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Estratto da:
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INTRODUCTION

The glasses AgI:Ag₂O:B₂O₃ are characterized by values of d.c. ionic conductivity covering a range of several orders of magnitude as a function of the AgI and Ag₂O content. The conduction mechanism has not yet been fully understood: in particular it is controversial whether all Ag⁺ ions are equivalent or the Ag⁺ ions bonded to iodine play a predominant role (1,2). To solve the problem a deeper structural knowledge is necessary.

While the structure of the boron-oxygen network has been quite well established by NMR, Raman and IR measurements, little is known about the local arrangement of the mobile cations. Due to its selectivity, XAS is particularly suited to study the short range coordination of silver and iodine. The measurements are performed at the wiggler source in Frascati.

RESULTS AND DISCUSSION

1. Binary matrix

EXAFS measurements at the L₃ and K edges of Ag allowed to study the Ag-O coordination in the binary matrix AgₓOnB₂O₃ (n=2,3,4,6). The details of the EXAFS analysis, performed by taking crystalline Ag₂O as model compound, are reported elsewhere (3,4). The results are summarized in Fig.1.

The interatomic distance Ag-O, which is r=2.04 Å in Ag₂O, varies from r=2.23 to 2.05 Å to 2.30 to 0.05 Å in the glasses, slightly decreasing when the Ag₂O content increases. This trend can reflect the strengthening of the structure due to the progressive change of the boron coordination from planar triangular to tetrahedral when Ag₂O is added to the B₂O₃ former
Fig. 1 - Results of the EXAFS analysis for the binary glasses Ag$_2$OnB$_2$O$_3$ (n=2,3,4,6). The open circle represents the model compound Ag$_2$O.

oxide. For the glass n=2 the best fit to the experimental EXAFS requires a further Ag-O coordination at r=1.99 Å, consistent with the presence of non-bridging oxygens in the borate network for high Ag$_2$O contents.

The coordination numbers are scattered around the value N=2. The shape of their distribution as a function of n is similar to that of the disorder parameters $\Delta_{Os}$; the scattering around the values 2 (for N) and zero (for $\Delta_{Os}$) is attributed to the correlation between N and $\Delta_{Os}$, which cannot be completely resolved by the fitting procedure due to the shortness of the useful k range. The EXAFS results are consistent with the hypothesis that N=2 and that the disorder parameters of the glasses are not sensibly higher than that of crystalline Ag$_2$O.

The existence of a locally ordered structure around the modifier cation agrees with the results obtained on sodium borate glasses by EXAFS and XRD(5,6) and on sodium phosphate glasses by neutron diffraction(7). The coordination number is however lower (N=2) for Ag in borate glasses and for Na in phosphate glasses than for Na in borate glasses (N=5-6).

The EXAFS result is strongly supported by the similarity of the fine structures at the edge Ag L$_3$ (due to transitions p $\rightarrow$ s,d) of the glasses and of Ag$_2$O, characterized by a white peak. The structures at the edge L$_1$ (s $\rightarrow$ p) of the glasses and of Ag$_2$O are instead completely different. This could be explained if one supposes that the linear O-Ag-O coordination present in Ag$_2$O has to be somewhat distorted to fit into the voids of the borate network. This distortion should affect by far more the directional p orbitals (edge L$_1$) than the isotropic s or the quite flexible d orbitals (edge L$_3$).
2. Ternary glasses

In Fig. 2 the fine structures at the edge Ag L₃ for the glasses (AgI)ₓ(Ag₂O₇B₂O₃)₁₋ₓ
with n=4 and x varying from 0 to 0.55 are shown and compared with those of crystalline
Ag₂O and AgI. The white peak is present in the spectra of all glasses, its strength de-
creasing when increasing the AgI content.

If one can consider the white peak as a fingerprint of an O-Ag-O distorted coordination, typical of the bond of silver with the boron-oxygen network, its strength can monitor the fraction of silver ions coordinated to the boron-oxygen network. Both the height and the area of the peaks of the ternary glas-
eses, when normalized to the corresponding val-
ues of the binary glass (n=4, x=0), do not dif-
fer from the fraction of silver ions coming from the binary matrix by more than 20%.

This indicates that the great majority of the Ag ions of the binary matrix maintains un-
changed their bond with the boron-oxygen net-
work when AgI is added.

Further work is in progress to clarify the coordination Ag-I as a function of x, by analizng the EXAFS at the edge K of silver and at the edge L₃ of iodine.

References:
(4) G.Dalba, P.Fornasini, F.Rocca, E.Bernieri, E.Burattini and S.Modilio, to be published.