Electronic Structure and Structural Studies of VO_2 Nanoparticles by Means of Nonresonant Inelastic X-ray Scattering and X-ray Diffraction under Pressure

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The temperature-induced metal-insulator transition (MIT) in Vanadium dioxide VO_2 has attracted much attention since its discovery 50 years ago. VO_2 shows a resistivity jump of more than four orders of magnitude in addition to structural phase transition at about 340 K. The MIT for VO_2 has been extensively studied as functions of temperature, pressure, and dopant content. However, the finite-size effect on the MIT has not been clear. It is necessary to use bulk sensitive measurements in order to investigate the MIT of nanostructures where surface cleaning is difficult. In this study, we have investigated the truly bulk electronic states of the VO_2 nanoparticles using nonresonant inelastic x-ray scattering (NIXS).

Recently, a monoclinic metallic phase has been observed under the pressure of more than 10 GPa at room temperature [1]. It revived the discussion on the relative role of electron-electron interaction and electron-lattice interaction in the MIT. Pressure dependence should be enhanced for fine particles due to lattice softening. In this study, we have also measured the pressure dependence of x-ray diffraction (XRD) for VO_2 nanoparticles up to ~3 GPa.

VO_2 nanoparticles with an average diameter of ~18 nm were prepared by ball milling from VO_2 microparticles (99 %, Furuuchi Chemical Corporation). NIXS measurements of VO_2 microparticles and nanoparticles were carried out at BL12XU. NIXS data were collected at room temperature. The total energy resolution of experiments was about 1.5eV at 9887 eV using Si(333) DCM beam and spherical bent Si(555) analyzers. The powder XRD experiments were carried out at BL12B2 line using the VO_2 nanoparticles. The samples were pressurized using a Merrill-Bassett diamond anvil cell. XRD data were collected at room temperature. The wavelength of the incident x-ray was set to 0.5 Å.

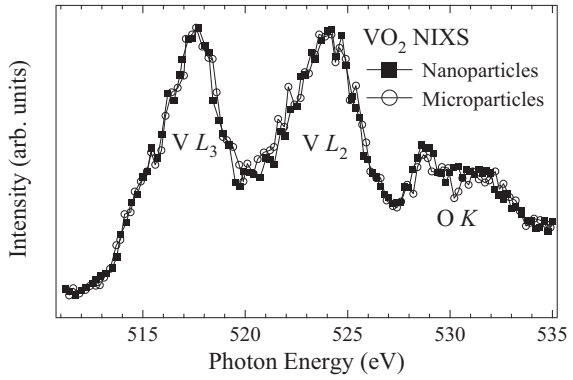

Fig. 1: NIXS spectra for VO_2 microparticles and nanoparticles.

The irradiation of x-ray over two hours turned black-colored VO_2 into orange-colored V_2O_5. Therefore, we moved the irradiation position of samples every 16 minutes in the NIXS measurements. Figure 1 shows NIXS spectra for the VO_2 microparticles and nanoparticles, corresponding to x-ray absorption spectra in V L_3, L_2 and O K regions. The difference between the spectra for the microparticles and nanoparticles is not clear due to not only poor S/N ratio but also poor resolution. Further experiments are needed for better S/N ratio and higher resolution.

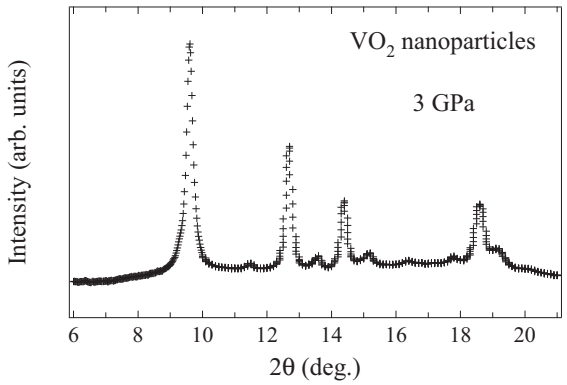

Fig. 2: XRD pattern for VO_2 nanoparticles under the pressure of ~3 GPa.

Figure 2 shows the low angle region of the XRD pattern for the VO_2 nanoparticles under the pressure of ~3 GPa. This is almost identical to the pattern under atmosphere pressure. Further experiments under higher pressure are needed for the observation of a new phase in VO_2 nanoparticles.

Reference

[1] E. Arcangeletti, L. Baldassarre, D. Di Castro, S. Lupi, L. Malavasi, C. Marini, A. Perucchi, and P. Postorino, Phys. Rev. Lett. **98**, 196406 (2007).