Crystallography

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Crystal structures and the oxygen deficiency of tetragonal and monoclinic zirconium oxide nanoparticles

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Introduction

Phase stability and particle size dependence in pure zirconium oxides have extensively been studied by numerous researchers. Recently, Tsunekawa *et al.* (2005) indicated that the valence of Zr ions in the zirconium oxide nanocrystallites decrease with decreasing particle size, suggesting the occurrence of oxygen deficiency δ in $ZrO_{2-\delta}$ ($0<\delta\leq1$), where the δ is the vacancy concentration. Although the nanocrystallites include both the tetragonal and monoclinic phases, the oxygen deficiency of each phase has not been directly determined yet. The purpose of the present work is to determine the oxygen deficiencies in the both tetragonal and monoclinic phases of a nanocrystalline sample from precise diffraction experiments. Furthermore we investigate the electron-density distribution of the nano-sized tetragonal $ZrO_{2-\delta}$. (Yashima & Tsunekawa, *Acta Crystallogr.*, **B61** (2005) 161-164).

Experiments

We performed synchrotron X-ray powder diffraction experiments of a zirconium oxide nanocrystalline sample using the multiple-detector system installed at the BL-$4B_2$ experimental station of the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. Powder diffraction data from the sample at 298 K in air were collected in asymmetric flat-specimen reflection geometry with a fixed incident angle of 7.0 deg. Scanning parameters were as follows: step interval of 0.010 deg., counting time of 4.5 s $step^{-1}$, and diffraction angle 2θ range from 8° to 140°. The crystal structures of the zirconium oxide nanocrystallites were refined by the Rietveld method with a computer program RIETAN-2000 (Izumi & Ikeda, 2000). Electron-density distribution of the tetragonal zirconium oxide nanocrystallites was investigated by a maximum-entropy method (MEM). The calculations were done using a computer program PRIMA.

Results and discussion

All the reflections were indexed with the tetragonal (Space group, $P4_2/nmc$) and monoclinic (Space group, $P2_1/c$) phases. In a preliminary Rietveld analysis, the occupancy factors of oxygen atoms in the tetragonal and monoclinic phases were refined independently. The occupancy factor of oxygen atoms of monoclinic phase was 1.12(4), thus it was fixed at 1.00 in the final refinement. This suggests that the monoclinic phase has no oxygen deficiency. Figure1(A) shows the refined crystal structure of the tetragonal phase. The occupancy factor of oxygen atom in the tetragonal phase was refined to be 0.984(4). This suggests that the tetragonal $ZrO_{2-\delta}$ has oxygen deficiency (δ=0.031(7)). Corresponding chemical formula of the tetragonal phase was $ZrO_{2-\delta}$ (δ=0.031(7)). On the contrary, the monoclinic phase did not have oxygen deficiency within the experimental error. The MEM electron-density map shown in Fig. 1(B) is consistent with the refined crystal structure of the tetragonal phase. The electrons are located at the positions of Zr and O atoms. No extra peaks are observed in the MEM electron-density map. The MEM density map also suggests the anisotropic distribution of the cation, which could be ascribed to the thermal motion or static disorder. There exist larger and smaller distributions of electron around the cation along the longer and shorter Zr-O bonds, respectively. The MEM density map in Fig. 1(C) indicates a covalent bonding between Zr and O atoms. The bond with shorter Zr-O length *r* has stronger bonding, while the bond with longer distance *R* has weaker bonding.

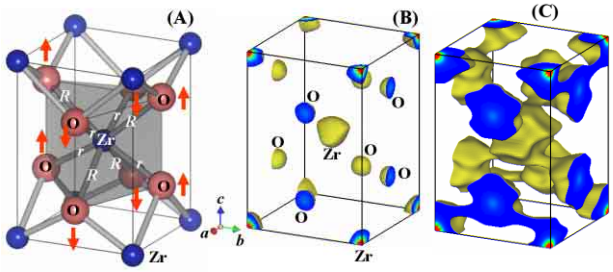

Fig. 1. (A) Refined crystal structure and equi-electron-density surfaces (B) at 10 and (C) at 1 $Å^{-3}$ of the tetragonal zirconium oxide nanoparticles. Two bond lengths between the cation and anion are *R* = 2.3562(6) Å and *r* = 2.0805(5) Å. Arrows stand for the displacements of oxygen atoms along the *c* axis (0.237(1) Å). Figures were drawn with the VENUS program made by Drs. R. A. Dilanian and F. Izumi.

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