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Report:

Ionic conductivity in borate glasses containing a modifier oxide (Ag_2O in this case) and a doping salts (AgI), has been the object of many studies in the last years. However, the mechanism of fast ion conductivity has not yet been definitively clarified: the scarcity of short-range information prevents choosing between different proposed theories.
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 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-Ag_2O-B_2O_3 glasses is in progress at Trento University, using the available ESRF Beamlines (BM8 and BM29). The preliminary steps are the characterization of structure and dynamics of c-AgI and c-Ag_2O reference compounds. During the Exp. 08-01-199, Ag-K EXAFS measurements have been performed at BM08-GILDA in the temperature range 4-500 K at intervals of 50 K (in the 7-300 K range using a He gas flow cryostat; in the 77- 500 K range using a cold/hot finger sample holder in vacuum). The beamline was optimized in the high energy - flat crystal monochromator configuration, obtaining a high resolution (as documented by the sharp edge features on Ag and Ag_2O in comparison with previous available data) and high photon flux and stability. Good quality EXAFS data were obtained in transmission mode up to 20 $Å^{-1}$, also for the

highest T, 500 K . Figure 1 (left) shows typical spectra obtained (5 sec/point); for each temperature 2-3 spectra were measured and independently analyzed for statistical noise evaluation. The influence of temperature is quite different for the first and second shell, as can be clearly seen from Figure 1 (right).

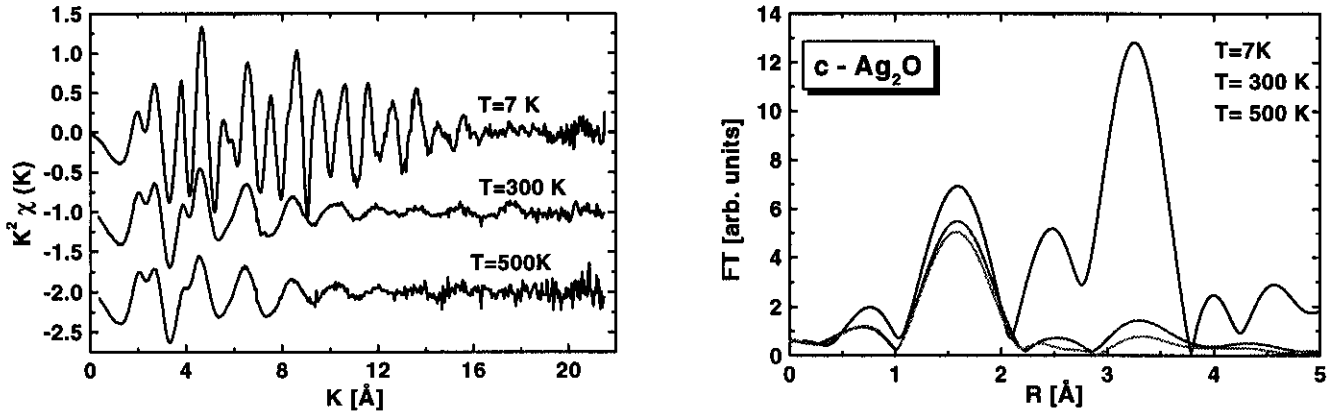

FIGURE 1: Experimental EXAFS signals (left) and corresponding Fourier Transform at three temperatures for c- Ag_2O.

The quantitative analysis of the first two coordination shells of Ag (2 oxygen and 12 silver, respectively) has been performed using the EXTrA software code (®-Univ. of Trento), by means of the ratio method, using the lowest temperature spectra of the two independent runs as reference.
In this way, it has been possible to extract the temperature dependence of the first three cumulants for the first Ag-O shell up to 500 K; for the second shell, the very high Debye Waller factor allowed a reliable cumulant analysis only up to room temperature.

From the analysis of C_2, the Einstein frequency corresponding to the Ag-O and Ag-Ag effective bond stretching constant in Ag_2O were evaluated as 11.1 THz and 1.2 THz respectively. These quite different values may be compared with the calculated vibrational density of states: a qualitative agreement is found with the two main peaks. A more accurate evaluation of the influence of different phonons is now in progress.

From the first three cumulants (by using the $C_3/2C_2$ correction method), the thermal expansion relative to the first Ag-O distance has been calculated: the obtained value ΔR=0.04 Å (from 7 to 500 K) is in good agreement with the available experimental data.
We note that this value indicates a strong positive thermal expansion in the whole temperature range; on the contrary, the preliminary analysis of binary silver borate glasses (very recent exp. 08-01-225, Feb. 2000) shows a reverse tendency for the Ag-O coordination, similarly to our previous evidence for I-Ag bonds in ternary glasses.
The effects of thermal (in particular the transverse vibrations) and static contribution to disorder seem to be quite different for the c-Ag_2O and glasses: the analysis of binary glasses as a function of Ag content and temperature is currently in progress.

Publications from ESRF work:
- G. Dalba, P. Fornasini, F. Rocca and F. Monti: *Short range order in borate glasses investigated by x-ray absorption spectroscopy*, in: Proceedings of the 3nd Int. Conf. on Borate Glasses, Crystals and Melts, 1999. A.C. Wright, S. A. Feller (Eds), Borate glasses Crystals and Melts, Soc. Glass. Technol., Sheffield (1999)