ESRF	**Experiment title:** **Local Structure and Dynamics in Silver borate glasses.**	**Experiment number**: 08-01 225
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Report:

Since the first pioneering studies on AgI, Silver-containing compounds represent a potential field for the application of EXAFS. In particular, there is a long-lasting interest towards multi-component borate glasses containing both Ag_2O (as modifier) and AgI (as dopant), for their potential utilisation in the field of solid electrolytes.

EXAFS on these materials has already provided unique information on the local structure and vibrational dynamics of iodine and silver atoms. However, the previous measurements performed at the Ag-K edges were not fully satisfactory, because of the low resolution and low beam intensity of the old synchrotron radiation sources. The experimental difficulties are increased by the unusual very low coordination of Ag-O bonds and by the contemporary presence of different local sites for the same kind of atoms. Our previous studies showed also a quite high influence of disorder, which requests a refined cumulant analysis.

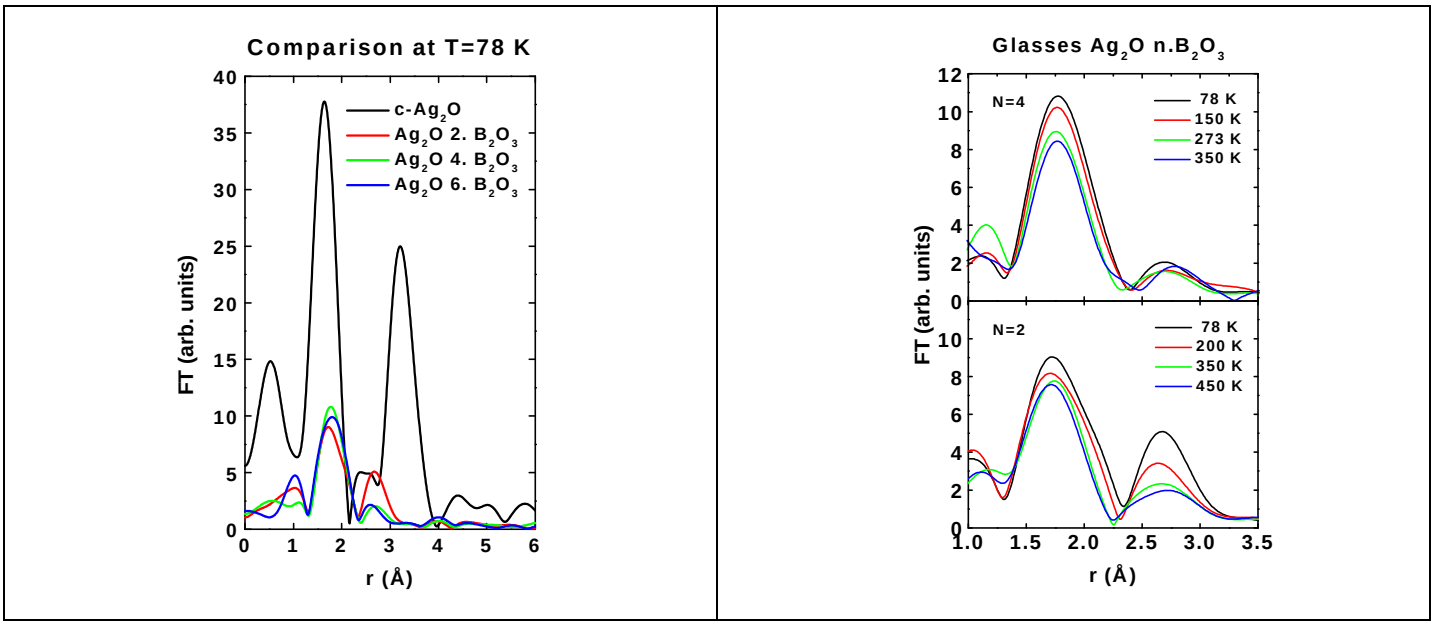
The performances of the actual EXAFS beamlines of ESRF allow now to improve the quality of experimental data, in order to solve the still open problems on the local structure and to obtain new information on the dynamics (i.e. on the different bond strengths, which can influence the ion mobility in the glasses).

A long-term research program on $AgI\text{-}Ag_2O\text{-}B_2O_3$ glasses is in progress at Trento University, using the available ESRF Beamlines. The preliminary steps were the characterisation of structure and dynamics of c-AgI and c-Ag_2O reference compounds (see Report 08-01 199). The experience gained with crystals is now being exploited to study the glasses.

Aim of the present experiment, was the study of binary glasses $\mathbf{Ag_2O\ .nB_2O_3}$ as a function of temperature and Ag content.

In the Exp. 08-01-225, performed during the CRG Italian beam time, Ag-K EXAFS measurements have been performed at BM08-GILDA in the temperature range 77-450 K using a cold/hot finger sample holder in vacuum. These are the first temperature dependent measurements performed on silver borate glasses modified

by silver oxide. The beamline was set on the flat crystal monochromator configuration (with mirrors), obtaining high photon flux and stability. Good quality EXAFS data were obtained in transmission mode up to 20 Å-1 , also for the highest temperature. A first summary of obtained data is presented in the next Figures, where the Fourier Transform signals can be compared.



The most important information from the *left Figure*, is the very reduced intensity of the first shell peak of glasses, corresponding to the Ag-O bond. The EXAFS analysis using the c-Ag_2O as reference, indicates a coordination number N_c about 1 (N_c=2 for the c-Ag_2O). The real meaning of this so low coordination is still an open question, because XRD and Neutron measurements estimated a much higher N_c.

The role of Silver as modifier of the borate glass network and the influence of high static disorder are currently taken into account to develop a structural model using the short-range information coming from EXAFS and the medium-range one coming from Diffraction experiments.

From both Figures, some differences can be recognised for the glass n=2, where the highest Ag-content induces clustering of metallic particles (as documented by the well defined Ag-Ag peak in the range 2.5-3 Å). A careful cumulant analysis of the Ag-O coordination indicates the presence of different static disorder for glasses with n=2 and 4.

In all the glasses, the average distance Ag-O was found about 0.3 Å larger than in c-Ag_2O. The temperature dependence of Ag-O coordination for the glasses with N=2 and 4 has been also studied by cumulant analysis method. While, however, the distance Ag-O in the crystal regularly grows with temperature (about 0.03 Å from 0 to 400 K), a neat contraction is observed in the glass N=4 (for this glass is about -0.02 Å from 0 to 400 K).

A convincing interpretation of the negative thermal expansion in the binary glass has not yet been reached, the main difficulty being the probable existence of several short range Ag-O bonds, which produce a non-negligible, if not predominant, structural contribution to the EXAFS Debye-Waller factor and possibly to thermal expansion. Further work is in progress to disentangle the thermal from the static contributions to disorder.

These results, although still preliminary, open new perspectives for the study of the local origin of thermodynamic properties of glasses.

Recent published papers from this Research Program:

+ G. Dalba, P. Fornasini, F. Rocca and F. Monti, Short range order in borate glasses investigated by x-ray absorption spectroscopy, Phys. Chem. Glasses 41, 290-295 (2000).
+ P. Fornasini and F. Rocca, X-ray Absorption Spectroscopy: characterisation of thermal and structural disorder, Asian Journal of Physics 9, 569-578 (2000).