

Temperature dependence of pre-edge features in Ti *K*-edge XANES spectra for $ATiO_3$ ($A = Ca$ and Sr), A_2TiO_4 ($A = Mg$ and Fe), TiO_2 rutile and TiO_2 anatase

Tatsuya Hiratoko,^a Akira Yoshiasa,^{a*} Tomotaka Nakatani,^a Maki Okube,^b Akihiko Nakatsuka^c and Kazumasa Sugiyama^d

^aGraduate School of Sciences and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan, ^bMaterials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa 226-850, Japan, ^cAdvanced Materials Science and Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan, and ^dInstitute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan.
E-mail: yoshiasa@sci.kumamoto-u.ac.jp

XANES (X-ray absorption near-edge structure) spectra of the Ti *K*-edges of $ATiO_3$ ($A = Ca$ and Sr), A_2TiO_4 ($A = Mg$ and Fe), TiO_2 rutile and TiO_2 anatase were measured in the temperature range 20–900 K. Ti atoms for all samples were located in TiO_6 octahedral sites. The absorption intensity invariant point (AIIP) was found to be between the pre-edge and post-edge. After the AIIP, amplitudes damped due to Debye–Waller factor effects with temperature. Amplitudes in the pre-edge region increased with temperature normally by thermal vibration. Use of the AIIP peak intensity as a standard point enables a quantitative comparison of the intensity of the pre-edge peaks in various titanium compounds over a wide temperature range.

Keywords: pre-edge peak; Ti *K*-edge; temperature dependence; Ti compounds; absorption intensity invariant point.

1. Introduction

The pre-edge peak structure in *K*-edge XANES spectra of 3*d* transition metals is sensitive to the electronic and geometrical structure around the X-ray absorbing central atom (Yamamoto, 2008). Characterization of pre-edge features is useful for understanding materials in the fields of physics, chemistry and earth sciences (Boye *et al.*, 2011; Gomes *et al.*, 2011; Yogi *et al.*, 2011).

Pre-edge peak features of the Ti *K*-edge have been studied by comparison of XANES spectra of different compositions (Grunes, 1983; Ravel *et al.*, 1993; Ravel & Stern, 1995; Farges *et al.*, 1997). Three obvious pre-edge peaks of six-coordinated titanium oxide are observed in many compounds. When Ti occupies an octahedral coordination site, the five *d* orbitals are split into t_{2g} and e_g orbitals according to the ligand field theory. The pre-edge structure of the Ti-*K* absorption edge of six-coordinated titanium oxide has long been debated owing to its complicated structure with three peaks (Grunes, 1983; Brydson *et al.*, 1989; Uozumi *et al.*, 1992; Wu *et al.*, 1997; Ankudinov *et al.*, 1998; Vedrinskii *et al.*, 1998; Joly *et al.*, 1999). Joly *et al.* (1999), by performing polarization XANES spectrum measurement of the rutile-type TiO_2 single crystal and calculating by the finite difference method, was successful in reproducing the three pre-edge peaks experimentally. The three pre-edge peaks are usually called *A1*, *A2* and *A3* in the order of increasing energy value, with the *A3* peak closest to the post-edge energy. The *A1* and *A3* peaks are assigned to the electric quadrupole and electric dipole transitions, respectively. The *A2* peak is a mixture of quadrupole and dipole transitions.

Temperature variations in the intensity of pre-edge peaks have been measured in various titanium compounds (Engel *et al.*, 1987; Durmeyer *et al.*, 1990; Vedrinskii *et al.*, 1997; Nozawa *et al.*, 2005; Sato *et al.*, 2005; Hashimoto *et al.*, 2007; Durmeyer *et al.*, 2010). Hashimoto *et al.* (2007) measured the Ti *K*-edge XANES spectra of several titanates ($PbTiO_3$, $BaTiO_3$, $SrTiO_3$, $CaTiO_3$, Mg_2TiO_4 , TiO_2 rutile, TiO_2 anatase) at various temperatures. However, a sufficient comparative study and detailed interpretation of temperature dependence over a wide temperature range of pre-edge peaks intensity has yet to be conducted in various titanium compounds.

In this paper we present a quantitative experiment for pre-edge peaks in various titanium compounds over a wide temperature range and investigate how the intensity of pre-edge features changes with temperature.

2. Experimental

All specimens [TiO_2 rutile (99.999%), TiO_2 anatase (99.999%), $CaTiO_3$ perovskite (99.99%), $SrTiO_3$ perovskite (99.99%), Mg_2TiO_4 spinel (99.99%) and Fe_2TiO_4 spinel (99.99%)] were commercial chemicals (Furu-uchi Chemical Co. Ltd) and were examined by X-ray diffraction methods. 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. Adjusting sample content allowed all samples to show edge-jumps of 0.7 ($\Delta\mu d$), where μ is the linear absorption coefficient and d is the sample thickness. XAFS spectra near the Ti *K*-edge were measured in transmission mode at

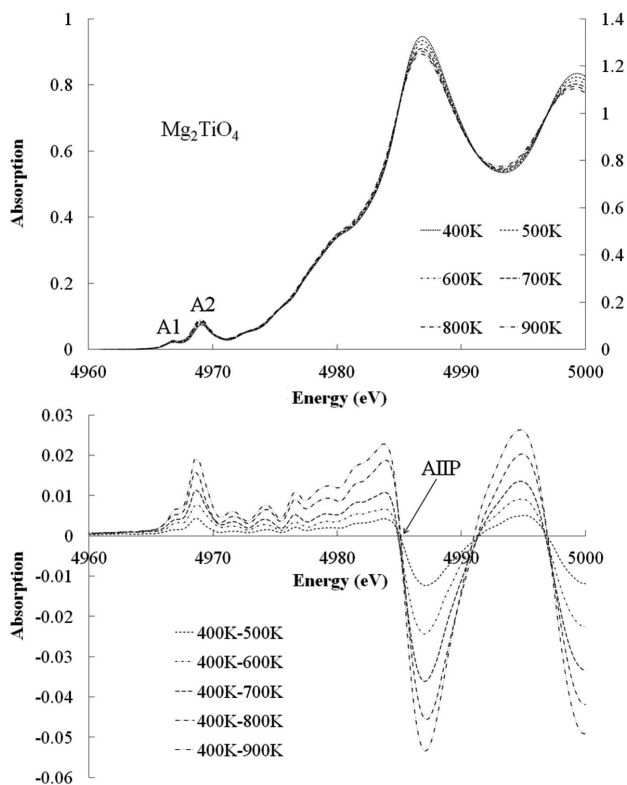


Figure 1
Ti *K*-edge XANES spectra of Mg₂TiO₄ at various temperatures.

beamlines BL-9C and BL-12C of the Photon Factory in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan (PAC No. 2011G611). Synchrotron radiation was monochromated by a Si (111) double-crystal monochromator. X-ray energy calibration was performed by setting the copper metal pre-edge absorption peak to 8978.8 eV. Mirrors were used to eliminate higher harmonics. Details of the measurements are given by Yoshiasa *et al.* (1997). X-ray absorption measurements in the temperature range 20–900 K were performed under a helium atmosphere.

3. Result and discussion

Fig. 1 and Figs. S1–S5¹ show Ti *K*-edge XANES spectra of all samples at various temperatures. In order to clarify the temperature dependence, the difference spectrum between the low-temperature spectra (300 K, 400 K and 500 K) and those at higher temperatures is plotted and shown in the lower portion of each figure. In every case examined an absorption intensity invariant point (AIIP), *i.e.* an energy point where the intensity does not change with temperature, was observed near each absorption edge for all samples. Arrows in the figures indicate each AIIP. The spectrum intensity at the AIIP was set as 1.0 by normalizing the spectrum intensity for the samples, and the temperature dependence of the XANES pre-edge peaks among the samples was then compared. The left-hand scale of Fig. 1 and Figs. S1–S5 shows the measured value, while the right-hand scale shows that normalized by the AIIP.

¹ Figs. S1–S5 have been deposited. Supplementary data for this paper are available from the IUCr electronic archives (Reference: WA5046). Services for accessing these data are described at the back of the journal.

Table 1
AIIP energy and slope of peaks A1 and A2 for each compound.

Compound	AIIP energy	Slope of peak A1 (intensity/100 K)	Slope of peak A2 (intensity/100 K)
TiO ₂ rutile	4984 eV	0.0016 (1)	0.0057 (2)
TiO ₂ anatase	4983 eV	0.0014 (1)	0.0017 (1)
CaTiO ₃	4982 eV	0.0019 (2)	0.0056 (1)
SrTiO ₃	4981 eV	0.0016 (1)	0.0067 (1)
Mg ₂ TiO ₄	4985 eV	0.0017 (1)	0.0048 (1)
Fe ₂ TiO ₄	4983 eV		0.0017 (4)

AIIPs, where the intensity does not change with temperature near each absorption edge, are present in each sample. AIIP-based normalization allows the elimination of errors caused by the reference point itself changing with temperature. This use of AIIPs for normalization is effective when comparing the temperature dependence of the absolute intensity in XANES spectra. XANES amplitudes are clearly seen to damp at energies higher than the AIIP owing to Debye–Waller factor effects with increasing temperature; the line displays the attenuation of a sine curve. Conversely, amplitudes increase with temperature at energies lower than the AIIP.

The peak A2 was observed for all compounds, while peak A1 was seen in all compounds with the exception of Fe₂TiO₄. Figs. 2 and 3 show the temperature dependence of the intensity of pre-edge peak features near A1 and A2 for several samples. The intensity of peaks

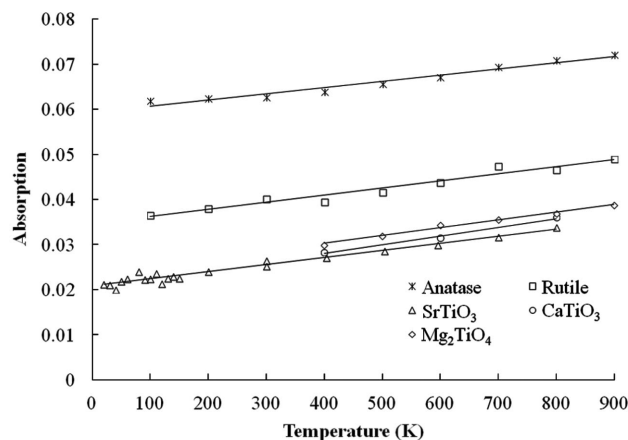


Figure 2
Temperature dependence of normalized pre-edge peak A1 intensity of the Ti *K*-edge for several samples.

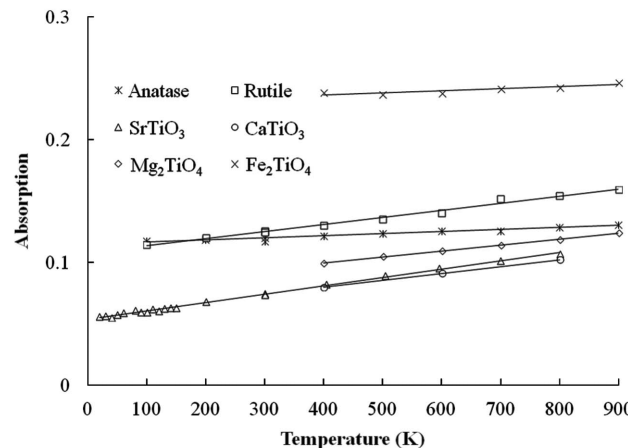


Figure 3
Temperature dependence of normalized pre-edge peak A2 intensity of the Ti *K*-edge for several samples.

A1 and A2 for all samples increased linearly with increasing temperature. Table 1 shows the AIIP energy for the compounds and the slopes of peaks A1 and A2 with temperature. Figs. 2 and 3 show that the gradient of the A1 peak intensity with temperature is identical for all compounds, while the gradient of the A2 peak intensity with temperature changes with composition. The rate of increase in the A2 peak intensity for TiO₂ anatase and Fe₂TiO₄ is quite small compared with the rest of the samples. The gradient of the A2 peak intensity for rutile and anatase suggests differences in local structure change with temperature. AIIP-based normalization has proven to be effective in physical-properties research.

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