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Temperature Dependence of the Pre-edge Features in the XANES Spectra of Tetragonal and Cubic $BaTiO_3$ and $PbTiO_3$

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1 Introduction

Temperature dependence of the intensities of the pre-edge peaks has been observed for various titanium compounds. Hashimoto et al.[1] measured the Ti K-edge XANES spectra of several titanates at various temperatures. The pre-edge peak intensities normally increase with temperature but the ferroelectric phases show different temperature dependences. The temperature dependence is not only because of a phase transition or local geometrical distortion of the titanium site but also because of the thermal vibration of the absorbing and scattering atoms. $PbTiO_3$ and $BaTiO_3$ perovskites have been intensively studied because of their ferroelectric property under ambient conditions and because they are useful as functional materials. We report quantitative comparison of the pre-edge peaks of $BaTiO_3$ and $PbZrO_3$ perovskite-type compounds in a wide temperature range using AIIP standardization and the change of the intensity of the pre-edge with temperature. [2].

2 Experiment

Single crystals of $BaTiO_3$ and $PbTiO_3$ perovskite were prepared and their structures were confirmed by X-ray diffraction at beamline BL-10A. The XAFS spectra near the Ti K-edge were measured in transmission mode at beamlines BL-9C [2]. The measurements were performed in the temperature range 20–900 K under a helium atmosphere. To clarify the temperature dependence, the difference spectra (D spectra) between the low-temperature spectrum and those at higher temperatures were determined. The D spectra at different temperatures were determined for the same sample. The reason for determining the D spectra is to detect only the temperature-dependent parts of the spectra. [2].

3 Results and Discussion

Figure 1 shows the pre-edge peak spectra of $BaTiO_3$ and $PbTiO_3$ at various temperatures. The arrows in the figures show the peak-top intensity change and energy shift with increasing temperature. The A2 peak intensity greatly decreases with increasing temperature and the peak-top energy shifts to the higher energy side. The shift values are in the range 0.2–0.3 eV, which are too large to be an energy shift of an electron orbital by thermal energy.

Figure 2 shows the pre-edge regions in the Ti K-edge XANES spectra and the D-spectra between the lowest temperature spectra and those at higher temperatures for $BaTiO_3$. The temperature dependence of the electron transitions can be extracted from the D spectra. The pre-edge peak positions of the A2 peaks are clearly different from the peak positions of the D2 peaks. The temperature dependence of the transition to each orbital is different. The transitions to orbitals with different temperature dependencies can be separated by determining the D spectra. The true temperature dependence of the transition to each orbital is obtained from the D spectra. The temperature dependence of A2 peaks can be explained by the position and decrease of the D2 valley in the D spectra.

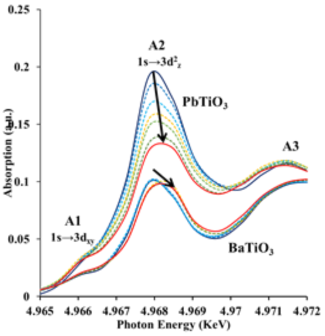

Fig. 1: Temperature variation of the pre-edge peaks in Ti K-edge XANES spectra of $BaTiO_3$ and $PbTiO_3$.

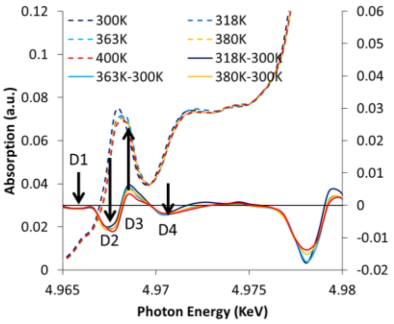

Fig. 2: Pre-edge peaks in the Ti K-edge XANES and the difference spectra of $PbTiO_3$ (difference between the spectrum at 500 K and those at 600–800 K).

References

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