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SHORT RANGE ORDER IN SILVER BORATE GLASSES

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Résumé - La coordination N du cation Ag dans les verres Ag2O - B2O3 a été étudiée par EXAFS. On trouve N voisin de 2 et un facteur Debye-Waller qui suggèrent que l'ordre à courte distance des liaisons Ag-O est élevé. Ceci différencie les verres boratés des verres sodés. L'addition de Ag I ne modifie pas sensiblement la coordination Ag-O et la coordination Ag-I est voisine de 4.

Abstract - The coordination of the silver cation in the glasses Ag2O n B2O3 has been studied by EXAFS. The values of coordination number (N≈2) and Debye-Waller factor denote an high degree of short range order in the bond Ag-O. This differentiates silver borate glasses from sodium borate glasses. When the glasses are doped with AgI, the Ag-O coordination is found to remain substantially unmodified. The coordination Ag-I is 4-fold.

1 - INTRODUCTION

Silver borate glasses Ag2O n B2O3 can be obtained in a wide range of compositions /1/. Silver oxide modifies the structure of the B2O3 random network. As a result of NMR, IR and Raman measurements, it is now well established that the progressive addition of Ag2O up to an Ag2O/B2O3 molar ratio of about 0.3 (n≈2) changes the coordination of boron from triangular (BO3) to tetrahedral (BO4). For higher Ag2O contents evidence has been found of non bridging oxygens /2,3,4/.

In particular NMR results confirm the hypothesis, firstly proposed by Krogh-Moe, that the basic compositional groups found in silver and alkali borate crystalline compounds (diborate, triborate, etc) are present in the corresponding glasses too. While the structure of the boron-oxygen network has been to a great extent understood, little is known about the bond of silver ions to this network.

One of the main interests in silver borate glasses is connected with their ionic conductivity which can be increased to values of technological interest by addition of suitable amounts of AgI. The mechanism of ionic conduction in silver borate glasses doped with AgI is not yet completely understood. In particular it is controversial whether all silver ions contribute to the conduction in the same way or silver ions bonded to iodine play a predominant role. The knowledge of the bond of silver ions to the boron-oxygen network in the glasses with and without AgI, besides its structural interest, can contribute to clarify the mechanism of ionic conduction.

In this paper we present experimental results on the coordination of
silver ions in binary glasses Ag$_2$O:B$_2$O$_3$ and ternary glasses AgI:Ag$_2$O:B$_2$O$_3$, obtained by EXAFS spectroscopy. EXAFS has proved to be a powerful tool for the investigation of the short range order in noncrystalline materials. In particular for multicomponent systems EXAFS, due to its selectivity, can give direct information about the coordination of single atomic species. This selectivity is very important for silver borate glasses, for which the peak at about 2.3 Å in the RDF is due to two different pair correlation functions (Ag-0 and 0-0). EXAFS measurements have been performed at the edges K and L$_3$ of silver and, for the glasses with AgI, also at the edge L$_3$ of iodine.

2 - BINARY GLASSES Ag$_2$O n B$_2$O$_3$

EXAFS has been measured at the edge Ag K for the glasses n=4,6 and for crystalline Ag$_2$O. The amplitudes of Fourier transforms are shown in Fig.1. The first peak, due to the coordination Ag-0, is well defined for all the spectra. Two main features are evident in Fig.1: a) the Ag-0 distance is larger in the glasses than in crystalline Ag$_2$O by about 0.3 Å; b) the height and width of the first shell peaks are comparable for the three spectra.

The Fourier filtered EXAFS signal of the first coordination shell in the glasses has been quantitatively analyzed by a best fit procedure utilizing backscattering amplitude and phases obtained from crystalline Ag$_2$O.

![Fig. 1 - EXAFS at the edge Ag K. Amplitude of Fourier transform for crystalline Ag$_2$O and for the binary glasses Ag$_2$OnB$_2$O$_3$, n=4,6. The main peak is due to the coordination Ag-0.](image-url)
The Ag-0 distance is 2.27±0.05 Å for both the glasses n=4,6. The coordination number is N=2.1±0.4 for the glass n=4 and N=2.3±0.4 for the glass n=6. Only slight differences have been found between the Debye-Waller factors of the glasses and of crystalline Ag₂O.

The errors quoted for the distances and coordination numbers are a conservative estimate which takes into account the low signal to noise ratio of the experimental data.

EXAFS at the edge Ag L₃ was measured for the glasses n=2,3,4 /5/. The signal is very short due to the onset of the edge L₂. As a consequence the resolving power in the r space is lower than for the EXAFS at the edge K. On the other hand the lower energy of the edge L₃ allows an higher resolving power in the energy space.

A preliminary analysis of the EXAFS at the edge Ag L₃ revealed the presence of small amounts of crystalline silver in the glasses, confirmed then by a careful diffractometric analysis.

In the EXAFS at the edge Ag K no clear evidence of crystalline clusters had been found probably because of the short lifetime of the excited K state and of the consequent decreasing sensitivity beyond the first shell.

By comparing the Fourier transforms of the glasses with that of metallic silver, the fraction of silver organized in crystalline clusters was evaluated for each glass (10% in the worst case). Its contribution was then subtracted from the EXAFS signal of the corresponding glass.

The Fourier transforms of the resulting EXAFS signals are shown in Fig.2.

![EXAFS at the edge Ag L₃](image)

**Fig. 2 - EXAFS at the edge Ag L₃.** Amplitude of Fourier transform for the binary glasses n=2,3,4. The main peak is due to the coordination Ag-0. The peak at about 4 Å is tentatively attributed to a distance Ag-Ag.
Crystalline Ag₂O cannot be utilized as model compound for a quantitative analysis because of the presence of strong near edge structures which considerably shorten the useful EXAFS range /5/.

The glass n=4, already characterized by the K edge EXAFS, has then been utilized as model compound for the glasses n=2,3.

The best fit analysis gives the same Ag-0 distance and coordination number for the glass n=3 as for the model compound n=4.

For the glass n=2 the best fit is obtained with two oxygen shells, the first one at r=1.97±0.05 Å with N=0.7±0.5, the second one at r=2.27±0.05, as for the other glasses, with N=2.3±0.5. The presence of a shell at a shorter Ag-0 distance confirms the existence of non bridging oxygens at high Ag₂O contents.

In Fig.2 a peak is present at about 4 Å in all the spectra. The peak is too broad to allow an unambiguous quantitative analysis. A tentative attribution can be made to a coordination Ag-Ag.

The main result of this EXAFS study on the binary matrix Ag₂O:B₂O₃ is the evidence of an high degree of order and a low coordination (N<2) in the nearest neighbours shell of silver ions.

According to this result, the silver ions are not randomly distributed in the interstitials sites of the glass network but are bonded to oxygens in a well defined configuration.

This confirms our previous conclusions obtained from a comparative analysis of the fine structures at the edge Ag L₃ of the glasses n=2,3,4 and Ag₂O /5/. The presence of a white peak in all these spectra had been interpreted in terms of similarity of the density of states of d symmetry in the bottom of the conduction band of Ag₂O and of the glasses.

The present EXAFS results can be compared with a structural analysis performed on crystalline Ag₂O 4B₂O₃ /6/. In this compound Krogh-Moe found two sites for silver: Ag(1) surrounded by 7 oxygens from 2.23 Å to 3.02 Å, Ag(2) by 8 oxygens from 2.39 Å to 3.00 Å. EXAFS on this compound would be characterized by a coordination number and a Debye-Waller factor significantly higher than those found in the present analysis of the glasses.

In alkali borate glasses Na₂O:B₂O₃ both EXAFS and X ray diffraction indicate that the number of oxygens atoms coordinated to the metal cation is about 5 /7,8/. The bond of the silver cation to the boron-oxygen network thus differs from that of the sodium cation. This means that a common microscopic picture cannot be easily built. A deeper understanding of these structural differences could help to better comprehend why values of ionic conductivity remarkably different are found for different cations.

3 - TERNARY GLASSES (AgI)ₓ(Ag₂0ₓB₂0₃)₁₋ₓ

EXAFS at the edge L₃ of iodine, measured for the glasses n=4 x=.55, n=3 x=.3, n=3 x=.6, shows a first coordination shell strikingly similar to that of β-AgI /9/.

The best fit of experimental data, utilizing amplitude and phases of β-AgI, is obtained for r=2.75±0.05 Å and N=4±0.5 in the three glasses. Iodine ions in glasses are thus tetrahedrally coordinated to silver ions like in crystalline AgI.

This similarity lacks for what concerns the Fourier transformed spectra beyond the first shell: the glasses are characterized by a more disordered situation /10/.

The EXAFS at the K edge of silver allows to discriminate the two first shell coordinations of silver: Ag-0 and Ag-I.

A quantitative analysis has been carried out for the glass n=4 x=.55 utilizing as model compounds β-AgI and the binary glass n=4 for the coordinations Ag-I and Ag-0 respectively /10/.

The Ag-0 distance is 2.23±0.05 Å, almost the same as in the binary
glass, within the quoted accuracy. The Ag-I distance is \(2.73 \pm 0.05\) Å, slightly shorter than the corresponding crystallographic distance in \(\beta\)-AgI.

The values \(N\) obtained by the best fit procedure are consistent with the hypothesis that the coordination numbers remain 2 for Ag-O and 4 for Ag-I and that the fraction of silver ions coordinated to oxygen and to iodine are determined by stoichiometry.

These results strengthen a previous hypothesis on the microscopic structure of ternary glasses: AgI doesn't dissolve homogeneously into the binary matrix but tends to reproduce distorted tetrahedral units without sensibly affecting the structure of the host matrix /4/.

EXAFS measurements are in progress at various \(n\) and \(x\) concentrations to test this hypothesis also in glasses with very low AgI content.

REFERENCES