Electronic Structure Change with the Transition Temperature of Anatase-Rutile TiO2

Minami Kondo and Masaru Takizawa

Department of Physical Sciences, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu 525-8577, Japan

Titanium dioxide (TiO_2) exists in three distinct phases: anatase, rutile, and brookite. Notably, both the anatase and rutile phases exhibit highly stable crystal structures. In this study, we investigated the transition of anatase TiO_2 to the rutile phase under the influence of thermal heating, utilizing X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS).

The XRD data were acquired using the Rigaku Mini flex-II, with the characteristic X-ray wavelength being Cu K α = 1.5418 Å. Additionally, XAS measurements were performed at BL-8 of SR center, Ritsumeikan University.



Fig. 1 XRD measurement results of anatase TiO_2 after thermal heating.

Figure 1 illustrates the XRD measurement results for anatase TiO₂ before and after thermal heating. Following heating at 900 °C for 20 hours, the anatase TiO₂ phase remained unchanged, and no transition occurred. However, after heating at 1000 °C for 10 hours, the rutile phase emerged. The ratio of anatase to rutile presence was approximately 7:3. Furthermore, after heating at 1000 °C for 20 hours, the entire sample transitioned to the rutile phase.

To investigate the electronic structure, the XAS measurement results for anatase TiO_2 before and after thermal heating are depicted in Fig. 2. Analyzing the O *K*-edge spectrum around 530 eV, we observe significant changes attributed to the desorption of adsorbed oxygen upon heating.

Furthermore, examining the Ti L-edge around 460 eV and the O K-edge around 543 eV, we note shifts in peak positions. These observations suggest that surface electronic structures also undergo changes during phase transitions induced by the heating process.

XRD and XAS measurements reveal that a phase transition occurs between 900 °C and 1000 °C for anatase TiO₂. Typically, anatase TiO₂ gradually undergoes phase transition, initiating around 600 °C and completing the transition at 700 °C. Notably, the phase transition temperature is susceptible to variation based on the specific manufacturing method employed for anatase TiO₂ production.



Fig. 2 XAS measurement results of anatase TiO_2 after heating.

References

[1] S. A. Kim *et al.*, J. Solid State Chem., 315 (2022) 123510.

[2] E. Kordouli et al., J. Solid State Chem., 232 (2015) 42.

[3] S. Wang et al., Appl. Surf. Sci., 263 (2012) 260.