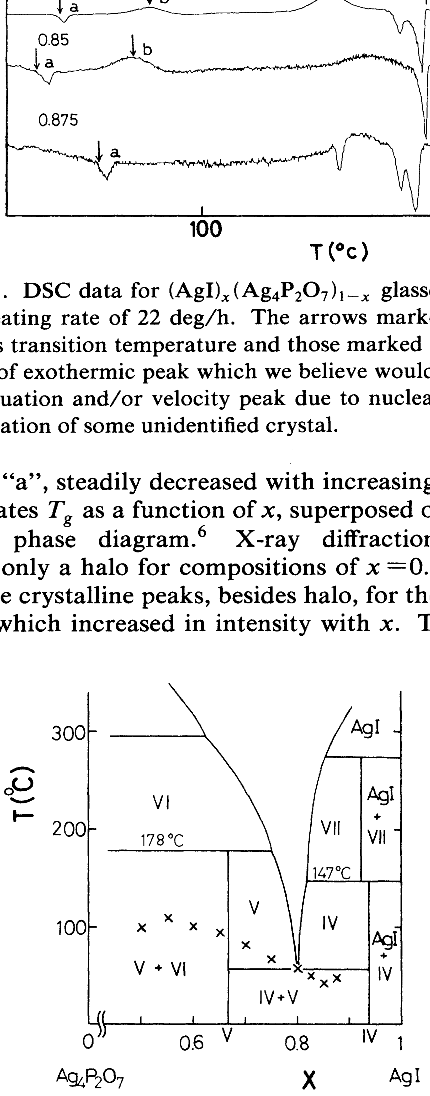

FIG. 2. Glass transition temperature, marked x, superposed on the phase diagram of $(\mathrm{AgI})_x(\mathrm{Ag_4P_2O_7})_{1-x}$ (Ref. 6). Here phases IV, V, VI, and VII are of the compositions $\mathrm{Ag_{19}I_{15}P_2O_7}$ $(x=\frac{15}{16})$, $\mathrm{Ag_6I_2P_2O_7}$ $(x=\frac{2}{3})$, $\mathrm{Ag_9IP_4O_{14}}$ $(x=\frac{1}{3})$, and $\mathrm{Ag_{16}I_{12}P_2O_7}$ $(x=\frac{12}{13})$, respectively. For clarity the term "and the melt" is omitted in the regions adjacent to liquidus.

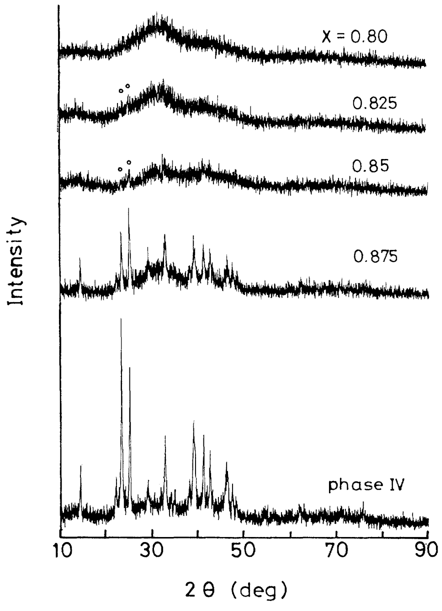

FIG. 3. X-ray (CuKα) powder diffraction of $x=0.80$ to 0.875 samples, as well as of phase IV crystal, of composition $\mathrm{Ag_{19}I_{15}P_2O_7}$, made by sintering appropriate mixture of AgI and $\mathrm{Ag_4P_2O_7}$ in vacuo at 200 °C for 24 h and cooled slowly to room temperature. The $x<0.80$ samples showed only a halo so therefore they are not shown here. Two dominant peaks for phase IV are marked by ○.

The broad exothermic peak at 150 ~ 170 °C and the sharp endothermic peak at ~180 °C were assigned, respectively, as due to nucleation and/or crystallization of phases V and VI (of the compositions $\mathrm{Ag_6I_2P_2O_7}$ and $\mathrm{Ag_9IP_4O_{14}}$) and incongruent melting of phase V to phase VI, because, as the AgI content was reduced, the former peak grew at the expense (so to speak) of the latter. Wide scatter in the location of the former peak may reflect a scatter in the onset temperature for nucleation from sample to sample. That these peaks would be of unstable origin comes from the fact that, when the scanning rate was increased to, say 3 °C /min, they were swept away. In the temperature range studied, we saw another exothermic peak for $x=0.80$ to 0.85, marked "b" in Fig. 1. We will discuss this later. The endothermic peak at 170 °C, found for the $x=0.80$ to 0.875 glasses, may also be of the quasistable phase not shown in the phase diagram.

Figure 4 shows some typical data of the sound velocity and attenuation as a function of temperature. Figure 5 shows x dependences of the sound velocity at 25 °C, as a representative of the sound velocity in the solid state, v_s, and at 180 °C, as a representative in the liquid state, v_l. For comparison, the v_s value for the α-AgI crystal[7] was also shown. Using the density, ρ, measured (Fig. 6), the elastic constant, c, which is the sum of contributions

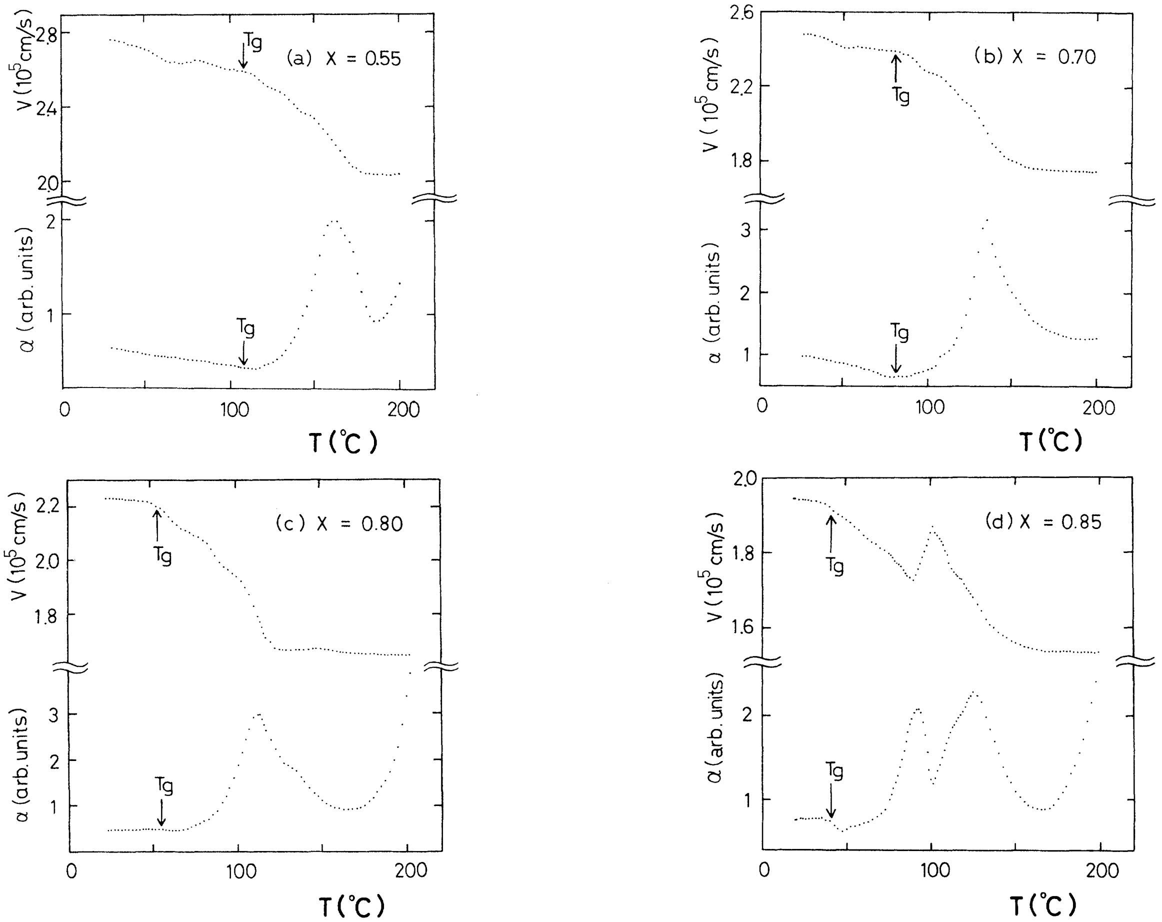

FIG. 4. Typical data of ultrasonic attenuation, α, and velocity, v, for $x=0.55$ to 0.85 samples measured using 1 MHz longitudinal waves. The arrow indicates glass transition temperature, T_g.

from bulk and rigidity moduli, was evaluated from

$$v_s=(c/\rho)^{1/2}\ . \qquad (1)$$

Figure 7 illustrates x dependences of c for our glasses, as well as for the $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$ glasses reported.[3] With increasing AgI content, ρ increased linearly up to $x=0.80$, but turned to a decrease afterward, and seemed to converge into the α-AgI value. Therefore, it is suggested that the density of the crystalline phases present (phase IV) in the samples of $x\geq 0.825$ is less than that of the glassy matrix.

The infrared study on the $(\mathrm{AgI})_x(\mathrm{AgPO_3})_{1-x}$ glasses[3] revealed that the phosphate network was not modified so severely by the addition of AgI. If this holds true even in our glasses, simple penetration of the AgI clusters into the voids provided by the oxysalt may be responsible for the observed changes in v_s and ρ.

For the $x=0.50$ to 0.75 glasses we saw single attenuation peak and three-stepped velocity dispersion which is ascribed as due to relaxation of the SCL. For the $x=0.80$ glass, a small peak appeared at 150 °C in the velocity curve, besides relaxational dispersion of the SCL.[2] This peak may correlate with a shoulder in the higher temperature side of the dominant attenuation peak, and with a small exothermic peak at 107±3 °C, marked "b" in Fig. 1, and is assigned as due to nucleation and/or crystallization of some unknown crystal because, with an increase in x, the velocity peak shifted to lower temperatures in near parallel to the corresponding exothermic peak (Fig. 8).

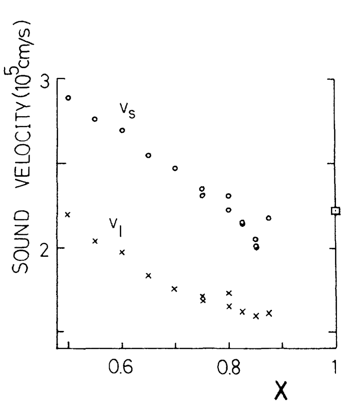

FIG. 5. Sound velocity at 25 °C, denoted v_s, as a representative of the velocity in the solid state, and at 180 °C, denoted v_l, as a representative in the liquid state. The square at far right represents room-temperature sound velocity for α-AgI (Ref. 7).

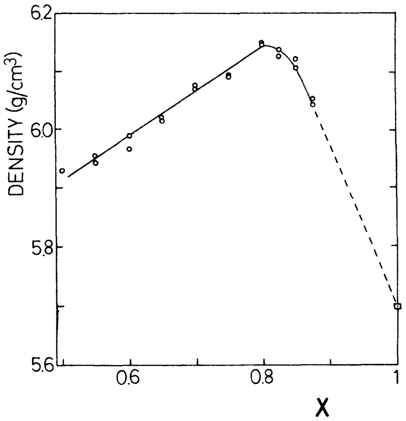

FIG. 6. Density, ρ, as a function of AgI content, x. The square at far right represents the density of α-AgI.

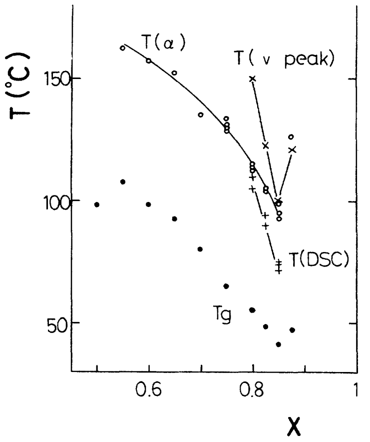

FIG. 8. Composition dependences of glass transition temperature, T_g; the temperature at the lower-temperature attenuation peak, $T(\alpha)$; the temperature at the velocity peak, $T(v$ peak); and the temperature at the exothermic peak other than that near 150-170 °C, T(DSC).

For the $x=0.85$ glass two attenuation peaks were clearly identified although they were heavily overlapped for the $x=0.825$ glass. The lower-temperature peak was assigned as due to relaxation of the SCL, because temperatures of this peak and of the dominant attenuation peaks in the $x \leq 0.825$ glasses changed almost in parallel to T_g (Fig. 8). On the contrary, the higher-temperature peak was assigned to the nucleation (and/or crystallization) of some unknown crystal. Tentative assignment was phase VII or some quasistable phase not shown in Fig. 2, but not phase IV, because then we should have seen the 147 °C endothermic peak in DSC even for the $x=0.825$ and 0.85 glasses.

Let us discuss, naively, the origin of the velocity peak for the $x=0.85$ glass. In the DSC of this glass, we saw a broad exothermic peak at ~74 °C caused, possibly, by nucleation and/or crystallization. However, under actions of forced vibration at 1 MHz, the SCL was so stirred and homogenized that the necessary coagulation for nucleation of the fragments (which constitute the SCL) was restricted and postponed to higher temperatures, around 123 °C. The nuclei or crystallites thus generated during ultrasonic oscillation would induce a velocity rise but, once generated, would relax in a similar fashion as the fragments in the SCL do, to give the attenuation peak and velocity dispersion. This may be the reason why the velocity rises to give a peak and why the velocity peak is located below the temperature of the corresponding attenuation peak.

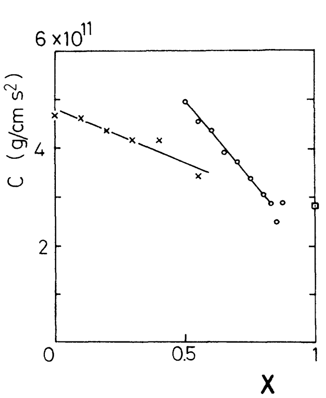

FIG. 7. Elastic constant, c, deduced from Eq. (1), as a function of AgI content, x, for our system (○), as well as that of $(AgI)_x(AgPO_3)_{1-x}$ glasses reported (Ref. 3) (×) and of α-AgI (Ref. 7) (□).

Figure 9 shows comparison of the ultrasonic, as well as DSC and x-ray (CuKα) diffraction, data for two samples of the $x=0.875$ glass. The DSC and x-ray diffraction showed only a small difference in relative peak magnitude, but the ultrasonic data showed large differences, with three attenuation peaks and corresponding velocity peaks, labelled a, b, and c, beyond three steps of velocity dispersion due to glass transition. The absence of a broad exothermic peak, marked "b" in Fig. 1, implies that these three peaks are different in origin from the peaks observed for the $x=0.80$ to 0.85 glasses. In view of almost identical locations for both the v and α peaks, the formation of some unstable nuclei and their subsequent melting can be one of the possibilities. Anyway, one can see from Fig. 9 that the ultrasonic technique is a very sensitive tool, even more sensitive than the DSC and x-ray diffraction, for studying small changes and small differences in the structure.

Theoretically the relaxation process satisfies the relation[9]

$$\alpha = c w^2 \tau / (1 + w^2 \tau^2) , \tag{2}$$

where

$$\tau = (1/v_0) \exp(H/kT) \tag{3}$$

is the relaxation time, w the acoustic angular frequency, v_0 the vibration frequency of the relevant mobile species, and H the corresponding activation energy. For the relaxational process of the fragments in the SCL we can accept, intuitively, the occurrence of the attenuation peak at $w\tau=1$, because transmission of the external sound wave would be disturbed most effectively when the period of the movement of the fragment matches the period of ultrasonic stress.

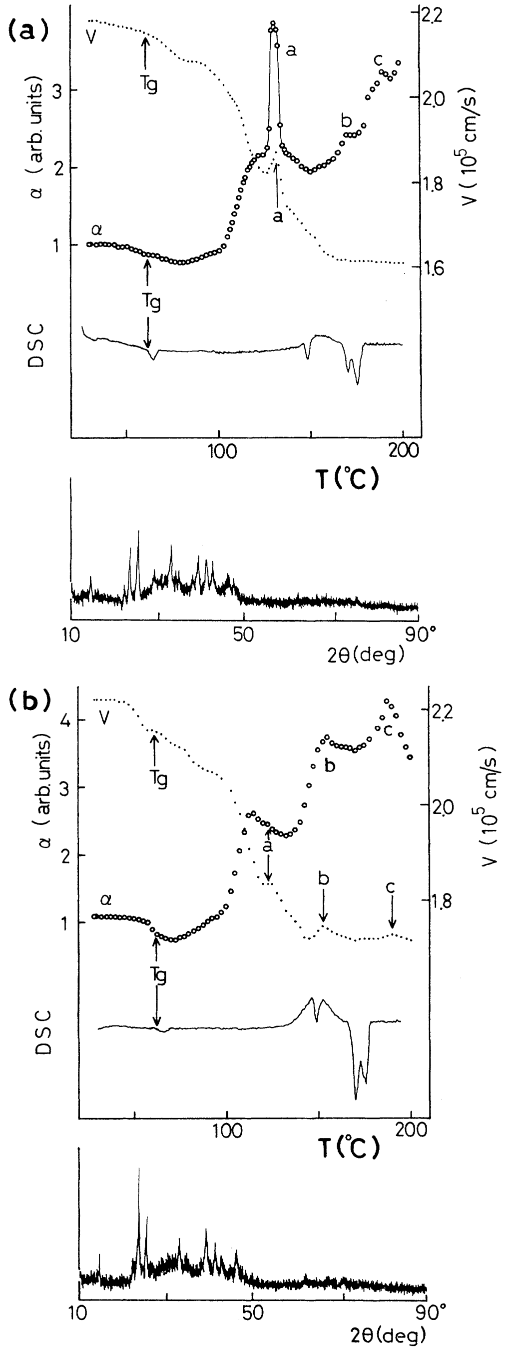

FIG. 9. Comparison of sound velocity and attenuation, as well as DSC and X-ray (CuKα) diffraction data, for two $x=0.875$ samples. Three attenuation and/or velocity peaks, labelled a, b, and c, were observed beyond three steps of velocity dispersion due to glass transition. DSC and x-ray diffraction data showed only a small difference in relative peak magnitude, but ultrasonic data seemed to be more sensitive on small differences in the structure.

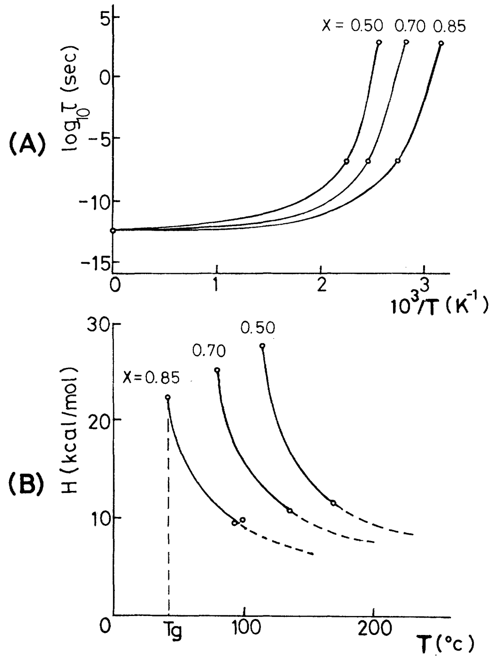

FIG. 10. Non-Arrhenius behavior of the relaxation time, τ, for viscous flow of the SCL, where it is assumed that τ at T_g is 10^3 sec (Ref. 10), that $\omega\tau=1$ at the lower-temperature attenuation peak, and that $\tau(T\rightarrow\infty)$ is 2.9×10^{-13} sec for Ag-I oscillation (Ref. 8) (a). (b) shows change in the dominant activation energy, H, with temperature, which is evaluated from Eq. (3).

Contrary to the solid state, the liquid shows drastic variation in H with temperature.[10] It is generally believed that the relaxation time at T_g is of the order of 10^3 sec at the very slow heating or cooling rate of the measurements.[10] If v_0 in our glasses is assumed to be 115 cm^{-1} for Ag-I oscillation,[8] then the logarithmic plots of τ as a function of reciprocal temperature strongly deviate from the Arrhenius behavior (Fig. 10a). If it is assumed that Eq. (3) holds true even in the liquid state, Fig. 10b yields a rough sketch of the activation energy as a function of temperature, similar to the curve reported for glycerol.[10] This implies that, as the AgI content increases, the activation energy for relaxation of the fragments in the SCL tends to decrease.

IV. CONCLUSION

Ultrasonic study on $(\mathrm{AgI})_x(\mathrm{Ag_4P_2O_7})_{1-x}$ glasses in the temperature range from room temperature to 200 °C revealed several interesting facts. First, as the AgI content was increased, the attenuation peak (and corresponding velocity dispersion) due to relaxation of the fragments which constitute the supercooled liquid shifted to lower temperatures, in near parallel to the glass transition temperature. This corresponded to lowering of the relevant activation energy. Second, for the $x\geq0.80$ glasses, we observed the second attenuation peak which increased in intensity with x. This peak was accompanied by the velocity peak, and was assigned to nucleation and/or crystallization of some unidentified crystal. Finally, it was shown that the elastic constant, c, deduced from Eq. (1), decreased almost linearly with increasing x, in similar fashion as did c of the $(\mathrm{AgI})_x(\mathrm{AgPO}_3)_{1-x}$ glasses.

Although we could not give definite assignments for the attenuation and/or velocity peaks and the shoulders observed, due partly to too-short temperature interval and too-complex system studied, the ultrasonic technique would be a promising, very sensitive tool giving fruitful insight into the phenomena of melting, nucleation, and crystallization and so on, especially when simultaneous measurements with, e.g., DSC and x-ray diffraction can be made.

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