ESRF	**Experiment title:** **EXAFS studies of clustering in lead borate and silicate glasses**	**Experiment number:** **08 01 652**
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Report:

Introduction.

The formation of metallic clusters in oxide glasses remains a very important question in the field of glass nano-science. Beside its applications in optoelectronics (quantum dots), clustering is a process that affects a large number of practical properties, from conductivity to thermal expansion and the glass transition temperature. The formation of these metallic groups is also relevant to computer simulations, where the threshold and amount of clustering heavily influences the model results. This is even more true in the case of lead silicate and lead borate glasses and crystals.

Lead silicate glasses are practically important because of their high density and refractive index, and they have also shown other interesting optical properties *e.g.* photosensitivity and good nonlinear optical responses in the second and third nonlinear coefficients.

Unfortunately, only the first series consisting in lead borate glasses have been investigated. This choice was imposed by the large number of samples contrasting to a relatively short allocated beam-time.

Experiment.

Glasses were prepared by conventional rapid-cooling, roller-quenching techniques.

EXAFS measurements were carried out in transmission mode at the L_3 edge of Pb (13.035 KeV) on powder samples deposited on Millipore filter membranes. The measurements about PbO (tetragonal and orthorhombic) , Pb_3O_4 as well as Pb metallic foil were performed at 77K to use them as reference compounds. Five samples of lead borate glasses, J PbO. (100-x) B_2O_3 +3H_2O with J = 0.4, 0.5, 1.2, 2 and 3 (which correspond to 28.6% , 33.3%, 54.5%, 66.6% and 75% PbO concentrations) , were measured at room temperature. On the basis of our previous experience with glassy compounds, two-three spectra were recorded for each composition, in order to achieve enough N/S ratio and accuracy.

Results.

A XANES analysis on all the borate glasses samples was firstly carried out. A range of 100 eV around the L_3 edge of lead was examined looking at the derivative of the spectra. In all the samples, but the least concentrated (J=0.4) two peaks aside the L_3 main peak, in the pre-edge region at -8.1 eV and past the edge at 12.5 eV, were recorded. These features are related to the $2p \rightarrow 6d$ and $2p \rightarrow$ non-bonding d levels transitions respectively [1] and are typical of a pure PbO compound. They do not change the energy position with varying the PbO concentration. For the least concentrated sample the peak past the main edge was absent.
EXAFS signal was then extracted and analysed using IFEFFIT [2] software package. The modulus of the Fourier transform of the signal evidenced a neat variation depending on the PbO percentage. A feature originating from the convolution of two distances behind the first shell appeared. Its overall magnitude decreases when reducing the quantity of PbO in the glass. In the least concentrated sample it was absent. Experimental EXAFS spectra, when compared with the low-temperature references, exhibited a marked similarity with the tetragonal PbO (litharge,tetragonal or red PbO). In order to validate and to quantify the degree of similarity, a further analysis based on FEFF algorithm was carried out afterward. The results and the successive fit procedure indicated a good agreement with the previous experimental comparison. A first shell analysis, obtained by taking out only the first peak in the Fourier transform, evidenced a tetrahedral structure with the Pb atom in the vertex of the pyramid. It was well reproduced by the first shell in the red PbO. An indication about the order behind the first shell was obtained extending the fitting procedure to larger distances. A fit with theoretical amplitude and phases of metallic lead was absolutely incompatible with the experimental signal. Other plausible structures like that of Pb_2O_3 and massicot (orthorhombic, yellow) PbO were ruled out because of leading to very poor fit results.

Conclusions.
The present EXAFS measurements on borate glasses obtained with varying the content of PbO evidenced some precise characteristics. The lead oxide added to the borate matrix is inclined to dispose itself in tetragonal form and, more precisely, it tends to the red PbO structure. This is confirmed by the XANES analysis which evidences the two peaks in the pre- and post-edge region typical of a PbO structure. It is, at the same time, confirmed by EXAFS: both by the experimental comparison with the reference and by the signal's fit of the several glass samples with the theoretical EXAFS reconstruction. This last analysis confirms that the first shell is entirely constituted by oxygen in the red PbO structure. Furthermore, the indication that also the second shell starts to follow the same structure of PbO is the second result. More precisely, the higher the concentration of PbO the higher the number of oxygen atoms that assume the second shell PbO structure. As for the most diluted sample, the litharge PbO structure is confirmed for the nearest oxygen atoms but no kind of longer range order was evidenced by the XAFS technique. In conclusion it can be assessed that in the measured samples there was no evidence of Pb metallic clustering even at the higher concentration of PbO, preferring the Pb atoms to retain the original bond with oxygen.

Bibliography.
[1] K. J.Rao and J. Wong, J. Chem. Phys. **81** (11) 4832 (1984)
[2] M. Newville, P. Livins, Y. Yacoby, E. A. Stern, and J. J. Rehr, Phys. Rev. B47, pp14126--14131 (1993).