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EXAFS on Silver Borate Glasses

P. Fornasini and G. Dalba

Dipartimento di Fisica, Università di Trento, I-38050 Povo, Italy

F. Rocca

IRST and Centro di fisica degli stati aggregati e di impianto ionico del CNR
I-38050 Povo-Trento, Italy

E. Bernieri and E. Burattini

INFN, PWA group, I-Frascati, Italy

1. Introduction

Fast ion transport properties in crystalline and amorphous solids have been widely studied in the last years. In particular, new glasses have been produced, exhibiting a conductivity due to alkali or silver ions much higher than the corresponding crystalline compounds.

The great variety of materials sharing these properties has stimulated the search for specific structural characteristics or at least for the simultaneous occurrence of conditions favouring the ionic transport, like the presence of a great number of interconnected low-energy sites and the open structure of the material. It is thus interesting to understand the short and mid-range structures of the fast ion conducting glasses to build up a microscopic picture of each material.

The present work concerns glasses of the type $(\text{AgI})_x(\text{Ag}_2\text{O} \text{ n } \text{B}_2\text{O}_3)_{1-x}$ where

$$n = [\text{B}_2\text{O}_3]/[\text{Ag}_2\text{O}] \quad x = [\text{AgI}]/([\text{Ag}_2\text{O}] + [\text{AgI}])$$

These glasses can be produced in a wide range of compositions and are thus well suited for a detailed study of the dependence of their microscopic properties both on the composition of the binary matrix $\text{Ag}_2\text{O} \text{ n } \text{B}_2\text{O}_3$ and on the AgI content.

Previous measurements have shown that, when the Ag_2O content is progressively increased, the coordination of boron is modified and various structural groups grow up following the model of Krogh-Moe.

The insertion of AgI into the binary matrix increases the number of low-energy sites and favours their interconnection, inducing a remarkable increase of the ionic conductivity [1].

Due to its ability to select the atomic species, EXAFS can provide a determinant help in understanding the surroundings of the mobile ion Ag^+ . However, the high photon energy of the K edge of silver on the one hand, the short useful k range at the L_3 edges of silver and iodine on the other, require a careful comparative investigation of all the available experimental data.

The EXAFS measurements have been performed at room temperature with synchrotron radiation at the Wiggler facility in Frascati. The Si(111) monochromator allowed to maximize the photon flux at the higher energies, to the detriment of the resolving power. New measurements are planned using a Si(220) monochromator to achieve a higher resolving power.

2. Binary matrix Ag_2O in B_2O_3

The edges L_3 and K of silver have been studied in the binary matrix. The EXAFS at the L_3 edge is too short to give accurate quantitative information. It has been possible, however, to remark that both amplitude and phase of the fundamental oscillation don't change in a sensible way when n is varied ($n=2,3,4$), indicating a substantial identity of mean distances and coordination numbers of the first shell. A qualitative analysis of second shell effects on the EXAFS signal suggests that a higher degree of order is present beyond the first shell in the glasses with higher B_2O_3 content [2].

Preliminary measurements at the Ag K edge allowed to obtain quantitative information concerning the first shell. A good fit of the experimental data has been obtained for Ag-O distances $2.27 \pm 0.05 \text{ \AA}$ (glass $n=4$) and $2.31 \pm 0.05 \text{ \AA}$ (glass $n=6$) utilizing the phase-shifts from the standard compound Ag_2O . These distances, remarkably higher than in crystalline Ag_2O (2.044 \AA), are comparable to the shortest Ag-O distance (2.23 \AA) measured in the crystalline compound $\text{Ag}_2\text{O} \cdot 4 \text{ B}_2\text{O}_3$ by X-ray diffraction [3].

3. Ternary glasses $(\text{AgI})_x (\text{Ag}_2\text{O} \text{ in } \text{B}_2\text{O}_3)_{1-x}$

For the ternary glasses the EXAFS analysis is possible both at the K edge of silver and at the L_3 edge of iodine. Crystalline $\beta\text{-AgI}$ has been used as standard compound.

The k range at the L_3 edge of iodine is quite short ($2.3\text{-}8 \text{ \AA}^{-1}$); the Fourier transforms $F(R)$ are however meaningful (Fig. 1).

The iodine ions in $\beta\text{-AgI}$ are surrounded by 4 silver ions at a distance of 2.81 \AA and 12 iodine ions at 4.58 \AA . In the Fourier transform of $\beta\text{-AgI}$ the

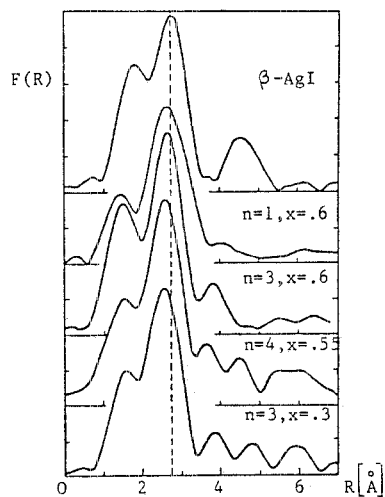


Fig.1. EXAFS at the I L_3 edge. Fourier transforms for $\beta\text{-AgI}$ and ternary glasses in order of decreasing AgI molar content.

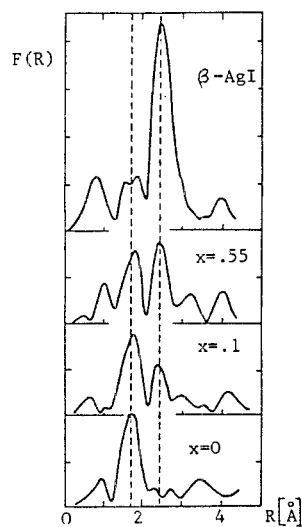


Fig.2. EXAFS at the Ag K edge for $\beta\text{-AgI}$ and ternary glasses with $n=4$.

first two coordination shells are clearly distinguishable. The satellite peak at 1.8 \AA is remarkably strong, due to the resonant behaviour of the backscattering amplitude of silver between 3 and 8 \AA^{-1} (Fig.3). The amplitude of the backtransformed signal exhibits a deep minimum at $k=5.8 \text{ \AA}^{-1}$; this shape is remarkably different from that calculated by Teo and Lee; it is, on the contrary, consistent with both the amplitudes measured for cadmium [4] and that calculated for tellurium by a spherical wave theory [5].

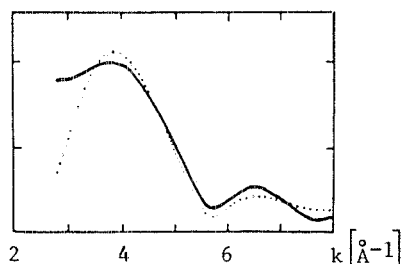


Fig.3. EXAFS at the I L₃ edge. Amplitude of the backtransformed signal for β -AgI (dotted line) and for the glass $n=3$, $x=0.3$ (continuous line).

The Fourier transforms of the ternary glasses exhibit a first-shell structure very similar to that of β -AgI. The position of the peak at 2.8 \AA slightly shifts towards smaller values of R when the molar fraction of AgI decreases. A more complete data analysis will clarify whether this effect is due to a true shrinkage of the I-Ag distance or to a progressive lack of symmetry of the first coordination shell of iodine.

A comparative analysis of the radial distribution function $F(R)$ (Fig.1) and of the amplitudes of the backtransformed signal (Fig.3) shows a remarkable similarity of the surroundings of iodine between the glasses $n=3$ and β -AgI. The similarity is weaker for the glasses $n=1$ and $n=4$. In particular a reduction of the signal amplitude is observed for $n=1$ with respect to $n=3$. This can be related to a greater easiness, for the silver ions, to be bound to the BO_4 units of the binary matrix at low n values.

The EXAFS at the K edge of silver can discriminate the fraction of silver ions coordinated respectively to iodine and to oxygen. In the Fourier transforms shown in Fig.2 for β -AgI and for glasses $n=4$ at various x concentrations the peaks of oxygen and iodine are clearly singled out. The analysis of the peak height reveals that at low x values the fraction of silver ions coordinated to iodine is higher than that expected from stoichiometry.

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