

Studies of the temperature dependence of the short range structure and local dynamics in silver borate glasses

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EXAFS temperature dependent measurements have been carried out on the borate glass doped with silver iodide, $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$, at the K-edges of Ag and I, in the range 39–500 K. Local negative thermal expansion has been measured in the explored temperature range; in the same range, crystalline AgI shows a positive trend. This behaviour, already found for another silver borate glass containing a higher content of silver iodide, was interpreted in terms of a relaxing of the AgI amorphous network within the silver borate host matrix. In the light of the results obtained for the glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$, having a much lower AgI concentration and showing an almost equal thermal expansion, a different interpretation is now necessary. The Ag–I first shell distance contraction is a specific characteristic of the AgI amorphous network within the silver borate host matrix: temperature increase favours shorter average distance of the mobile Ag^+ cations from I ions. The host matrix influences, however, the local thermal disorder around Ag and I species.

The conduction mechanism in AgI doped silver borate glasses is still not completely understood despite a wide experimental and theoretical effort. This is due in part to an incomplete knowledge of the microscopic structure around the mobile cations,⁽¹⁾ which could provide information about the migration pathways of the cations and the interplay between AgI and host

borate matrix. The short-range order in glasses, namely the coordination with nearest and next nearest neighbours, represents the link between chemical bonds on one side and structural units of glasses on the other. A good knowledge of the short-range order is important not only to support the reliability of medium and long range models but also to clarify dynamical and transport properties.⁽²⁾

The treatment of the effects of vibrational and structural disorder on XAFS, although very promising, still represents a partially unsolved problem. The increasing quality of experimental data and the progress in the procedures of data analysis allow one to go beyond the harmonic approximation in the treatment of vibrational disorder. Important results have been recently obtained, both in crystals^(3–5) and in glasses,⁽⁶⁾ by performing highly accurate EXAFS measurements as a function of temperature and by analysing the spectra by the cumulant expansion technique. This method allows one to exploit the sensitivity of EXAFS to anharmonicity effects and to the correlation of atomic motion. Thus original information on the local thermal expansion on the effective bond stretching force constants of selected atomic pairs and on the dependence of structural disorder on temperature can be obtained. These results show that EXAFS is sensitive to local dynamical properties that can be different from average thermodynamical parameters.

This paper presents our most recent study on the local thermal behaviour of the silver borate glass doped with AgI: $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$. The measurements

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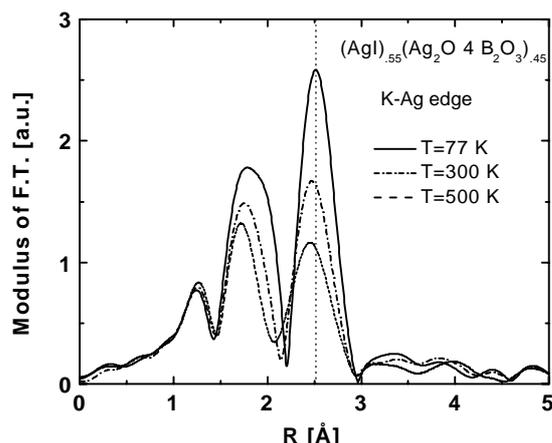


Figure 1. Modulus of the Fourier transform (FT) of the EXAFS signal at the K-edge of Ag, at some selected temperatures, for the glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$

have been made as a function of temperature at the Ag and I K-edges. Other EXAFS temperature dependent studies were carried out at the I K-edge on a glass with the same composition but characterised by a higher AgI and a lower B_2O_3 content.⁽⁶⁾ The structural results on $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$ glass are here discussed with reference to the results previously obtained on the glass with higher AgI concentration.

Experimental

The glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$ has been prepared by conventionally quenching the melt in a stainless steel mould. The presence of crystallites in the glass is ruled out by x-ray diffraction measurements. At microscopic analysis the glass appears homogeneous.

The temperature dependent EXAFS measurements at the K-edge of Ag, in the range 78–500 K, have been done at the beamline BM8 Gilda of the European Synchrotron Radiation Facility (ESRF) (Grenoble, France). The measurements at the K-edge of I have been done at the ESRF public beamline BM29, in the range 39–300 K. The EXAFS data analyses have been carried out in terms of cumulants using the phase difference and amplitude ratio technique according the procedure reported in Ref. 7. The cumulant series was truncated at the fourth order term.⁽⁸⁾ The lowest temperature spectra, at 39 (I K-edge) and 78 K (Ag K-edge), were taken as reference for back scattering amplitude, phase shifts and inelastic terms. The analysis of the phase differences allowed us to determine the values, relative to the references, of the first two odd cumulant $\Delta C_1^*(T) = \Delta R$ and $\Delta C_3(T)$, i.e. the variation of the first shell bond length and the asymmetry coefficient.⁽⁸⁾ From the logarithms of amplitude ratios, the coordination number and the first two even relative cumulants ΔC_2^* and ΔC_4 were evaluated. Here we report the values of ΔR and ΔC_2^* , i.e. the EXAFS Debye–Waller factor, as a function of temperature.

Results

An EXAFS signal $k\chi(k)$ with a good signal to noise ratio was obtained for both spectra up to 14 \AA^{-1} ; k is the wave vector defined as $k = [(2m_e/\hbar^2)(E - E_0)]^{1/2}$, where

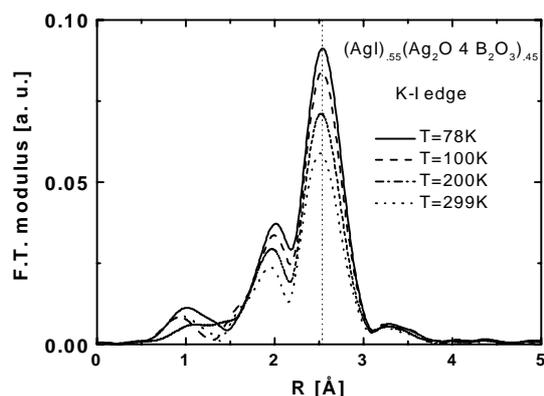


Figure 2. Modulus of the Fourier transform (FT) of the EXAFS signal at the K-edge of I, at some selected temperatures for the glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$

E_0 is the position of the photoelectron energy origin. In Figures 1 and 2 the modulus of the Fourier transform (FT) of the EXAFS signal is shown for some selected temperatures. The FTs in Figures 1 and 2 describe the different neighbourhoods of Ag and I, respectively. Around Ag atoms, at least three different sites can be envisaged in the range 1.5 and 3 Å: in the first site, Ag is surrounded by O nearest neighbours belonging to the silver borate network, in the second one, Ag is surrounded by I nearest neighbours belonging to the AgI network; in the third one, Ag is bonded to both O and I atoms. At increasing temperature, we may expect that the relative number of Ag cations in these sites changes. We will discuss this fact later on. So the FT in Figure 1 represents a complex atomic situation: the peak between about 1.5 and 2.1 Å is partially related to the O atoms, nearest neighbours of Ag in the silver borate network, while the one whose maximum is at about 2.5 Å, is related to the I nearest neighbours of Ag in the AgI network; a pre-peak, due to the modulated backscattering amplitude of I, contributes to the first peak as well. Moreover, in the range 2.5–3 Å, a small contribution due to short Ag–B bonds can also be present. The vertical dashed line in Figure 1 points out the shift of the Ag–I peak at increasing temperatures.

A clearer picture emerges from the point of view of I atoms, Figure 2, since here the peaks between about 1.5 and 3 Å come only from the Ag nearest neighbours of the AgI network. In Figure 2 the FT of the EXAFS at the K-edge of I is presented for some temperatures. The pre-peak at about 2 Å is due to the typical shape of the backscattering amplitude of heavy elements like Ag. The vertical dashed line points out the shift of the I–Ag peak at increasing temperatures.

The contribution to the EXAFS signal at the K-edge of Ag, relative to the coordination Ag–I, was singled out by back transforming in the range 2.1–3 Å. No Fourier filtering of the EXAFS contribution of the first shell Ag–O coordination was tempted owing to a partial not negligible overlap of the I pre-peak with the Ag–O peak. By Fourier filtering both the peaks in the range 1.4–3 Å⁻¹ and using a multi-parameters fitting procedure it is possible to disentangle the struc-

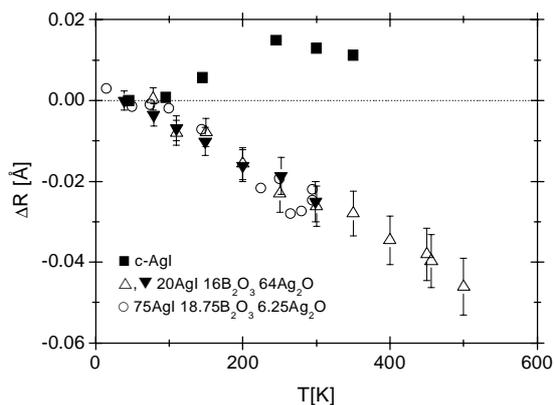


Figure 3. Temperature dependence of the relative variations of the first shell bond distance for the glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$, here referred with the formula $20\text{AgI} \cdot 16\text{B}_2\text{O}_3 \cdot 64\text{Ag}_2\text{O}$. Two independent sets of distances are presented: Ag-I (from the K-edge of Ag, white triangles) and I-Ag (from the K-edge of I, black triangles), respectively. Each relative variation is referred to the spectrum measured at the lowest temperature (the Ag data (white triangles) were vertically shifted to match the values of I data (black triangles)). Data corresponding to c-AgI (squares) and to the glass with higher AgI concentration $75\text{AgI} \cdot 18.75\text{B}_2\text{O}_3 \cdot 6.25\text{Ag}_2\text{O}$ are presented for comparison

tural parameters relative to both coordination shells: this analysis is complicated by possible correlations of best fitting parameters and will be presented in a forthcoming paper. The EXAFS signal at the K-edge of I, related solely to the I-Ag coordination, Figure 2, was singled out by back transforming the corresponding peak in the range $1.4 \div 3 \text{ \AA}^{-1}$. The results obtained from the analysis at the I K-edge are more accurate than those obtained from the K-edge of Ag.

In Figure 3 the relative variations of the first shell bond distance, seen from the two different observation points, I (black triangles) and Ag (white triangles), are shown. Each relative variation is referred to the spectrum measured at the lowest temperature (the Ag data (white triangles) were vertically shifted to match the values of I data (black triangles) at the same temperature). It is worth noting the good agreement, within the error bar, of the data, collected in two independent set of measurements at two different beamlines. A negative thermal expansion of the Ag-I average bond length, in the whole observed temperature range, is evident. In contrast with the glass, the thermal expansion of the first shell distance of crystalline β -AgI is positive.

In Figure 4 the mean square relative displacement (MSRD), $\Delta C_2^{\%}$, measured from the two atomic observation points, is presented. MSRDs have been determined using the lowest temperature spectrum of the each sample as a reference. $\Delta C_2^{\%}$ is a measure of the vibrational and temperature induced structural disorder. In the same figure the MSRD temperature dependence of crystalline β -AgI is reported for comparison.

Discussion

The study of thermal behaviour from a local perspective can provide fresh insights into many phenomena of technological and fundamental interest in crystals⁽⁵⁾ and in multicomponent glasses.⁽⁹⁾ In crystals, positive

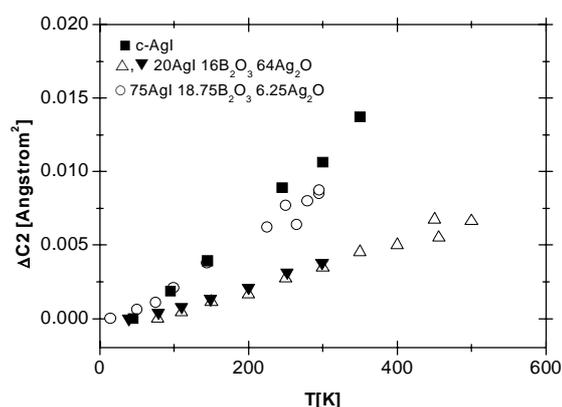


Figure 4. Temperature dependence of the mean square relative displacement (MSRD), $\Delta C_2^{\%}$, determined from Ag and I K-edge absorption measurements, for the glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$ (triangles). Two independent sets of MSRDs are presented: one obtained from the K-edge of Ag (white triangles) and the other from the K-edge of I (black triangles). Data corresponding to c-AgI (squares) and to the glass with higher AgI concentration, $75\text{AgI} \cdot 18.75\text{B}_2\text{O}_3 \cdot 6.25\text{Ag}_2\text{O}$, are presented for comparison. MSRDs have been determined using the lowest temperature spectra of each compound as reference

and negative thermal expansions have been found for near neighbours distances.⁽³⁻⁵⁾ These phenomena have been interpreted in terms of local dynamical and geometrical effects induced by temperature increase.

Let us try to interpret the contraction of the Ag-I average bond length of the glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$ with increasing temperature (Figure 3, triangles) and the thermal behaviour of the MSRD (Figure 4, triangles). In silver borate glasses doped with AgI, we must also take into account the high mobility of Ag^+ cations, because the individual position of each cation can change continuously when temperature is sufficiently high to allow jumps between adjacent sites.

The first evidence of a negative local thermal expansion in glasses was found in the silver borate glass $75\text{AgI} \cdot 18.75\text{Ag}_2\text{O} \cdot 6.25\text{B}_2\text{O}_3$, prepared by twin roller rapid quenching^(6,9) (Figure 3, circles). By this preparation technique, glass formation in the system AgI-Ag₂O-B₂O₃ ($\text{Ag}_2\text{O}/\text{B}_2\text{O}_3=3$) has been observed up to 78 mol% AgI.⁽¹⁰⁾ Within the glass formation limit, the glasses with 70–78 mol% AgI exhibit an inhomogeneous microstructure with dispersed AgI rich amorphous particles. By increasing the AgI concentration, in very limited compositions, 80–84 mol% AgI, the ionic superconducting α -AgI phase is stabilised at room temperature.^(11,12)

The glass $(\text{AgI})_{0.55}(\text{Ag}_2\text{O} \cdot 4\text{B}_2\text{O}_3)_{0.45}$ in comparison with the glass $75\text{AgI} \cdot 18.75\text{Ag}_2\text{O} \cdot 6.25\text{B}_2\text{O}_3$, has a lower AgI content (~20 mol%) and a host matrix with a higher B₂O₃ content (~64 mol%), (as a matter of fact, its formula, using the same notation as in Ref. 10, is $20\text{AgI} \cdot 16\text{B}_2\text{O}_3 \cdot 64\text{Ag}_2\text{O}$). Moreover, the two glasses, as already mentioned, differ in the preparation technique and homogeneity.

Further information can be obtained by analysing the temperature dependence of the second cumulant $C_2^{\%}$. In crystals, $C_2^{\%}$ is a measure of the vibrational disorder while, in amorphous systems, it contains a high

structural contribution which can be temperature dependent. The MSR D here reported represents only the vibrational and structural temperature dependent contribution, Figure 4, the static contribution at the lowest temperature is not shown. Despite physical and chemical differences, the two glasses show almost the same negative thermal expansion coefficient (Figure 3, triangles and circles). In contrast, the MSR D of the glass with higher AgI content (Figure 4, circles) is larger than the one of the glass with lower AgI content (Figure 4, triangles) and closer to that of *c*-AgI (Figure 4, squares).

The local thermal behaviour of the glass 75AgI.18.75Ag₂O.6.25B₂O₃ was interpreted⁽⁵⁾ assuming that the local vibrational properties sampled by EXAFS strongly depend on the nearest neighbour interaction, and, in some cases, are very similar in crystalline and noncrystalline compounds of equal composition and similar local coordination. This hypothesis was based on the fact that in *a*-Ge the structural component of disorder is almost independent on temperature showing, in such a way, that the local vibrational properties of *a*-Ge are similar to those of *c*-Ge.⁽¹³⁾ Likewise⁽⁶⁾ it seemed reasonable to assume that the local vibrational disorder of the amorphous AgI component of the glass has a thermal behaviour similar to that of *c*-AgI. On the basis of this assumption $\Delta C_{\frac{1}{2}}^*$ should increase as a function of temperature almost with the same rate for both glasses and *c*-AgI. The differences found between *c*-AgI and the glass 75AgI.18.75Ag₂O.6.25B₂O₃ suggested that the temperature dependence of ΔR , and $\Delta C_{\frac{1}{2}}^*$ was not of purely vibrational origin, but was strongly influenced by structural modifications induced by temperature.^(6,9)

The negative local thermal expansion and the dependence of the structural disorder on temperature was then attributed to a weakening of the bonding between the amorphous AgI network and the host borate matrix with a consequent relaxing of the AgI network. With increasing temperature, a modified equilibrium between the spatial constraints imposed by the borate network and the high mobility of Ag cations may lead to the loosening of the chemical bonds between AgI and silver borate matrix.

On the basis of this interpretation we expected a stronger influence of the host matrix on the thermal expansion of the glass 20AgI.16Ag₂O.64B₂O₃, with lower AgI content (20%). We have instead measured the same contraction (Figure 3, circles and triangles). Anyway a slower growth of $\Delta C_{\frac{1}{2}}^*$ has been found for the glass with the lower AgI content (Figure 4, triangles) with respect to the glass with higher AgI content (Figure 4, circles). These results imply that the silver borate host matrix, although it influences the local or-

der of I and Ag species, does not play a direct role in the local negative thermal expansion. The interpretation of this phenomenon seems then to be a peculiarity of the AgI amorphous network within the host glassy matrix. The decrease of the mean value of the first shell Ag-I distance distribution with temperature could be attributed to an enrichment of the population of Ag⁺ sites closer to the I atoms of the amorphous AgI network. Such sites are favoured by the temperature increase.

Conclusions

In this paper we have studied the first shell coordination Ag-I in the glass (AgI)_{0.55}(Ag₂O.4B₂O₃)_{0.45} as a function of temperature. We have found that: (a) the mean value of the Ag-I distance undergoes a contraction with increasing temperature in the range 39–500 K; (b) the temperature dependent MSR D is lower than in *c*-AgI. These two facts have been related to structural modifications both on the silver borate matrix and AgI amorphous network. However, the contraction of the Ag-I first shell distance seems to be a peculiarity of the AgI network. A deeper understanding of these phenomena needs, however, systematic EXAFS studies on glasses AgI-Ag₂O-B₂O₃ with different silver borate matrix and ionic conductivity.

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