XANES and EXAFS Modelling of Configurational Disorder in Silver Borate Glasses

G. Dalba[1], P. Fornasini[1], A. Kuzmin[2], F. Monti[3], A. Sanson[1], O. Sipr[4] and F. Rocca[5]

[1]INFM and Dipartimento di Fisica, Università di Trento, Via Sommarive 14, 38050 Povo (Trento), Italy
[2]Institute of Solid State Physics, University of Latvia, Kengaraga street 8, 1063 Riga, Latvia
[3]Dipartimento di Informatica, Università di Verona, Strada le Grazie 15, 37134 Verona, Italy
[4]Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, 16253 Prague, Czech Republic
[5]CNR-IFN, Istituto di Fotonica e Nanotecnologie del Consiglio Nazionale delle Ricerche – Sezione "CeFSA" di Trento, I-38050 Povo (Trento), Italy

Abstract

The sensitivity of X-ray absorption spectroscopy (XAS) to the local structure around a selected atomic species (symmetry, distances and angles) is commonly exploited to quantitatively describe systems where all the configurations around the absorbing atoms may be approximated by the mean one. However, in many cases of disordered systems a simple description of the local structure with single-configuration models cannot be reconciled with experimental spectra.

In this paper the necessity to analyse the XAS spectra by considering a multiplicity of atomic structural configurations is demonstrated in the case of silver borate glasses.

The local coordination around Ag cations in $(Ag_2O.nB_2O_3)$ glasses has been studied by comparing the XAS experimental spectra at the Ag K edge with theoretical XANES and EXAFS spectra obtained by a configurational average of model structures.

In order to provide a reasonable agreement with experiment, these models have to take into account that there are many geometrically distinct Ag neighbourhoods present in the system, and that the measured XANES and EXAFS signals are in fact averages over spectra originated at all the non-equivalent photoabsorbing sites (multi-configuration approach).

1. Introduction

The sensitivity of X-ray absorption spectroscopy (XAS) to the local structure of the absorbing site (symmetry, distances and angles) is generally exploited to quantitatively describe systems characterised by single or few atomic configurations.

However, the use of routine best-fitting procedures to fit experimental spectra can give rise to unreliable results, when applied to systems where several atomic configurations around the absorbing species are present, as in the case of some glasses.

In this paper we present a study about the structural configurations of the Ag cation in borate glasses $Ag_2O \cdot nB_2O_3$. Silver borate glasses constitute a widely studied class of materials, especially when mixed with AgI to form fast ion conducting glasses, which can be used as solid electrolytes [1].

The local coordination of silver cations has been studied by various spectroscopic and structural techniques both in binary $Ag_2O \cdot nB_2O_3$ and ternary (i.e., with AgI) glasses [2–4]. The first X-ray absorption spectroscopy (XAS) experiments on binary glasses identified a mean Ag-O distance of about 2.3 Å, and suggested a structural model where silver is bridging between two oxygen atoms in a quasi linear configuration, like in c-Ag_2O [5, 6]. However most recent calculations, based on reverse Monte Carlo (RMC) analysis of neutron scattering data, show evidence of a broader distribution, with the presence of different local sites around Ag cations, having a higher average coordination number [7].

In particular, the pair correlation functions $G_{ij}(r)$ for $Ag_2O \cdot nB_2O_3$ simulated by Swenson *et al.* [8] by RMC show that the first peak of the partial $G_{AgO}(r)$ is relatively sharp and symmetrical around 2.4 Å. The corresponding coordination number is estimated to be about 3.3, in good agreement with the experimental value of 3.7 ± 0.5 previously determined by neutron diffraction [8]. On the contrary, both $G_{AgB}(r)$ and $G_{AgAg}(r)$ show a very broad peak, extending from about 2.5 Å and reaching its maximum value at about 3.1 Å [7].

Since the presence of static disorder reduces the XANES and EXAFS signals in a different way, we undertook in a previous work [9] a comparative analysis of XAS spectra calculated for the near edge region. As a first step, all the known crystalline sites for Ag in borate crystals were simulated and compared with experimental XANES spectra by increasing the number of nearest neighbours and the static disorder. Both XANES and EXAFS signals could not be reproduced by any of these sites [10]. As a second step, some simple geometrical structures were built, in order to evaluate the number and kind of nearest neighbours necessary to reproduce at least the general shape of XANES. The best agreement was reached with a configuration of 8 atoms, distributed within a radial distance of about ~3 Å, that were displaced angularly and/or radially starting from a cubic model. From the previous [9] XANES simulations, we concluded that the most plausible model for the local coordination of Ag in borate glasses is characterised by a first shell Ag-O_4 at a distance $R = 2.2$–2.3 Å, the remaining atoms being distributed randomly at longer distances. We also verified that the substitution of some next nearest neighbours oxygen atoms with boron slightly improves the agreement with experimental spectra. In any case, the agreement was only qualitative but it gave a clear indication that a single-configuration model is not able to reproduce the experimental spectra.

In the followings, we will present some examples about the use of a multi-configuration approach.

2. Experimental and Theoretical Details

X-ray absorption spectra were measured at the Ag K-edge using the synchrotron radiation from the ESRF storage ring (Grenoble, France) at the GILDA BM08 beamline. A transmission scheme with a Si(311) crystal monochromator and two ion chambers filled with argon gas was used. Three sets of measurements were performed: (*i*) crystalline c-Ag_2O at 77 K; (*ii*) glasses g-$Ag_2O \cdot 4B_2O_3$ and g-$Ag_2O \cdot 2B_2O_3$ in a range of temperatures

from 77 to 450 K; (*iii*) a set of glasses g-Ag$_2$O·nB$_2$O$_3$ with $n = 2,3,4,6,8$ at $T = 77$ K.

The obtained X-ray absorption spectra were analysed using two methods.

1) The XANES part was simulated by real-space full-multiple-scattering calculations [11] for a set of trial structures. We used the *rsms* code, which is an amended descendant of the *icxanes* code [12] and is maintained by O. Sipr [13]. In order to put into evidence the net effect of structural changes, the same scattering potential was chosen for all the trial structures. We resorted to a non-self consistent potential constructed along the Mattheiss prescription for a silver orthoborate crystal. We checked that the particular choice of the potential is not crucial for the aim of our study. Since no significant core-hole effect has been observed, we used a potential which neglects the core-hole.

2) The EXAFS signals were extracted in a conventional way using the EDA software package [14] and analysed as described below. To determine structural parameters from the EXAFS spectra of glasses, one needs to know the amplitude and phase shift functions for required atom pairs. In this work we have used theoretical *ab initio* model within FEFF8 formalism [15], which was tested using reference c-Ag$_2$O compound with well known structure. The calculated c-Ag$_2$O EXAFS signal was in excellent agreement with the experimental, confirming the good accuracy of the theoretical amplitude and phase shift functions for Ag-O and Ag-Ag atom pairs.

The EXAFS signals of glasses were extracted on the same energy scale as for the reference c-Ag$_2$O compound. Their Fourier transforms consist of a broad asymmetric single-peak and do not show any evidence of the contribution from outer coordination shells. This allows to perform the analysis of the first peak using the original EXAFS spectra without employing the Fourier filtering procedure.

The EXAFS signals were best fitted using two techniques, which allow to reproduce the atomic structure up to ∼3.2 Å. The first one is a model-independent approach, implemented by the EDARDF code [16]. It allows to reconstruct the total radial distribution function (RDF) without any assumption on its shape. As an example, the RDFs obtained for the glasses at 77 K are shown in Fig. 1.

The second one is a conventional Gaussian multi-shell best-fit, starting from results obtained by using the EDARDF code. In particular, up to three shells were used to reproduce the EXAFS signal, with a maximum number of nine fitting parameters, three (N, R, σ^2) for each shell.
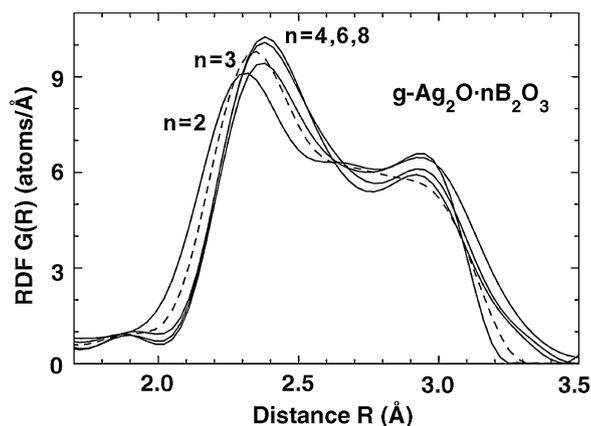

Fig. 1. RDFs in g-Ag$_2$O·nB$_2$O$_3$ glasses at 77 K, as obtained by EDARDF code.

3. Results and discussion

3.1. *General conclusions from EXAFS analysis*

The RDF around silver ions in silver borate glasses has complex asymmetric shape. As a first approximation, based on the chemical composition of these glasses and general rules of glass network formation, the RDF can be decomposed into two parts: (*i*) the nearest oxygen atoms, which form the first coordination shell of silver ions, and (*ii*) the outer neighbours, presumably oxygens and borons which form the glass network. The oxygen atoms in the first shell show a broad but well defined distribution peaked at ∼2.3 Å. At the same time, the group of more distant neighbours has a wide distribution, extending from 2.4 to 3.2 Å. Such a shape of the RDF significantly complicates the analysis, since it cannot be easily approximated by a simple analytical function. Another problem is related to the composition of the outer neighbours. The expected intermixture of oxygen and boron atoms and the similarity of their scattering amplitude and phase shift functions do not allow to separate unambiguously these two contributions. In fact, we have analysed two extreme models: in the first one, all atoms in the outer group were assumed to be oxygens and, in the second one, all atoms were assumed to be borons. The obtained results show that an exchange of oxygen atoms with borons slightly affects the values of structural parameters (N, R, σ^2), but does not substantially change the asymmetric shape of the RDF.

The approximation of the total RDF with three Gaussian functions allows to conclude that there are about 4 oxygen atoms in the first coordination shell of silver and about 4–5 oxygen/boron atoms in the next outer shells.

3.2. *Multi-configuration analysis*

On the basis of the EXAFS results, we have studied the evolution of the simulated XANES spectra, by varying in a systematic way the "1 + 8 atoms cubic cluster" previously identified: atoms were grouped into two shells, allowing different parameters (radial distances and angles, coordination numbers, type of atoms) to be independently varied. Finally, for each set of variable parameters, a mean XANES spectrum was generated by averaging over many configurations obtained from a particular distribution of possible clusters. The choice of shape of the distribution of allowed parameters is one of the crucial points of the procedure. As an illustration of our procedure, we investigate in Fig. 2 the effect of a gradually introduced randomization of the test models geometry. The top curve corresponds to a semi-ordered model with Ag at the cube centre and eight neighbouring atoms located along the cube diagonals: four oxygens form the first shell at $R = 2.3$ Å, four borons form the second shell with R covering equidistantly the 2.5–3.0 Å interval and a partial disorder is introduced via distributing these neighbouring atoms among the cube corners in all possible ways. Then we introduced angular randomization of the second-shell atoms (i.e. their angular coordinates are uniformly distributed over the full space angle) and on top of that also a radial randomization (radial distances of second-shell atoms are uniformly distributed in the interval 2.5–3.0 Å). The remaining theoretical curves describe models with additionally imposed randomization of the first-shell atoms: either only in angular coordinates (fourth curve from the top in Fig. 2) or both in angular and radial coordinates (fifth curve from the top). In the last case, the radial distances of the first shell atoms uniformly deviate from their middle value of 2.3 Å by at most 0.2 Å. A complete description of our constructing the structural models is under publication [10].
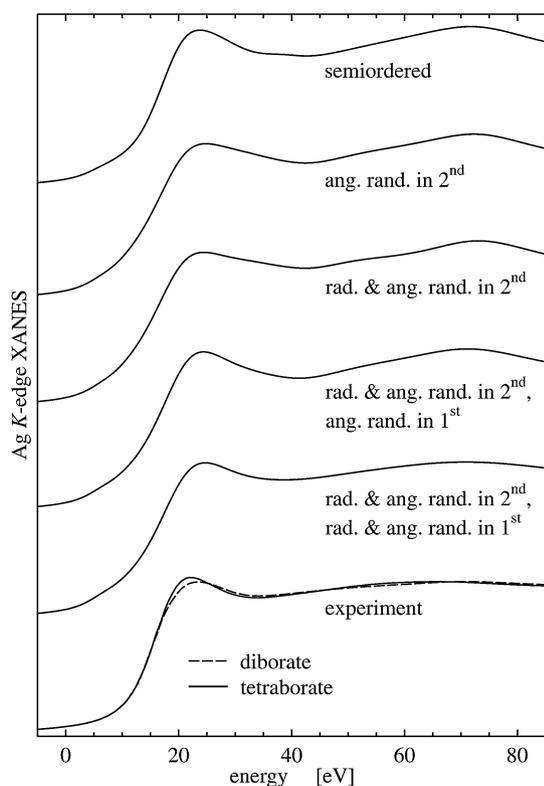
Fig. 2. Configurationally averaged XANES spectra obtained by gradually introducing the randomization in the structure of test models, as described in the text.

Fig. 3. Comparison of experimental EXAFS with calculations for structural models obtained by gradually introducing randomization, as described in the text.

In this way, a much better agreement with XANES experimental spectra has been obtained, but it is still difficult to identify the *good* model, if any. We have thus developed a new software code, able to calculate and average not only XANES, but also EXAFS spectra from each set of *randomly* generated clusters. Preliminary results are very promising, as shown in Fig. 3, where theoretical EXAFS curves for models explored in Fig. 2 are presented (third from the top curve represent a model with angular randomization applied for the first-shell atoms, below is the curve for a model with both angular and radial randomization of the first shell atoms and bottom curve corresponds to both angular and radial randomization in both the first and the second shells). It is quite clear (as expected) that EXAFS is much more sensitive to details of the distribution of radial distances, while XANES is more able to appreciate the influence of angular parameters, which change the multiple scattering contributions.

A first result of the comparison between XANES and EXAFS is the identification of the "wrong" distributions of generated clusters. Moreover, a careful analysis of the trends of the obtained spectra allows us to check the actual influence of each parameter on the configurationally-averaged spectra and to identify for each parameter the most probable value.

We should remember, however, that for silver borate glasses (and in general for systems where a description in terms of single-configuration is not realistic) the obtained values do not describe the local structure of Ag ions, but only a *mean* situation. In fact, the experimental spectrum is due to the superposition of several absorption spectra, corresponding to silver atoms in a quite different configuration. Work is in progress to go beyond the limits of the *random* generation of possible local clusters, aiming to build a bestfit procedure able to manage with more physical constraints for the identification of local sites of Ag ions in borate glasses.
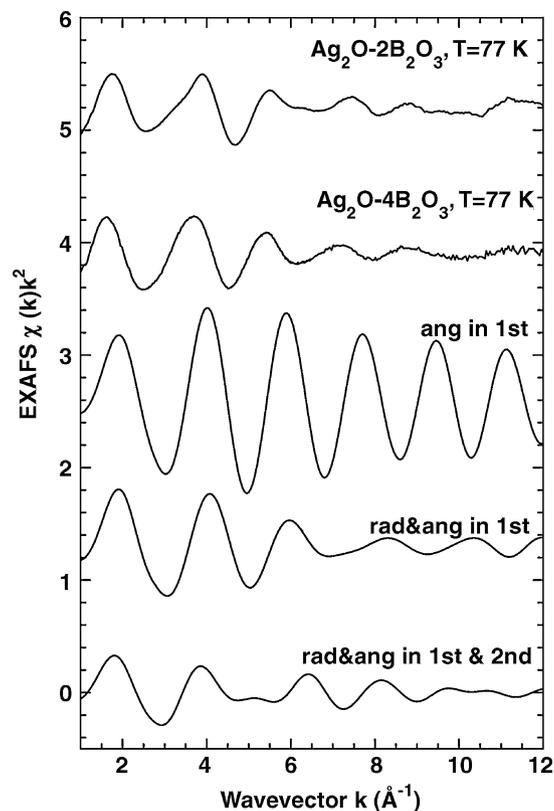
References

1. Minami, T., J. Non-Cryst. Solids **73**, 273 (1975).
2. Varsamis, C. P., Kamitsos, E. I. and Chryssikos, G. D., Phys. Rev. B **60**, 3885 (1999).
3. Swenson, J., Börjesson, L. and Howells, W. S., J. Phys: Condens. Matter **11**, 9275 (1999).
4. Cervinka, L., Bergerová, J., Dalmaso, A. and Rocca, F., J. Non-Cryst. Solids **232–234**, 627 (1998).
5. Dalba, G. *et al.*, S., J. Non-Cryst. Solids **91**, 153 (1987).
6. Rocca, F., Dalba, G., Fornasini, P. and Monti, F., in "Proc. Second. Int. Conf. Borate Glasses, Crystals and Melts", Abington, 1996, (edited by A. C. Wright, S. A. Feller, and A. C. Hannon), (Society of Glass Technology, Sheffield, 1997), p. 295.
7. Swenson, J., Borjesson, L., McGreevy, R. L. and Howells, W. S., Phys. Rev. B **55**, 11236 (1997).
8. Swenson, J., Borjesson, L. and Howells, W. S., Phys. Rev. B **52**, 9310 (1995).
9. Sipr, O., Dalba, G. and Rocca, F., Phys. Chem. Glasses **44**, 252 (2003).
10. Sipr, O., Dalba, G. and Rocca, F., Phys. Rev. B **69**, 134201 (2004).
11. Vvedensky, D. D., "Unoccupied Electron States", (Edited by J. C. Fuggle and J. E. Inglesfield), (Springer, Berlin, 1992), p. 139.
12. Vvedensky, D. D., Saldin, D. K. and Pendry, J. B., Comput. Phys. Commun. **40**, 421 (1986).
13. Sipr, O., Rocca, F. and Dalba, G., J. Synchrotron Rad. **6**, 770 (1999).
14. Kuzmin, A., Physica B **208/209**, 175 (1995).
15. Ankudinov, A. L., Ravel, B., Rehr, J. J. and Conradson, S. D., Phys. Rev. B **58**, 7565 (1998).
16. Kuzmin, A., J. Physique IV (France) **7**, C2-213 (1997).