EXAFS Study of the Local Environment of Pb Impurity in $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$

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Ferroelectric properties of perovskite solid solutions are studied extensively for many years. It was known that substitution of the A atoms in the perovskite ABO_3 structure for Pb strongly affects the ferroelectric properties of crystals. For example, doping of $BaTiO_3$ by Pb increases the phase transition temperature [1] and the doping of $SrTiO_3$ [2] and $CaTiO_3$ by Pb results in the appearance of ferroelectricity in these incipient ferroelectrics. To understand better the microscopic mechanisms of these effects, the local environment of Pb impurity atoms in $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ was studied in this work by EXAFS technique.

EXAFS measurements were made on the K1.3b station of synchrotron radiation source "Sibiria-2" at Kurchatov Institute. Spectra were collected at 300 K in fluorescence mode at the L_{III}-edge of Pb (13055 eV) and K-edge of Sr (16115 eV). The samples of $Ba_{0.9}Pb_{0.1}TiO_3$, $Sr_{0.8}Pb_{0.2}TiO_3$, $Sr_{0.98}Pb_{0.02}TiO_3$ and $Ca_{0.9}Pb_{0.1}TiO_3$ were prepared by thermal decomposition of coprecipitated oxalate complexes.

The EXAFS spectra were analyzed in the conventional way [3]. To find the local distortion about the Pb atom, a model was used, in which the (100) displacement of the central Pb atom and Debye-Waller factors for atoms in 3–5 nearest shells were varied with taking into account the lattice parameter obtained from independent X-ray diffraction experiment.

Strong distortion of the local environment of Pb impurity atoms was revealed by the data analysis. Debye-Waller factors for the first (Pb-O) shell in all three perovskites were much larger than this factor for the first Sr-O shell in $SrTiO_3$. Large Debye-Waller factors resulted in disappearance of the contribution of the first shell to the EXAFS spectra already at $k > 4$ Å^{-1}. At the same time, the contribution from the second (Pb-Ti) shell was clearly visible in spectra up to 10 Å^{-1}. This means that doping by Pb results in strong random tilting of neighboring TiO_6 octahedra without changing the Pb-Ti interatomic distance. Moreover, the data analysis revealed noticeable (0.1–0.15 Å) off-center displacement of the Pb atoms from the A sites in $SrTiO_3$ and $BaTiO_3$ crystals, the magnitude of the displacement being much larger than the relative displacement of Ti and Ba atoms in tetragonal $BaTiO_3$ (0.05 Å [1]). Therefore, the doping of perovskite crystals by Pb results in two effects that can alter the phase transition temperature: 1) the appearance of dipole moments of off-center Pb atoms, and 2) the appearance of strong rotational disorder of TiO_6 octahedra.

References

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