

Angular dependence of Nb K-edge XAFS spectra of Nb doped TiO₂

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1 Introduction

Nb-doped TiO₂ show n-type semiconducting properties. In order to characterize the performance of the Nb dopant it is important to obtain the structure and location of the Nb dopant. However, there were two different doping sites ever proposed. Sasahara reported that the Nb was typically present in the interstitial position on the surface as Nb⁵⁺ [1]. Zimmerman interprets the ESR signals using the Nb⁴⁺ substitution on the Ti⁴⁺ site and hopping conductivity [2].

In this work, we measured angular dependence of Nb K-edge XAFS spectra of Nb-doped TiO₂ single crystal (rutile) and identify the location of the dopant Nb.

2 Experiment

The single crystal of Nb-doped TiO₂ was purchased from Shinko-sha (0.05 wt%; 5 Ωcm). XAFS spectra were measured using a Si(311) double crystal monochromator at NW10A of Photon Factory Advanced Ring (PF-AR). The fluorescence XAFS spectra were obtained by using 19 elements SSD. All measurements were carried out at room temperature. The [110] direction of the single crystal was along the oriented surface normal. The angle Θ between X-ray polarization vector ϵ and [110] direction was defined within the plane which was determined by [110] and [001] around the [110] direction.

3 Results and Discussion

Figure 1 shows the observed XANES of Nb in the TiO₂ single crystal (a) and calculated result (b). The observed Nb K-edge XANES shows clear angular dependence. The theoretical calculation were obtained by using FEFF[3]. In this model, X-ray absorbing Nb was substituted with a Ti site of the rutile TiO₂. In Fig. 1(a), A and B were changed depending on the angle Θ . The calculated results show the similar trends in the strongest peaks A and B at $\Theta=90^\circ$ (Fig. 1(b)).

Figure 2 shows Fourier transformed the observed EXAFS oscillations. The $\chi(R, 90)$ have a larger peak around $R = 0.25$ nm. EXAFS curve fitting analysis shows that the peak is composed Nb-Ti path to the nearest Ti site located on [001] in rutile TiO₂ structure well corresponding to the substituted model.

Nb at the interstitial site could not reproduce the XAFS oscillations.

4 Conclusions

The angular dependence of XAFS spectra has good agreement with the theoretical calculations based on the Nb substituted with Ti position of rutile TiO₂.

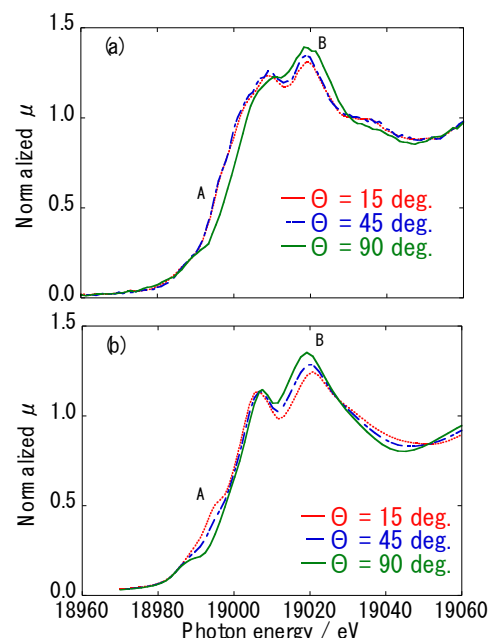


Fig. 1: Angular dependence of Nb K-edge XANES spectra of Nb doped TiO₂. Θ is angle between [110] and X-ray polarization vector ϵ . (a) experimental and (b) calculated results.

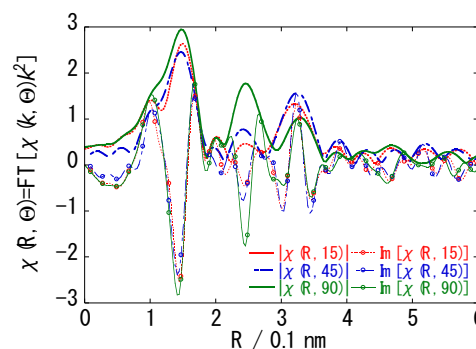


Fig. 2: Angular dependence of Fourier transform (FT) of k^2 -weighted Nb K-edge EXAFS oscillations $\chi(k)$ of Nb doped TiO₂. Θ is same as in Figure 1. (k -range in the FT is 20-110 nm⁻¹)

References

- [1] A. Sasahara and M. Tomitori, *J. Phys. Chem. C* **117**, 17680 (2013).
- [2] P. H. Zimmermann, *Phys. Rev. B* **8**, 3917(1973).
- [3] J.J. Rehr *et al.*, *Phys. Chem. Chem. Phys.* **12**, 5503 (2010).

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