

Temperature Dependence of XANES Spectra for ATiO_3 , A_2TiO_4 and TiO_2 Compounds with Structural Phase Transitions

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Abstract. Ti K-edge X-ray absorption near edge structure (XANES) spectra of various titanates was measured at various temperatures. The composition, structure and temperature dependence of XANES spectra was investigated especially on the phase transition. Ti atoms are located in TiO_6 octahedral sites for the all samples. Ti K-edge XANES spectra change largely with different compositions, while the temperature dependence of XANES spectra is small in each compound even if undergoing structural phase transition. For the temperature dependence, the pre-edge intensity has two types of behavior. One is decreasing as temperatures increase, the other is increasing. The former is for PbTiO_3 and BaTiO_3 perovskite and the later is for CaTiO_3 and SrTiO_3 perovskite, Mg_2TiO_4 spinel and TiO_2 rutile.

Keywords: XANES, Titanate, pre-edge

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INTRODUCTION

PbTiO_3 and BaTiO_3 perovskites have been intensively studied for a long time, because of having ferroelectric properties at ambient condition and being very useful as functional materials. In particular, some X-ray absorption fine structure (XAFS) studies were carried out to investigate the mechanism of ferroelectric-paraelectric phase transition for these materials [1-5]. They determined the temperature dependence of local distortion around the absorber using EXAFS analysis for PbTiO_3 and also interpreted the change in the XANES spectra, especially the pre-edge features. They showed that the intensity of the pre-edge depends on the degree of distortion around the Ti atoms.

In this study, we measured the Ti K-edge XAFS spectra of several titanates, such as ATiO_3 (perovskite and ilmenite-type structure, $\text{A}=\text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}, \text{Pb}$), A_2TiO_4 (spinel-type structure, $\text{A}=\text{Mg}, \text{Fe}$) and TiO_2 (rutile and anatase structure) for various temperatures from 18 K to 1100 K and investigated how the

XANES spectra changed with composition, structure and temperature.

EXPERIMENTAL

Commercial chemicals of TiO_2 rutile (99.999%), BaTiO_3 perovskite (99.99%) and PbTiO_3 perovskite (99.9%) were used and the crystals of CaTiO_3 and SrTiO_3 perovskite [6], MgTiO_3 ilmenite and Mg_2TiO_4 and Fe_2TiO_4 spinel were synthesized and all specimen were identified by X-ray diffraction. The appropriate amount of fine powder sample and boron nitride powder was 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 ($\Delta \mu d$), where μ is the linear absorption coefficient and d is the thickness. The measurements of the Ti K-edge XANES spectra were carried out in transmission mode at beam line BL-7C and BL-12C of the Photon Factory in KEK, Tsukuba. X-ray absorption measurements in the temperature range from 18 K to 1100 K were made under a helium atmosphere. The synchrotron radiation was monochromatized by a Si(111) double crystal

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monochromator. Mirrors are used to eliminate higher harmonics. Details of the measurements are given in reference [7].

RESULTS AND DISCUSSION

Figure 1 shows the Ti K-edge XANES spectra for each titanate sample at room temperature. Ti atoms occupy TiO_6 octahedral sites for all samples measured in this study. At room temperature, CaTiO_3 and PbTiO_3 are orthorhombic, BaTiO_3 is tetragonal and SrTiO_3 is cubic, respectively. Perovskite-type ATiO_3 compounds reveal several phase transitions. CaTiO_3 and BaTiO_3 have the same space group at room temperature, but the XANES spectra are not similar to each other. The temperature dependence of the XANES spectra for these materials is very small, even though phase transitions occurred. SrTiO_3 , BaTiO_3 and PbTiO_3 perovskite undergo structural phase transitions in the temperature ranges of this study, SrTiO_3 ; rhombohedral-tetragonal-cubic, BaTiO_3 and PbTiO_3 ; tetragonal-cubic, but no significant change of the XANES spectra was observed at above and below the transition point. These structural transitions of

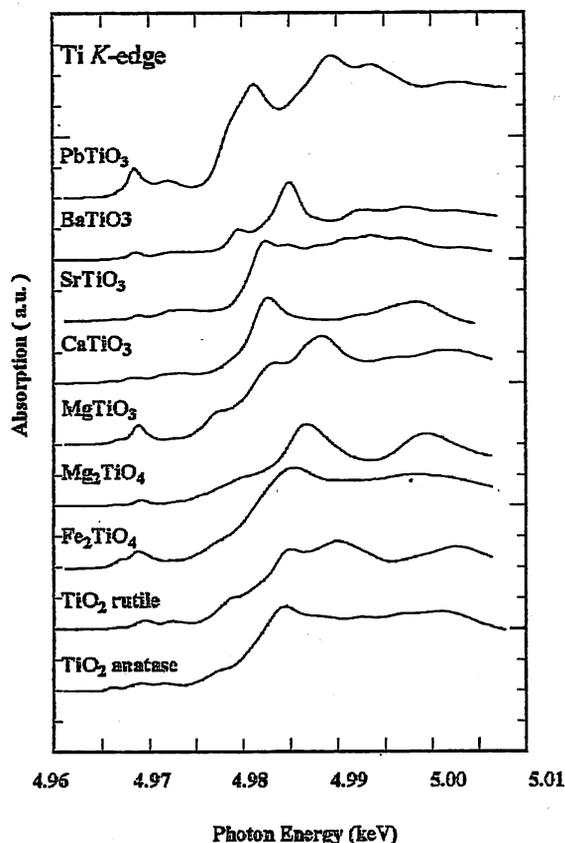


FIGURE 1. Ti K-edge XANES spectra of titanate samples at room temperature.

perovskite are caused mainly only by rotation of the TiO_6 octahedron, therefore the local structure around Ti atom is not changing much. On the other hand, the XANES spectra for TiO_2 are different between anatase and rutile structure, although these two compounds have the same composition.

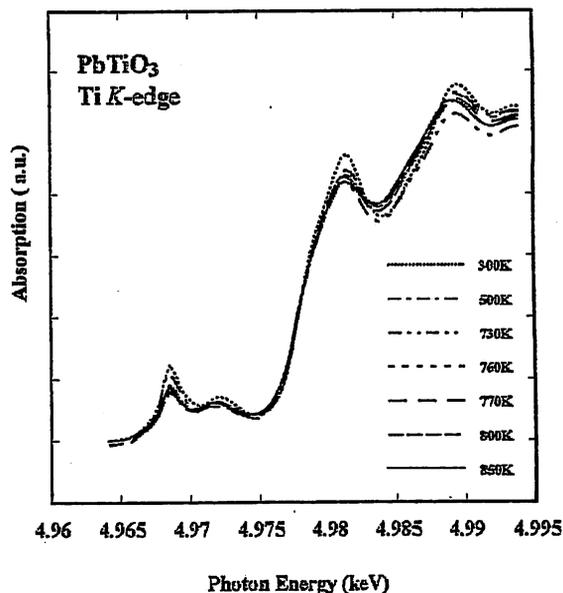


FIGURE 2. Ti K-edge XANES spectra of PbTiO_3 perovskite at various temperatures from 300 K to 850 K. PbTiO_3 perovskite is tetragonal at room temperature and cubic at temperatures higher than 760 K.

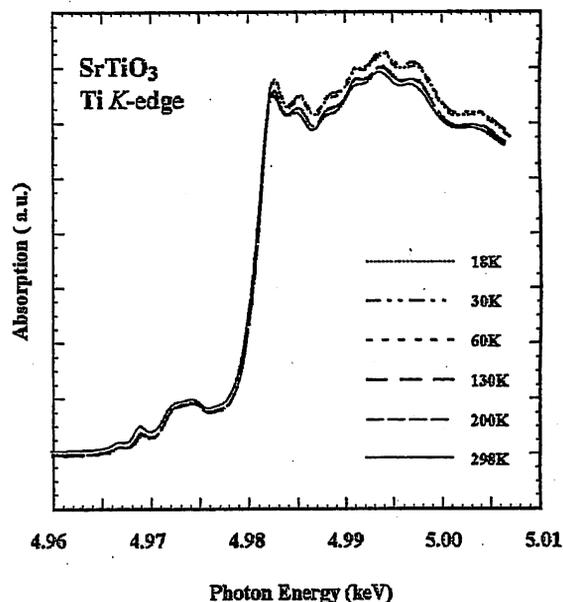


FIGURE 3. Ti K-edge XANES spectra of SrTiO_3 perovskite at various temperatures from 18 K to 298 K. SrTiO_3 perovskite is cubic system higher than 130K.

The electronic state of Ti atoms reflects the chemical bond with oxygen and also with the A site atoms via oxygen atoms. The electronic state of the absorber atom is reflected in the XANES spectra. Thus the different XANES spectra show the different electronic state of the Ti-O bonds in each compound. Even if the Ti atom for these titanates has the same coordination and valence electrons in the TiO_6 octahedron, the oxygen atoms around Ti have different electronic state and orbitals affected by the A site atoms.

Figures 2 and 3 show the temperature variations of Ti K-edge XANES spectra for PbTiO_3 and SrTiO_3 , respectively. The edge jump intensity for each spectrum for each compound was normalized at the threshold energy point. The amplitude of the post-edge XANES spectra for all compounds decreases as the temperatures increase.

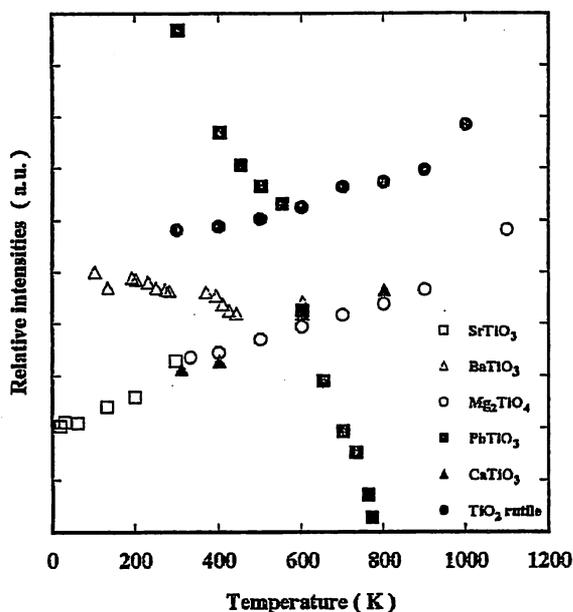


FIGURE 4. The relative intensities of pre-edge of Ti K-edge XANES spectra for several samples vs. temperature. These intensities of pre-edge peaks increase slightly as temperatures increase except PbTiO_3 and BaTiO_3 .

The XANES spectra of the higher-energy region are more strongly affected by the thermal vibration of the atoms than that of the lower-energy region, as the amplitudes of post-edge peaks decrease with temperatures.

The temperature dependence of the pre-edge intensity has two types of behaviors. Figure 4 shows the relative intensities of the pre-edges for SrTiO_3 , BaTiO_3 , Mg_2TiO_4 , PbTiO_3 , CaTiO_3 and TiO_2 rutile vs. temperature. One is decreasing as the temperature increases, the other is increasing. The former is for the PbTiO_3 and BaTiO_3 perovskites and the later is for the CaTiO_3 and SrTiO_3 perovskites, for Mg_2TiO_4 spinel and for TiO_2 rutile. Miyanaga *et al.* (2002) reported that the pre-edge indicated the distortion of Ti-O bonds and the pre-edge intensity becomes smaller when the distortion of the Ti atom decreases as temperatures increase for PbTiO_3 . In this study, we find that the pre-edge peak intensity increase for the other compounds, although the distortion should become smaller as temperatures increase. These two different behaviors of the pre-edge intensity suggest that the increase and decrease of X-ray absorptivity at various temperatures is fluctuated by the hybridized orbital proportion and symmetry. Therefore these intensities of the pre-edge are dependent on composition, structure and temperature.

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