

Temperature Dependence of the Pre-edge Features in the XANES Spectra of Tetragonal and Cubic ATiO₃ (A = Sr, Ba and Pb) and PbZrO₃

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1 Introduction

Characterization of the pre-edge structure in the K-edge XANES spectra of 3d and 4d transition metals is useful for understanding materials in the fields of physics, chemistry and earth sciences. Perovskite-type ATiO₃ (A = Sr, Ba and Pb) compounds undergo several structural phase transitions. PbTiO₃ and BaTiO₃ perovskites have been intensively studied because of their ferroelectric property under ambient conditions and because they are useful as functional materials [1,2]. Here, we report quantitative comparison of the pre-edge peaks of ATiO₃ (A = Sr, Ba and Pb) and PbZrO₃ perovskite-type compounds in a wide temperature range using AIP standardization [3] and the change of the intensity of the pre-edge with temperature [4].

2 Experiment

The XAFS spectra near the Ti and Zr K-edge were measured in transmission mode at beamlines BL-9C PF and NW10A AR, KEK. 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 reason for determining the D spectra is to detect only the temperature-dependent parts of the spectra. When only the temperature changes for the same sample, the difference spectrum shows only the temperature-dependent parts because the other factors cancel out. Figure 1a and 1b show the Ti K-edge XANES spectra of SrTiO₃ from 300 to 700 K and the D spectra obtained by taking the difference between the spectrum at the lowest temperature (300 K) and those at higher temperatures (400–700 K) [4].

3 Results and Discussion

Figure 2 shows the pre-edge peak spectra of BaTiO₃ and PbTiO₃ at various temperatures. For PbTiO₃, the A2 peak intensity greatly decreases with increasing temperature and the peak-top energy shifts to the higher energy side. The peak-top energy also shifts to the higher energy side for BaTiO₃. The shape of the A2 peak for PbTiO₃ is similar that for BaTiO₃. 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.

Figures 3 show 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

PbTiO₃. It is also confirmed that some orbitals overlap near the A2 peak and the A2 peak-top position does not represent the energy of the electronic transition. The pre-edge peak positions of the A2 peaks are clearly different from the peak positions of the D2 peaks. 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.

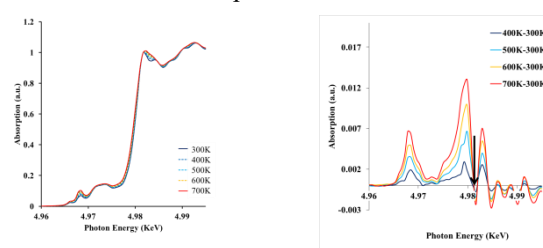


Fig. 1: a) Ti K-edge XANES spectra of SrTiO₃ at 300–700 K. (b) Difference spectra of SrTiO₃, which are the difference between the spectrum at 300 K and those at higher temperatures (400–700 K) [4].

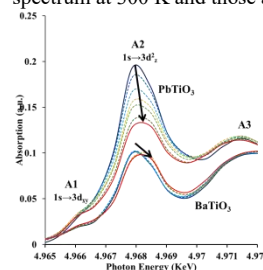


Fig. 2: Temperature variation of the pre-edge peaks in Ti K-edge XANES spectra of tetragonal perovskite-type BaTiO₃ and PbTiO₃ [4].

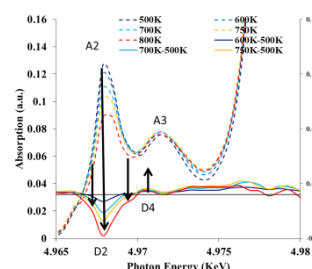


Fig. 3: Pre-edge peaks in the Ti K-edge XANES and the difference spectra of PbTiO₃ (difference between the spectrum at 500 K and those at 600–800 K) [4].

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 [2] Yoshiasa et al. *Acta Cryst.* B72 (2016) 381-388.
 [3] Hiratoko et al. *J. Synchrotron Rad.* 20 (2013) 641-643
 [4] Yoshiasa et al. *Phys. Status Solidi B* (2018) 1800050 (8pages) <https://doi.org/10.1002/pssb.201800050>
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