	Experiment title: XAFS study of the structural transformations in relaxor solid solutions	Experiment number: HS-2112
Beam line: ID26	Date of experiment: from: 23/04/03 to: 29/04/03	Date of report: 25/02/04
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Report:

The origin of relaxor behaviour of mixed-ion perovskites is of current interest [1,2] and the progress in this area relies on accurate information on the atomic structure which makes it possible to determine the values and orientation of local dipole moments. Obtaining such information is a challenging problem, as one has to characterize both structural and compositional disorder which is found to be an intrinsic feature of relaxor perovskites. Diffraction methods, being the most powerful means for characterization of the long-range structure, appear to be fairly 'blind' for local irregular deviation of atomic positions from the average ones. Thus additional experiments to provide insight into local structure are very important for the development of a comprehensive structural model of relaxor perovskites.

A study of the Ti environment in solid solutions of $PbNb_{2/3}Mg_{1/3}O_3$–$PbTiO_3$ (PMN-PT) as a function of Ti concentration, $Na_{0.5}Bi_{0.5}TiO_3$ and $K_{0.5}Bi_{0.5}TiO_3$ (KNBT) as a function of K concentration has been made using EXAFS spectroscopy. The aim of the study is to obtain information on the local structural distortions in the relaxor perovskites and their changes associated with the change of macroscopic symmetry at the so-called morphotropic phase boundary. The relation between the macroscopic and the local symmetries is the focus of the study.

Room-temperature fluorescent Ti K-edge spectra were measured at ID26. A Ge X-ray detector array was used to count the fluorescence output. The sample surface was oriented at approximately 45° to the incident X-ray beam and the detector.

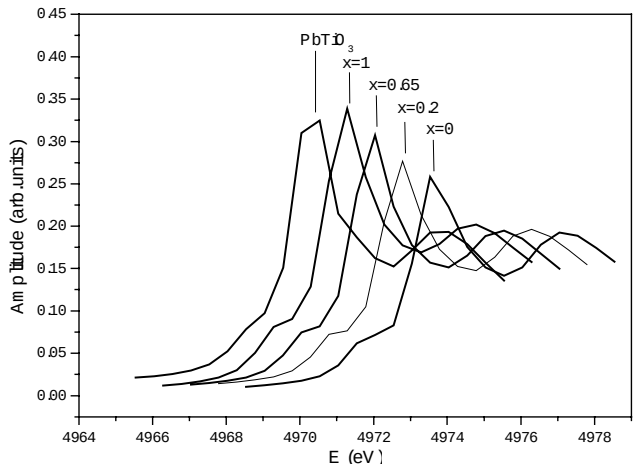

Fig.1 The compositional dependence of the pre-edge structure of $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$ solid solution compared with the $PbTiO_3$ pre-edge structure

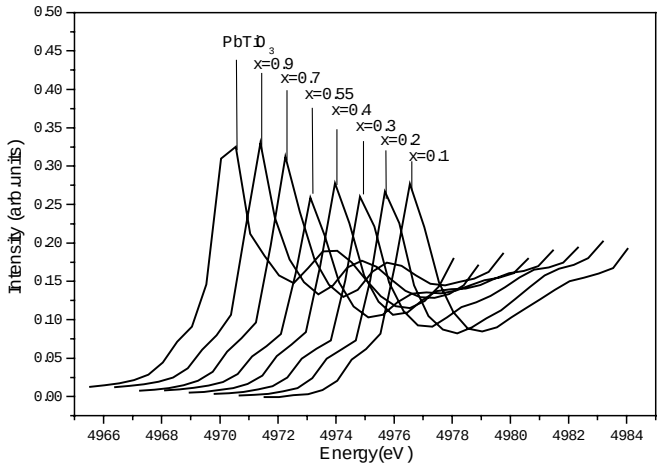

Fig.2 The compositional dependence of the pre-edge structure of $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ solid solution compared with the $PbTiO_3$ pre-edge structure

Information on the compositional dependence of Ti off-centre displacements in $(Na_{1-x}K_x)_{0.5}Bi_{0.5}TiO_3$ and in $Pb(Mg_{1/2}Nb_{1/2})_{(1-x)}Ti_xO_3$ has been obtained from the pre-edge peak intensity. In both systems Ti is found to be strongly off-centre over the whole compositional range.

The evolution of the pre-edge structure of KNBT and PMN-PT crystals with composition is shown in Fig.1 and 2 together with $PbTiO_3$ pre-edge used as a reference spectrum. The energy scale corresponds to the $PbTiO_3$ spectrum, while the other spectra are shifted along the axis in order to demonstrate the variation of the pre-edge peak intensity. It can be seen that in pure KBT the amplitude of the pre-edge peak is approximately the same as in $PbTiO_3$ and the integrated intensities of the peaks have very similar values. Thus the Ti displacement in KBT can be estimated to be equal to 0.25 Å. A gradual reduction of the pre-edge peak amplitude occurs as a result of substitution of K for Na. The reduction of the Ti displacement is not dramatic and most likely is just a result of the reduction of the unit cell parameters.

In $Pb(Mg_{1/2}Nb_{1/2})_{(1-x)}Ti_xO_3$ a slight decrease of Ti displacement with Mg(Nb) concentration is observed. The analysis of the Fourier transforms of the spectra show that in the both compoumds the local symmetry of Ti atoms differs from that imposed by the macroscopic symmetry and thus disorder of Ti displacements may be suggested. Most likely the direction of Ti displacement varies across the sample and depends on the local arrangement of atoms forming the Ti nearest environment.

References

1. Samara G A, Journal of Physics – Condensed Matter 2003 15 (9): R367-R411
2. Fisch R, Physical Review B 2003 67 (9): art. no. 094110