7C, 12C/2006G082

# Temperature dependence of XANES spectra for $ATiO_3$, $A_2TiO_4$, and $TiO_2$ compounds as analogue of the earth's lower mantle

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## Introduction

$ATiO_3$ perovskite (A: Ca, Sr, Ba, Pb) and $TiO_2$ has been intensively studied for a long time as functional materials. X-ray absorption fine structure (XAFS) studies were carried out to investigate about the mechanism of ferroelectric-paraelectric phase transition for these materials. In this study, we measured the Ti k-edge XAFS spectra of several titanates, such as $ATiO_3$ (perovskite and ilmenite-type structure, A=Mg, Ca, Sr, Ba, Pb), $A_2TiO_4$ (spinel-type structure, A=Mg, Fe) and $TiO_2$ (rutile and anatase structure) for various temperatures from 18K to 1100K and investigated how the XANES spectra changed by composition, structure and temperature.

## Experimental

All specimens were identified by X-ray diffraction. The appropriate amount of fine powder sample and boron nitride powder was mixed and pressed into pellet of <0.2 mm I thickness and 10.0 mm in diameter. All samples had edge-jumps with 0.7 ($\Delta\mu d$). The measurements of Ti k-edge XANES spectra were carried out in transmission mode at beam line BL-7C and BL-12C of the Photon Factory. X-ray absorption measurements in the temperature range from 18K to 1100K were made under a helium atmosphere. The synchrotron radiation was monochromatized by a Si(111) double crystal monochromator.

## 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 site for all samples measured in this study. The temperature dependence of the XANES spectra for these materials is very small, even though phase transitions were experienced. These structural transitions of perovskite are caused mainly only by rotation of $TiO_6$ octahedron, therefore local structure around Ti atom is little changing. 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 show the temperature variations of Ti k-edge XANES spectra for $SrTiO_3$. The edge jump intensity for each spectrum is normalized at threshold. The amplitude of post-edge XANES spectra for some compounds decreases as temperatures increase. The XANES spectra of higher-energy region are more strongly affected by the thermal vibration of atom than that of lower-energy region, then the amplitudes of post-edge peaks decreases with temperatures. For the temperature dependence of the pre-edge intensity has two types of behaviors. One is increasing as temperature increase, the other is decreasing. The former is $PbTiO_3$ and $BaTiO_3$ perovskite and the later is $CaTiO_3$ and $SrTiO_3$ perovskite, $Fe_2TiO_4$ and $Mg_2TiO_4$ spinel and $TiO_2$ rutile and anatase. In the present study, we find that the pre-edge peak intensity for the other compounds increase with temperature. These two different behaviors of the pre-edge intensity suggest that the increasing and decreasing of X-ray absorptivity and symmetry at various temperatures be fluctuated by the hybridized orbital proportion. The behaviors of the temperature dependence of the pre-edge are different by composition and structure.

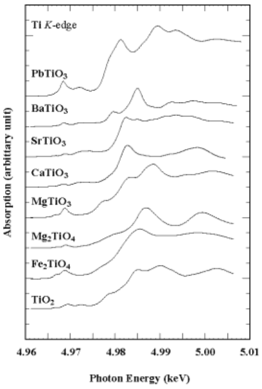

**Figure 1.** Ti k-edge XANES spectra of titanate samples at room temperature.

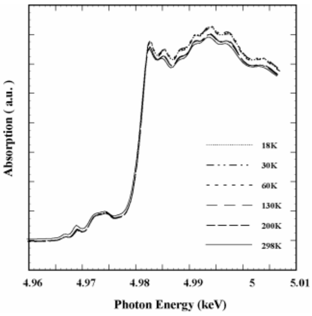

**Figure 2.** Ti k-edge XANES spectra of SrTiO3 perovskite at various temperatures from 18K to 298K.

## References

[1] T.Hashimoto et al. The American Institute of Physics,Conf. Proc. 882, 428 (2007)

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