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Abstract

This paper presents a summary of the results obtained by X-ray Absorption Spectroscopy on the coordination of Ag and I in the superionic glasses $(AgI)_x$ $(Ag_2O \ nB_2O_3)_{1-x}$. Two types of coordination have been discriminated for Ag: a relatively strong bond with two oxygens of the borate network, not affected by the presence of the dopant AgI and a bond with iodine, in which each iodine is on the average coordinated to four silvers, without however reproducing the regular crystal structure of AgI. Is is reasonable to assume the presence of a third intermediate situation: silver ions bridging between borate network and AgI-like islands, with mixed bonds $I - Ag - O$. The analysis of our data tends to exclude the presence of an ordered I-I coordination, in disagreement with the structural hypothesis based on the presence of microcrystalline clusters of the superionic phase of AgI.

Superionic conducting glasses have interest for their possible applications in the field of electrochemical devices. The ion-conducting properties of oxide glasses containing a modifier oxide and a doping salt have been widely studied because, for particular compositions of these glasses, the ionic conductivity can achieve values as high as $10^{-2} \ S \ cm^{-1}$ at room temperature [1]. No general agreement has however been reached about the explanation of the conduction mechanism: the choice between different theories is prevented by the lack of sufficient microscopic information. In particular, a better knowledge of the local structure surrounding the moving ion is highly desirable. In this paper we summarize the results obtained by X-ray Absorption Spectroscopy (XAS) on the coordination of silver and iodine ions in the glasses $(AgI)_x \ (Ag_2OnB_2O_3)_{1-x}$. XAS measurements have been done with Synchrotron Radiation at the Adone Wiggler facility (PWA) in Frascati.

In the superionic conducting glasses $AgI : Ag_2O : B_2O_3$ the moving ions are the Ag^+ ones and the conductivity strongly increases with the AgI content [2]. The local structure of the borate network is well known from NMR, IR and Raman spectroscopic results: the mixing of Ag_2O with B_2O_3 progressively changes the

coordination of Boron atoms from the planar triangular one of pure B_2O_3 glass to a tetrahedral one [3]. When this change is complete, non-bridging oxygens appear and their number progressively increases within the upper limit of the glass forming region. On the grounds of many spectroscopic studies it is generally thought that the local arrangement of borate units is not strongly modified by adding AgI to the glass matrix. The local environment of the mobile ion Ag^+ can be carefully studied by local sensitive spectroscopies as NMR and XAS, but up-to-date the study is still incomplete. The main open question concerns the characterization of the possible different coordinations of the Ag^+ ions with oxygen and iodine atoms. The presence or not of different local sites for the silver ions is still a controversial problem: the high mobility of ions probably masks the true situation and better experiments and theories are expected. Moreover, the temperature dependence of the ionic conductivity leads to hypothetize a different arrangement at low T with respect to that shown at room T. If the existence of different sites is proved, they should be related to different ion mobilities, because the different bonds and coordinations should strongly influence the ion dynamics. A second problem is the comparison of the iodine coordination in the glasses with the well known crystalline phases of AgI. Some phenomenological theories on fast ionic conduction hypothetize the presence of islands of the superconducting α phase of AgI; to test these theories the structural study of the glasses should determine not only the first shell coordination but also the medium range structure.

The main results we are presenting here were drawn from the XAS room temperature studies on K and L edges of silver and on L edges of iodine. The coordination of silver ions in the low conducting binary matrix $Ag_2OnB_2O_3$ has been determined. XAS measurements were performed at the K and L_3 edges of silver in glasses with $n = [B_2O_3]/[Ag_2O]$ varying from 2 to 6 and in the crystalline model compound Ag_2O. EXAFS analysis showed that for all considered glasses silver ions are bonded to 2 oxygen atoms like in c–Ag_2O with a Debye-Waller (DW) factor not appreciably higher than in c–Ag_2O. The mean $Ag-O$ distance was instead 0.23 Å larger than in c–Ag_2O. For the glass $n{=}2$ the best fit to EXAFS was obtained by considering two $Ag-O$ coordinations, one with the same distance, the other with a remarkably shorter distance: this shorter distance probably corresponds to the appearance of non-bridging oxygens at high Ag_2O contents [4]. The relatively high degree of local order and the low coordination in the first coordination shell of silver indicate that silver ions are not randomly distributed in the interstitial sites of the glass network, but are bonded in a well defined configuration to the boron-oxygen network. In c–Ag_2O the chain $O-Ag-O$ is linear, with an $Ag-O$ distance 2.04 Å; the increment of 0.23 Å in the $Ag-O$ distance suggested a tentative model for the bond of silver with the borate network in the glasses with low Ag_2O content (where all oxygens are bridging): silver could be strongly bonded to two oxygens belonging to an unique tetrahedron BO_4^-, with the chain $O-Ag-O$ bent at an angle of about 64 degrees [5]. This model was supported by a phenomenological interpretation of the fine structures within the first 10 eV above the edges Ag L_1 and L_3. The L_1 spectra of the glasses are remarkably different from those of c–Ag_2O, while the L_3 spectra of glasses and crystal are both characterized by a peak at about 1 eV and a shoulder at about 6 eV. The proposed distortion of the $O-Ag-O$ chain should affect by far more the directional p orbitals (edges L_1) than the more flexible d or the isotropic s orbitals (edges L_3) [6].

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In the ternary high conducting glasses $(AgI)_x(Ag_2OnB_2O_3)_{1-x}$ XAS has been utilized to study the local environments of both silver and iodine atoms by looking at the respective absorption edges.

EXAFS at the K edge of silver allowed to distinguish the two possible coordinations of silver with oxygen and iodine in glasses with $n=4$ and x varying from 0 to 0.55. The $Ag-O$ distance is independent from the AgI content; the mean $Ag-I$ distance is 2.75 Å, slightly lower than in crystalline $\beta-AgI$, where it is 2.82 Å. The edges AgL_3 are characterized by the peak at about 1 eV and the shoulder at about 6 eV already found in the binary matrix. These structures progressively decrease when increasing the AgI content and are completely absent in the spectra of pure $c-AgI$; they have thus been considered as fingerprints of the $O-Ag-O$ bond, their intensity monitoring the fraction of silver ions actually coordinated to the borate network. A quantitative analysis of the edge structures has shown that the fraction of Ag ions bonded to oxygen is that expected from stoichiometry, indicating that the strong bond of Ag with the borate network is not appreciably affected by the progressive introduction of AgI [6] .

Let us now consider the local coordination of iodine. The EXAFS results at the edge IL_3 for the glasses $(AgI)_x$ $(Ag_2O$ $4B_2O_3)_{1-x}$ indicate that the mean local environment of iodine changes when the AgI content increases [5] . The first-shell contribution to EXAFS, due to Ag ions, is consistent with a mean fourfold coordination of I with Ag like in crystalline AgI, where iodine is tetrahedrally coordinated to silver; the EXAFS signal is anyway slightly but progressively damped when the AgI concentration increases, indicating a slight decrease of the coordination number and/or increase of disorder.

A more complex situation is suggested by the behaviour of the second coordination shell of iodine. The glasses with the lowest content of AgI $(x=0.1)$ exhibit a clear second-shell contribution to EXAFS, which has been attributed to a high probability of second-shell correlations of iodine with the oxygens of the borate network via $I-Ag-O$ bonds. When increasing the content of AgI the second-shell contribution to EXAFS rapidly disappears, monitoring the progressive decreasing of the $I-Ag-O$ bonds. No second-shell contribution due to iodine atoms can be evidenced in EXAFS even for the highest AgI content $(x=0.55)$. This absence has been explained by assuming randomly distorted $I-Ag-I$ bonds which would correspond to a large spread in the distribution of $I-I$ distances and thus to a strong damping of the corresponding EXAFS signal. The average coordination of iodine with silver is fourfold, however it cannot be considered as regular in the glasses as in crystalline AgI. This conclusion is supported by the differences between the structures at both the L_1 and L_3 absorption edges of iodine in the glasses with respect to AgI [5] .

The absence in EXAFS of the contribution from an ordered $I-I$ second-shell coordination, in agreement with the results of X-ray diffraction measurements [7], and the differences in the structures at the I L edges exclude the presence of microcrystalline clusters of the superionic α phase of AgI in the glasses.

Let us now summarize and discuss the main conclusions extracted from the XAS room temperature results outlined above. Two types of coordination of silver have been clearly discriminated: the first one corresponds to a bond of silver with two oxygens of the borate network; this relatively strong chemical bond is not affected

by the presence of the dopant AgI; the second one corresponds to bonds of silver with iodine atoms, in which each iodine is on the average coordinated to four silvers. This coordination, however, does not reproduce the regular crystal structure of AgI. It is reasonable to assume the presence of a third intermediate situation: silver ions bridging between the borate network and the AgI-like islands, with mixed bonds: I-Ag-O.

New measurements at temperatures varying from 300 to 4 K are in progress in order to improve the physical information we can extract from EXAFS. Low temperature measurements, where the thermal damping effect is reduced, are expected to allow more accurate quantitative determinations of static structural parameters like coordination numbers and interatomic distances. As a matter of fact, recent EXAFS results on AgI [8] suggest that only at low temperature a carefull determination of the second shell contributions can be performed for the glasses, because the DW factor changes strongly with temperature and the static and thermal contributions are a-priori unknown. By analyzing the dependence of the EXAFS amplitude one expects the possibility of discriminating between the different strenghts of the chemical bonds of Ag with respectively oxygen and iodine. In fact, due to the high sensitivity of the EXAFS DW factors to the correlated motions of absorber and backscatterer atoms, a temperature dependent study should evidence the differences in the vibrational dynamics corresponding to each local coordination.

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