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Studies on microwave synthesis of VO_2 nanocrystals and thin films

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1 Introduction

Monoclinic vanadium dioxide VO_2 with a rutile-type structure (Fig. 1a) exhibits a reversible first-order metal-insulator transition (MIT) at a temperature of T_c = ~68 °C [1]. Around this transition temperature, the insulating monoclinic VO_2 changes to the metallic tetragonal VO_2, and the electrical and optical properties change significantly. As a result, applications for switches, sensors, and smart windows are being considered.

This MIT temperature can be controlled by substituting the V site with a different element such as W. To prepare nanoparticle-containing coating solutions for flexible films, we have been investigating the synthesis of $V_{1-x}W_xO_2$ nanocrystals. We report here the results of X-ray absorption spectroscopy (XAS) analysis of nanocrystals hydrothermally synthesized without microwave heating as a preliminary experiment.

2 Experiment

In a typical synthesis procedure, $VOSO_4 \cdot nH_2O$ and $CO(NH_2)_2$ were mixed in distilled water with continuous magnetic stirring to form a clear blue solution. Subsequently, an appropriate amount of hydrazine solution was added to this blue solution, which was then transferred into a Teflon-lined autoclave. After the hydrothermal treatment at 270 ºC for 24 h, the resulting precipitate was collected after being centrifuged and washed several times with distilled water and alcohol, and then freeze-dried. For the synthesis of W-doped VO_2, a required amount of tungstic acid was added before the autoclave was sealed.

The obtained samples were analyzed by X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), and differential scanning calorimetry (DSC). The XAS spectra of powder specimens were measured by transmission mode using synchrotron radiation at beamline BL-9C of Photon Factory in KEK. The computer program, ATHENA, [2] was used for the analysis of the XAS data.

3 Results and Discussion

Figure 1b shows STEM image of VO_2 nanocrystals synthesized by hydrothermal synthesis. The particle size of the VO_2 nanoparticles was approximately 20 nm. XRD analyses confirmed that single phase samples were obtained, and DSC measurements showed that the MIT temperature decreased with increasing W substitution.

Figure 2 presents V K-edge X-ray absorption near-edge structure (XANES) spectra of $V_{1-x}W_xO_2$ nanocrystals. The spectrum of the VO_2 nanocrystals was observed between the spectra of V_2O_3 and V_2O_5, indicating that the valence of vanadium seems to be tetravalent. This spectrum of the VO_2 nanocrystals was observed to be on the higher energy side compared to the calculated XANES spectrum by FDMNES code [3]. Although the MIT temperature changed significantly with W substitution, no change in the spectrum was observed within this range of substitution.

XRD peaks of the VO_2 nanocrystals disappeared when the sample was stored in air for a long period of time. XANES spectra indicated that the VO_2 samples stored in the air for several months had changed to a V_2O_5 like phase, suggesting a change in valence from V^{4+} to V^{5+}. Preventing such transformation of these nanocrystals will be an important technological challenge in the future.

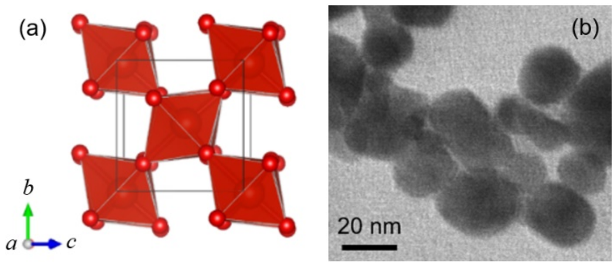

Fig. 1: Crystal structure and STEM image of the VO_2 nanocrystals synthesized by hydrothermal synthesis.

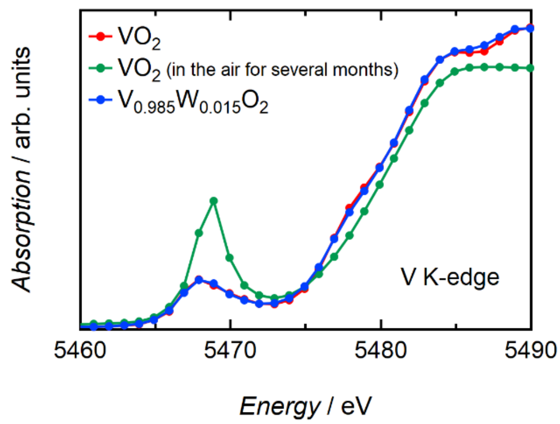

Fig. 2: V K-edge XANES spectra of $V_{1-x}W_xO_2$ nanocrystals synthetized hydrothermally.

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References

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