

Identification of valence state of Ti using NEXAFS

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Introduction

Ti is known to have important effects on mechanical and electrical properties of Al_2O_3 . On the other hand, Ti can have various valence states such as Ti^{2+} , Ti^{3+} , and Ti^{4+} . It is important to identify the valence state of the doped Ti in Al_2O_3 . In this study, the Ti-K NEXAFS from selected Ti-oxides are investigated to establish the method to identify the valence state of Ti. We compare the NEXAFS from the tetravalent oxides including rutile and anatase with that from the trivalent oxides, Ti_2O_3 . First principles band structure calculations using the orthogonalized linear combinations of atomic orbitals (OLCAO) method have been also performed.

Methodology

Ti-K NEXAFS were measured for rutile and anatase type of TiO_2 and Ti_2O_3 . The measurements were performed at BL12C in KEK-PF, Japan. Si(111) double crystals were employed as a monochromator. The spectra were obtained by the conventional transmission method.

In order to reproduce the experimental spectra, the first principles orthogonalized linear combinations of atomic orbitals (OLCAO) calculations were performed [1]. Full basis function sets, i.e., 1s to 5p for Ti and 1s to 3p for O, were employed in the self consistent calculation, whereas extended basis function sets, i.e., 1s to 6p for Ti and 1s to 4p for O were utilized in the spectral calculation to reproduce the features at the high energy region.

The core-hole effect was fully taken into account in the self-consistent iterations by removing an electron at the core orbital and putting it at the lowest unoccupied band. Both the final state and the ground state were separately calculated. Theoretical transition energy was evaluated as the difference in the total energy of the supercell between the ground and the final states. The transition matrix elements of the electric dipole transition between the ground and final states were computed for the theoretical spectrum.

Results and Discussion

Figure 1. shows Ti-K NEXAFS spectra of rutile and anatase structured TiO_2 , and Ti_2O_3 observed in the present study. The Ti-K NEXAFS can be divided into two parts, one is a set of small-peaks within 8eV from spectral onsets, and the other is that of the following large peaks. They are hereafter called “pre-peak” and “main-peak” for simplicity. Although the spectral features of the

Ti^{4+} compounds are slightly different from each other, the following two characteristics are commonly found. 1) The onset of the pre-peak is 4953eV. 2) The shoulder named peak B is found at 4966eV in the main-peak. On the other hand, the onset of the pre-peak and peak B in the main-peak appear at 4951eV and 4962eV in the spectrum of Ti_2O_3 . In order to ensure the spectral differences between the Ti^{4+} and Ti^{3+} oxides, those NEXAFS were compared with the theoretical spectra. In the calculations, 72, 108, and 120 atoms supercells were employed for rutile and anatase type of TiO_2 , and Ti_2O_3 , respectively. Although the onsets of the calculated spectra were shifted by +8eV, it should be noted that the calculation error is 0.2% of the absolute transition energy. The pre-peak A1 of rutile disappears in the theoretical spectrum, whereas it is clearly found in the experimental spectrum. Joly et al. and Shiery reproduced the pre-peak A1 by including the quadrupole transition [2, 3]. In contrast, the quadrupole term was not included in the present calculation. However, it is found that the other peaks are well reproduced by calculating the dipole transition matrix. In particular, the above spectral differences between the Ti^{4+} and Ti^{3+} oxides in experiments were well reproduced by the present calculations.

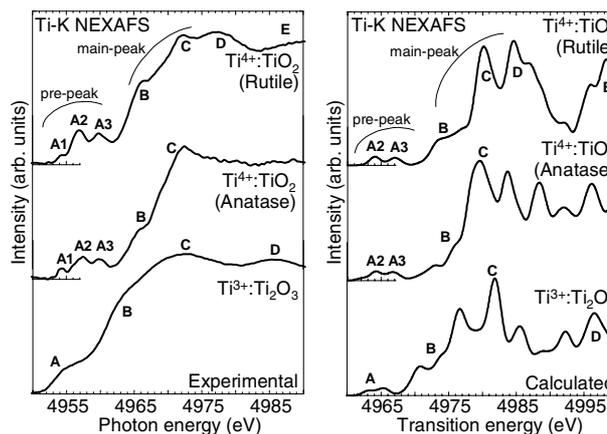


Fig. 1. Experimental and theoretical Ti-K NEXAFS from rutile, anatase, and Ti_2O_3 .

References

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