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Temperature dependence of Ti K-edge XANES spectra in various titanium oxides and the absorption intensity invariant point.

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1 Introduction

Temperature dependences of pre-edge peaks were observed in the various titanium compounds. 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 static distortion of titanium site but also to thermal vibration amplitude of the absorbing titanium atom. The aspect of temperature change in X-ray absorptivity at each peak position is fluctuated by the hybridized orbital proportion and the site symmetry. Sufficient comparative study and the detail interpretation of the temperature dependence of pre-edge peaks intensity is not made in various titanium compounds in wide temperature range. We present a quantitative experiment for the pre-edge peaks in various titanium compounds in a wide temperature range and investigated how intensity of the pre-edge peaks changed with temperature.

2 Experimental and analysis

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 ($\triangle \mu$ d), where μ is the linear absorption coefficient and d is the thickness. The measurement 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 (PAC No. 2011G611). The synchrotron radiation was monochromatized by a Si (111) double crystal monochromator. Mirrors are used to eliminate higher harmonics. Details of the measurements are given in reference [1]. X-ray absorption measurements in the temperature range from 20K to 900K were performed under a helium atmosphere.

Figures 1 shows the Ti K-edge XANES spectra of Mg2TiO4 at various temperatures. In order to clarify the temperature dependence, the difference spectra that is the difference between the spectrum at 400K and those of higher temperatures (900K-400K), are shown in the lower parts of Figures.

3 Results and Discussion

We have found that there is the energy point at which peak intensity does not change in temperature near the each absorption edge for all samples. This point should be called the absorption intensity invariant point (AIIP). The arrows indicate the AIIP in Figure. Using the AIIP peak intensity as a standard point, it is possible to present a quantitative comparison for the pre-edge peaks in various titanium 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. In Figure 1, the left side scale shows the measured value and the right side scale is normalized by AIIP. It is clearly indicated that the higher energy side from AIIP, the XANES amplitudes are dumping due to the Debye-Waller factor effects with increasing temperature. That is, it sees as attenuation of a sign curve. On the other hand the lower energy side before AIIP, the amplitudes increase with temperature. The AIIP energies are around 4.983 KeV.

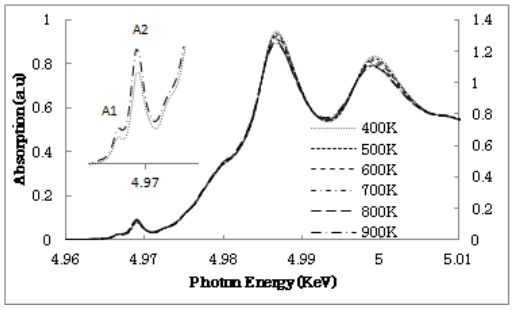

Fig1. Ti K-edge XANES spectra and differences of Mg2TiO4 at each temperature.

[1] T.Hiratoko, et al., Journal of Synchrotron Radiation, 20 (2013) 641-643.

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