Temperature dependence of Zr and Ti K-edge XANES spectra for para- and ferro-electric perovskite-type PbZrO₃, PbTiO₃ and BaTiO₃

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Abstract. Zr and Ti K-edge XANES spectra of PbZrO₃, PbTiO₃ and BaTiO₃ perovskite-type compounds were measured in the temperature range from 10K to 850K. Quantitative comparisons for the near-edge spectra were performed in a wide temperature range using the absorption intensity invariant point (AIIP) standardization. Clear temperature dependence for pre-edge shoulder is identified by the calculating the temperature difference of the XANES spectrum intensity. Decrease of pre-edge shoulder and peak intensity is observed only in the para- and ferro-electric phases and draw curves, not straight lines. The gradients for shoulder and pre-edge peak intensity are rich in a variety. The decrease in absorption of pre-edge peak and shoulder is speculated due to the shift from the off-centre position of the Zr atom with respect to the oxygen octahedron to center position. The Zr ion in the PbZrO₃ para-electric phase has same temperature behaviors of Ti ions in the ferroelectric perovskite.

1. Introduction
Characterization of pre-edge peak structure in K-edge XANES spectra of transition metals is useful for understanding materials in the fields of physics, chemistry and earth sciences. The pre-edge features are sensitive to the electronic and geometrical structure around the X-ray absorbing central atom. Temperature dependence on the intensity of pre-edge peaks were observed in various compounds [1-5]. Hashimoto et al. [3] measured the Ti K-edge XANES spectra of several titanates at various temperatures. They have revealed that the pre-edge peak intensities are normally increase with temperature but ferroelectric phases shows different type temperature dependences. Hiratoko et al. [5] succeeded in the quantitative comparative study of temperature dependence over a wide temperature range of pre-edge peaks intensity in various titanium compounds using the absorption intensity invariant point (AIIP) standardization. Large temperature dependence of pre-edge peaks originates in the quadrupole transition and the large density of d states below the p states. Temperature dependence is not only due to a phase transition or to a local geometrical distortion of titanium site but also to thermal vibration amplitude of the absorbing and scattering atoms [5]. The aspect of temperature...
change in X-ray absorptivity at each peak position is fluctuated by the hybridized orbital proportion and the site geometry. PbTiO$_3$ and BaTiO$_3$ perovskites have been intensively studied, because of ferroelectric properties at ambient condition and being very useful as functional materials. Several XAFS studies were carried out to investigate the mechanism of ferroelectric-dielectric phase transition for these materials [3,6-8]. Miyanaga et al. [8] proposed that the Ti ion occupies an off-center position of the distorted TiO$_6$ octahedral site and the geometrical distortion in tetragonal phase decreases with increasing temperature and A2 pre-edge peak intensity decreases. These results showed that the A2 pre-edge peak intensity depends on the degree of distortion around the Ti atoms. PbZrO$_3$ has a para-electric property. PbZrO$_3$ has the same perovskite type structure and phase transitions as BaTiO$_3$ and PbTiO$_3$. There are little researches of comparing them on detailed temperature dependence of XANES patterns because there is no clear pre-edge peak in Zr K-edge XANES spectrum. A sufficient comparative study and the detail interpretation of the temperature dependence of pre-edge and near-edge shoulder intensities have not been made in ferro- and para-electric perovskite-type compounds in wide temperature range. We present a quantitative comparison for the pre-edge shoulders in PbZrO$_3$, PbTiO$_3$ and BaTiO$_3$ perovskite-type compounds in a wide temperature range using the AIIP standardization and investigated how intensity of the pre-edge shoulders changed with temperature.

2. Experiment
The specimens of PbZrO$_3$ perovskite (99.99%), PbTiO$_3$ perovskite (99.99%) and BaTiO$_3$ perovskite (99.99%) were commercial chemicals (Furu-uchi Chemical Co. Ltd) and were examined by X-ray diffraction methods at beam line BL-10A of the Photon Factory in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan (PAC No. 2011G611 and 2013G542). Appropriate amounts of fine-powder sample and boron nitride powder were mixed and pressed into pellets of <0.2 mm in thickness and 10.0 mm in diameter. All samples had edge-jumps of 0.7 (Δμd), where μ is the linear absorption coefficient and d is the thickness. XAFS spectra near the Zr and Ti K-edges were measured in transmission mode at beamlines NW10A and BL-9C of KEK, Tsukuba, Japan. Synchrotron radiation was monochromatized by Si (311) or Si (111) double-crystal monochromator. X-ray energy calibration was performed by setting the copper metal pre-edge absorption peak to 8978.8 eV. X-ray absorption measurements in the temperature range 10–850 K were performed under a helium atmosphere. Details of the measurements are given by Yoshiasa et al. [9] and Hiratoko et al. [5]. Analysis of XAFS data was performed by using XAFS93 programs [10].

3. Results and discussion
3.1 AIIP-based normalization and temperature dependence of pre-edge peak intensity
Figs. 1-3 show the Zr and Ti K-edge XANES spectra for PbZrO$_3$, PbTiO$_3$ and BaTiO$_3$ perovskite-type compounds at various temperatures. In order to clarify the temperature dependence, the difference spectrum between the low-temperature spectra and those at higher temperatures is plotted and shown on the right side. The absorption intensity invariant point (AIIP) [5], i.e. an energy point where the intensity does not change with temperature, was observed near each main peak. Thick arrows in the figures indicate the AIIP. The physical meaning of AIIP will be regarded as extension of EXAFS baseline. Using the AIIP peak intensity as a standard point, it is possible to present a quantitative comparison for the pre-edge peaks in various compounds in a wide temperature range. We normalized the spectrum intensity for the samples in a way that the intensity at AIIP is 1.0 and compared the temperature dependence of the XANES pre-edge peaks among the samples. The AIIP-based normalization allows the elimination of errors caused by the reference point itself changing with temperature. XANES amplitudes at energies higher than the AIIP damp owing to Debye–Waller type effects with increasing temperature [5]. Amplitudes increase linearly with temperature at energies lower than the AIIP usually except for ferroelectric PbTiO$_3$ and BaTiO$_3$ phases. The height of pre-edge peak for ferro-electric perovskite increases with temperature [5,11].
Decreases in Ti K-edge peak A2 intensities were observed mainly in the ferroelectric tetragonal phases. The observations are consistent with previous results [3,6-8,12]. The pre-edge feature of ferroelectric perovskite tends to decrease toward Curie point (Tc) with increasing temperature. This decrease in absorption of pre-edge peak will be speculated due to the shift from the off-centre position of the Ti

**Figure 1.** (A) Zr K-edge XANES spectrum of PbZrO$_3$ at 10 and 210 K (AIIP: 18.025). (B) The difference spectra for PbZrO$_3$ that is the difference between the spectrum at 10K and those of higher temperatures (50K - 210K).

**Figure 2.** (A) Ti K-edge XANES spectrum of PbTiO$_3$ at 500 and 750K K (AIIP: 4.982). (B) The difference spectra for PbTiO$_3$ that is the difference between the spectrum at 500K and those of higher temperatures (600K - 850K).
atom with respect to the oxygen octahedron to center position. It should be also concluded that the decreasing in intensities observed in the para- and ferro-electric materials arise from the atomic movement from off-center to center position [11].

3.2 Decrease of pre-edge shoulder intensity and gradient against temperature.

A clear pre-edge peak isn’t observed in Zr K-edge for PbZrO3 and some shoulders appear on the low energy side of the main peak and AIIP position. These shoulders were named S1–S3. The assignments for electron transitions near the pre-edge and shoulders position were proposed by theoretical calculations [13,14]. The hybridizations between cation and oxygen are important in each compound. In the difference spectra between the low temperature and higher temperature spectra (Figs 1-3), clear negative and positive peaks can be distinguish according to the respective temperature dependences. Three negative peaks or shoulders are identified and observed only in the Ti and Zr K-edges for para- and ferro-electric PbZrO3, PbTiO3 and BaTiO3 by thin arrows in Figures. These peaks in PbZrO3 correspond to S1 – S3 shoulders. In para- and ferro-electric perovskite-type compounds, some pre-edge peak and shoulder intensities decrease with increasing temperature. The validity of observing the temperature dependence of XANES was indicated by the difference spectra between the low temperature and higher temperature spectra.

Figure 4 shows the comparison of temperature dependence of the S2 shoulder intensity for PbZrO3 and BaTiO3 and the A2 pre-edge peak intensity observed in BaTiO3 and PbTiO3. The intensities of shoulder S1 and peak A2 decrease clearly with increasing temperature and draw curves, not straight lines. The gradients for S1 shoulder and A2 pre-edge peak intensity are rich in a variety. It is known that the pre-edge peak intensity increase usually linearly with increasing temperature by harmonic thermal vibration and that the gradient of the pre-edge A2 peak intensity against temperature has two tendencies of rutile- and anatase-types [5]. It is important that the Zr ion in the PbZrO3 para-electric phase has similar temperature behaviors of Ti ions in the ferroelectric PbTiO3 and BaTiO3 perovskite. We guess that the decrease in pre-edge shoulder intensity occur by the same factor as the Ti K-edge peak A2 intensities in the ferroelectric phases. The decrease in absorption of pre-edge shoulder is speculated due to the shift from the off-center position of the Zr and Ti atom with respect to the oxygen octahedron to center position.
Figure 4. (A) Temperature dependence of normalized pre-edge peak A2 intensity of Ti K-edge for PbTiO3 and BaTiO3. (B) Temperature dependence of normalized pre-edge peak S2 intensity of Zr and Ti K-edges for PbZrO3 and BaTiO3 perovskite.

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