

Growth of rectangular hollow tube crystals with rutile-type structure in supercritical fluids

K Niwa¹, H Ikegaya², T Taguchi², S Muto³, T Tokunaga² and M Hasegawa¹

¹ Department of Crystalline Materials Science, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

² Department of Materials Science and Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

³ EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan

E-mail: niwa@numse.nagoya-u.ac.jp

Abstract. Super critical fluids are well known as suitable solvents for dissolution and extraction processes, because it exhibits extreme high solubility and reactivity. However further experimental development using supercritical fluid would offer new insight in material science, especially the synthesis and crystal growth of novel materials. We report the successful growth of single crystals with the rutile-type structure (TiO₂, Co-doped TiO₂, SiO₂, GeO₂ and SnO₂) in supercritical fluids (water or oxygen) using a laser heated diamond-anvil cell up to a pressure of 7 GPa. The resultant product showed the rectangular hollow tube morphology, a several tens of microns in length and a wall thickness of less than 500 nm. TEM analyses demonstrated that this rectangular hollow tube single crystals were surrounded by the {110} faces and grown along the [001] direction. The preferential growth of {110} faces is consistent with the lowest surface energy of {110} faces of the rutile-type structure. In addition, the rapid cooling rate in LHDAC and high solubility of supercritical fluids also play an important role for the formation of the rectangular hollow tube. The details of the synthesis procedure, characterization and growth mechanism are discussed in this paper.

1. Introduction

High pressure technique is powerful tool for synthesizing novel materials and in the field of geophysics and solid state physics. New transition metal nitrides were successfully synthesized via direct chemical reaction between pure elements and molecular nitrogen under a few tens of gigapascals, [1,2]. It is unavoidable that the high-pressure synthesized sample is normally small and often this results in difficulties for detailed characterization. Thus, in order to extract basic information such as crystal structure, composition and morphology, it would be very useful to obtain a single crystal.

Recently, we succeeded in growing rectangular hollow tube single crystals of rutile-type GeO₂ and TiO₂ in supercritical fluids (oxygen or water) using laser-heated diamond anvil cell (LHDAC) [3,4]. These results show the importance and availability of using supercritical fluid as a solvent in the crystal growth under extreme conditions. Here, we have studied the crystal growth of SiO₂ and SnO₂ which also show the rutile-type structure under high pressure. Furthermore, we have applied this high-



pressure technique to grow doped crystals and succeeded in growing the rutile-type Co-doped TiO_2 . Many dioxides crystallize to the rutile-type structure, thus our results offer great promise for understanding the fundamental crystal growth mechanism under extreme conditions and applications of high pressure techniques to crystal growth experiments.

2. Experimental set-up

LHDAC was used for high-pressure crystal growth experiments. Polycrystalline sintered MO_2 ($M = \text{Si}$, Ge and Sn) was sandwiched by KClO_4 on both sides and loaded into the sample cavity of DAC together with ruby chips as pressure markers [5] (see figure 1(a)). The sample was compressed to the desired pressure at room temperature and an infrared laser (fiber laser; $\lambda = 1.07 \mu\text{m}$ or CO_2 laser; $\lambda = 10.6 \mu\text{m}$) irradiated the sample periods of ~ 1 sec. Pt powder was mixed with SiO_2 as a laser light absorber, because SiO_2 is transparent at infrared wavelengths. Just after laser irradiation ($T < 3000 \text{ K}$), the sample was rapidly cooled to room temperature by closing the laser shutter. In the experiments to grow Co-doped TiO_2 crystals, Co-Ti alloys were used as the precursor. The Co-Ti alloys with atomic ratio of $\text{Co/Ti} = 5/95$ and $50/50$ were prepared by arc melting method, then thin Co-Ti alloy foil was loaded in the sample hole together with distilled water and ruby chips (see figure 1(b)). After being compressed to the desired pressure at room temperature, infrared laser was irradiated to the sample as well as the experiments of SnO_2 , GeO_2 and SiO_2 . The products were recovered into ambient condition and examined by X-ray diffraction (XRD) measurements, scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX). Some samples were further examined by transmission electron microscope (TEM) equipped with electron energy-loss spectroscopy (EELS) and wavelength dispersive spectroscopy (WDS). We have made more than twenty runs in this study, some of them are shown here. Details of the experiments are described elsewhere [3,4].

3. Results and Discussion

3.1. Experiments of SiO_2 , GeO_2 and SnO_2

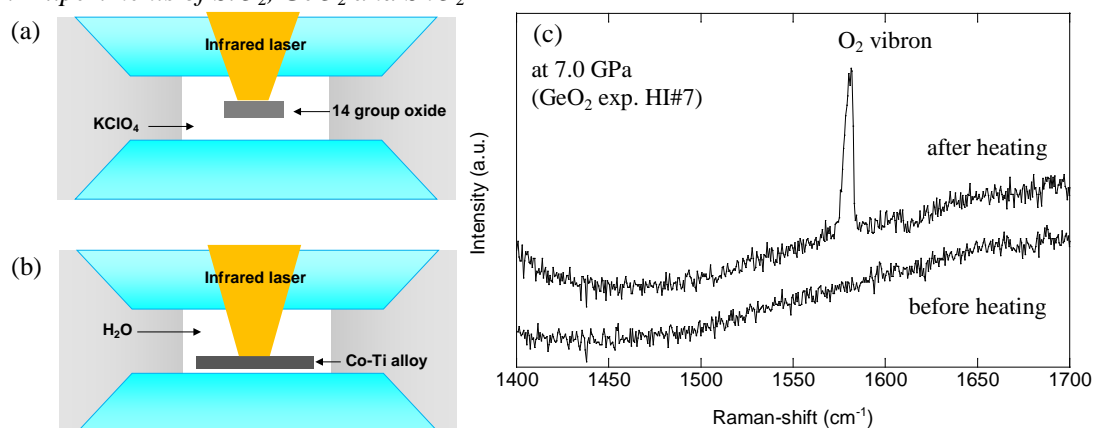


Figure 1. (a) and (b) Sample assemblies of DAC (c) Example of Raman spectra with respect to the frequency of O_2 vibron measured before and after laser heating at 7.0 GPa.

As clearly seen in figure 1(c) which corresponds to the Raman spectra of GeO_2 experiment, an intense Raman peak at 1580 cm^{-1} was observed after laser-heating at 7.0 GPa. This intense peak corresponds to the oxygen vibron [6] therefore, it was revealed that oxygen was produced via a decomposition reaction of KClO_4 when it is laser-heated at high pressures.

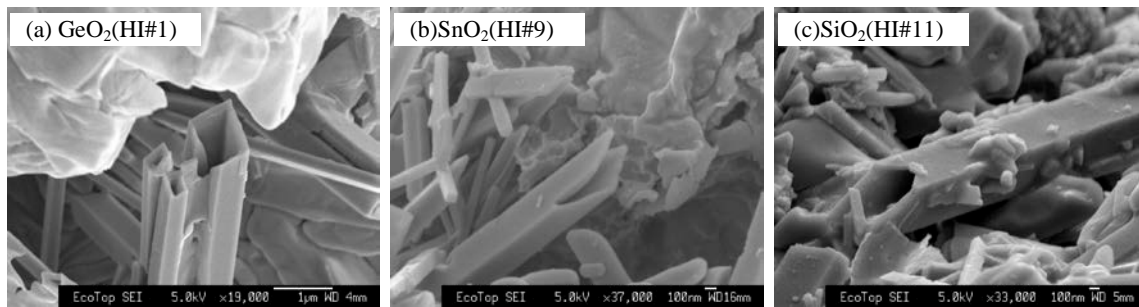


Figure 2. SEM images of recovered samples of (a)GeO₂, (b)SnO₂ and (c)SiO₂ experiments, respectively.

Figures 2(a)-(c) show the SEM images of run products corresponding to the experiments of GeO₂, SnO₂ and SiO₂, respectively. The rectangular hollow tube products with a few microns in length and a few hundreds nm in wall thickness were observed in KCl matrix. The texture and morphology of the recovered product were completely different from those of precursor (as-sintered oxides). The powder XRD patterns of the recovered samples demonstrated that the recovered products crystallized to the rutile-type structure and the lattice constants were consistent with the reported values [7,8]. Based on our previous characterization of the rectangular hollow tube rutile-type GeO₂ crystal by TEM/EDS [3], the rectangular hollow tube product was found to be a single crystals which were surrounded by the four equivalent {110} faces and elongated along the [001] direction. The crystal growth experiments of SiO₂ were difficult, because the rutile-type SiO₂ is stabilized at higher than ~10 GPa [9]. However, as a result of improvements of the experimental-set up such as selecting the laser source and modifying the sample assembly, we have succeeded in growing rectangular hollow tube crystals of the rutile-type SiO₂ at the pressure above 15 GPa, as well as the GeO₂ and SnO₂ crystals. Previous high pressure experiments by using Li₂WO₄ solution reported the growth of rectangular shaped rutile-type SiO₂ crystals and no hollow tube morphology [10]. To the best of our knowledge, this is the first report on the synthesis of rectangular hollow tube SiO₂ crystals by using LHDAC.

3.2. Experiments of doped oxides (Co-doped TiO₂)

Titanium dioxide (TiO₂) has been widely recognized as a remarkable photo-catalysis [11]. The catalytic power of TiO₂ strongly depends on the crystal structure, morphology and surface area etc., [12]. It has been reported that doping of other elements in TiO₂ induces novel magnetic or dielectric properties; e.g. TiO₂ with a few atomic percent of cobalt exhibited a ferromagnetic property with the high Curie temperature [13]. Therefore, it is important to investigate the effects of morphological changes on photo-catalytic and physical properties. In our previous studies, the rectangular hollow tube rutile-type TiO₂ crystals were successfully grown via direct chemical reaction between titanium metal and pure water at approximately 2 GPa [4]. We therefore, applied our crystal growth technique to develop the rectangular hollow tube shaped Co-doped rutile-type TiO₂. The experimental set-up was identical to that of our pure TiO₂ experiments [4], except the precursor. The XRD patterns of recovered run products demonstrated that the rutile-type phase, Co(OH)₂ and high pressure metal phase, were synthesized together with the residual alloy.

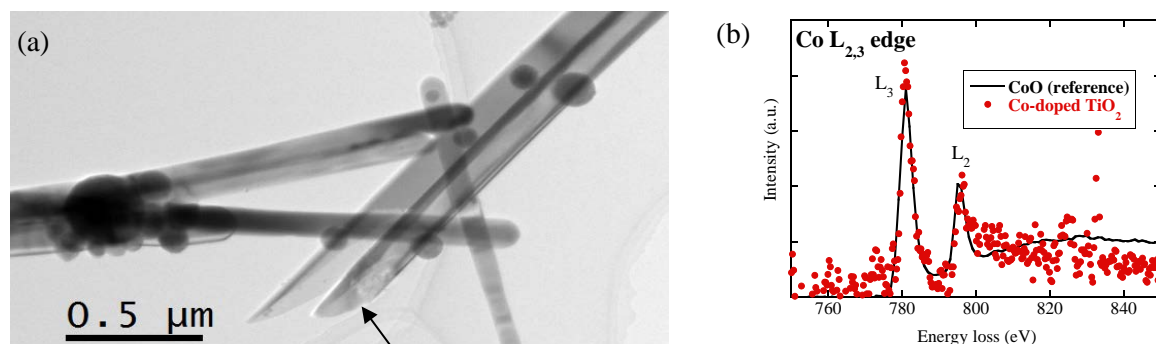


Figure 3. (a) TEM image and (b) EELS spectra of recovered sample and reference material of CoO in the energy loss range of Co-L edge.

Figure 3(a) shows a TEM image of the run product which was synthesized via chemical reaction between 50 atomic percent cobalt alloy and supercritical water at 2.9 GPa. It was found that many needle-like products existed in the matrix together with sphere shaped ones. Some of these needle-like shaped products are of rectangular hollow tube morphology. The existence of rectangular hollow tube product is consistent with our previous results on pure rutile-type TiO₂ [4]. These results indicate that these rectangular hollow tube crystals are of the rutile-type TiO₂. In order to evaluate the content of cobalt in the grown crystal, TEM-EELS and -WDS analyses were carried out on a single rectangular hollow tube crystal, indicated by the arrow in figure 3(a). The energy loss intensities with 781.65 and 797.25 eV are detected in the observed spectrum (see figure 3(b)). These peaks correspond to the Co-L₃ and L₂ white-line, respectively [14,15], which is consistent with those of a CoO reference. The WDS analyses were consistent with EELS. Therefore, Co²⁺ is likely to be stabilized in the rectangular hollow tube TiO₂ crystals. It seems difficult to evaluate the existence of Co³⁺, because of the low signal to noise ratio associated with the low cobalt content. Our chemical analyses demonstrated that the rectangular hollow tube TiO₂ crystal contained <1 atomic percent cobalt. This amount of cobalt is much lower than the initial atomic ratio of the starting alloy (50 atomic percent cobalt). Since the XRD pattern showed the existence of Co(OH)₂, little cobalt is likely to dissolve into TiO₂ and almost all of cobalt may react to form the Co(OH)₂, in case of using the present crystal growth technique under a few gigapascals.

3.3. Growth mechanism of rectangular hollow tube crystals

Present crystal growth experiments using LHDAC demonstrated that the rutile-type oxides were favored to form the rectangular hollow tube morphology. Previous studies also reported the successful growth of the rectangular hollow tube rutile-type SnO₂ crystals via thermal evaporation method [16]. No rectangular hollow tube crystals were obtained when we carried out the melting-solidification experiments of GeO₂ and SiO₂ in KCl as pressure medium. These experimental results strongly suggest that the rectangular hollow tube crystals are grown in non-equilibrium conditions such as extremely high solubility and rapid cooling rate.

The crystal growth mechanism of rutile-type compounds has been experimentally and theoretically investigated so far. The single crystal of rutile-type oxides which is grown in equilibrium condition normally shows the rectangular pillar morphology which has four equivalent {110} faces and elongated along the *c*-axis [17]. The largest surface area of {110} faces is consistent with their lowest surface energy as indicated by theoretical calculations [18,19]. In the non-equilibrium conditions mentioned above, the effects of surface energy become pronounced and so the low energy {110} faces are preferentially grown. This results in the growth of the rectangular hollow tube single crystals. The growth of rectangular hollow tube crystal is conceivable not only for the oxides but also for the other compounds which crystallize to the rutile-type structure. Further details of the growth mechanism are described in our previous studies [3,4].

4. Conclusion

We have succeeded in the growth of the rectangular hollow tube crystals of GeO₂, SnO₂ and SiO₂ in the wide pressure-temperature ranges by using LHDAC. The present results together with our previous studies indicate that the following factors are important for the crystal growth of rectangular hollow tube morphology; 1) Surface energy of rutile-type structure 2) High solubility of supercritical fluids 3) Very rapid cooling rate of LHDAC. In addition, the rectangular hollow tube less than 1 atomic percent Co-doped TiO₂ crystals have been also successfully grown at around 3 GPa. This means that the present crystal growth technique using LHDAC is applicable to the doped metal-oxides which have various kinds of interesting properties.

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