Preparation of Spherical Particles with Quartz Single Crystal

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Spherical particles with α-quartz single crystal were obtained from amorphous silica by heating in the atmospheric pressure. The silica particles containing a small amount of titanium oxide and calcium oxide were prepared from metal alkoxides and then were heated at 1000 °C in the atmospheric pressure. The resulting particle was determined to be a single crystal by means of a transmission electron microscopy and electron diffractometry.

Thermodynamically stable crystalline phases of silicon oxide at atmospheric pressure are quartz, cristobalite, and tridymite from low temperature.[1,2] Quartz single crystal has been widely applied for various electronic and optical devices such as an oscillator and wave guide because of the excellent property.[3–7] Industrial single crystal of quartz has been manufactured by the hydrothermal method at high temperature under high pressure.[6,7] By this method, a seed of single crystal of quartz is grown to an ingot so that it is difficult to form fibers, thin films, or particles.

Amorphous silica is obtained from the molten state or by the sol–gel process using tetraethylorthosilicate (TEOS). Amorphous silica is never crystallized to quartz by any heat treatment in the atmospheric pressure. If some metal oxides were contained in amorphous silica, it usually crystallizes to crystobalite by the heat treatment,[1] although some exceptional cases are known. For example, amorphous silica crystallized to quartz by heating in the LiCl–NaBr flux or by sintering with alkali metal oxides.[2,8] Furthermore, it is note worthy that amorphous silica containing a small amount of titanium oxide and alkaline earth metal oxide, which is prepared by using TEOS, titanium alkoxide, and alkaline earth metal alkoxides, is converted to quartz by the heat treatment in the atmospheric pressure.[9]

The crystallization behavior of amorphous silica prepared by the sol–gel process is interesting, as it crystallizes to quartz in the maintenance of the shape depending on the small amount of additives.[9] Amorphous silica as a quartz precursor is better to be prepared avoiding the molten state since the melt usually becomes to cristobalite or glass by cooling.[1] The sol–gel process is suitable for the preparation of the precursor because it is obtained from alcohol solution. Quartz crystallization of amorphous silica prepared by the sol–gel process has application potential for the formation of desired shapes such as monodispersed particles, thin films, and fibers. Quartz crystallization affected by the component and structure of the precursor, the heat treatment, and the nucleation were investigated.

Spherical particles were prepared by the Stöber method.[10] The solution containing 20.8 g of TEOS, 0.85 g of titanium tetrabutoxide (TBT), and 0.28 g of $CaCl_2$ in 50 cm^3 of methyl alcohol was added dropwise to the mixture of 0.8 dm^3 of methyl alcohol and 0.2 dm^3 of aqueous ammonia (25 wt %) by using a microtube pump (Iwaki Glass PST-103). During the addition, the mixture was stirred by using a magnetic stirrer. The adding speed of the solution was ca. 1 cm^3 min^{-1}. Particles were obtained by evaporating the disperse medium. These particles contain 3 components homogeneously and are abbreviated as Homo-3C. After adding the solution to the mixture of methyl alcohol and aqueous ammonia in the same way as described above, subsequently the solution containing 20.8 g TEOS in 20 cm^3 of methyl alcohol was added dropwise to the mixture. These resulting particles containing 3 components in the core and silica in the shell are abbreviated as Core-3C. Particles containing silica in the core and 3 components in the shell, abbreviated as Shell-3C, were prepared by adding TEOS and then the solution containing TEOS, TBT, and $CaCl_2$ to the methyl alcohol–ammonia water mixture.

The shape and average diameter of spherical particles were evaluated by a scanning electron microscopy (SEM; JEOL, JSM-5800LA). The crystallization behavior with the heat treatment was investigated by an X-ray diffractometer (XRD; Phillips, X-Pert Pro MPD). The morphology and crystallinity of particles were characterized by means of a transmission electron microscopy and electron diffractometry (TEM; JEOL, JEM-3000F). Particles for the TEM observation were dispersed in epoxy resin (Gatan; G2 Bond) and then were molded to a film. The film was polished to appear a hole by using a precision ion polishing system (Gatan; Model 691). The distribution of crystallized particles in the specimen was analyzed by comparison of the bright-field and dark-field images. The crystallinity of a particle was confirmed by a selected area electron diffractometry.

Homo-3C and Shell-3C were crystallized to α-quartz by the heat treatment at ca. 1000 °C for 1 h. However, heating at

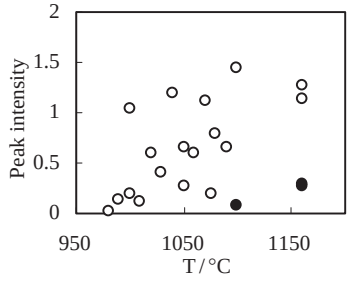

Figure 1. XRD peak height of heated particles vs. heating temperature. White and black circles indicate α-quartz and α-cristobalite, respectively. Peak intensities were based on peak heights of $CaCO_3$ added as the internal standard.

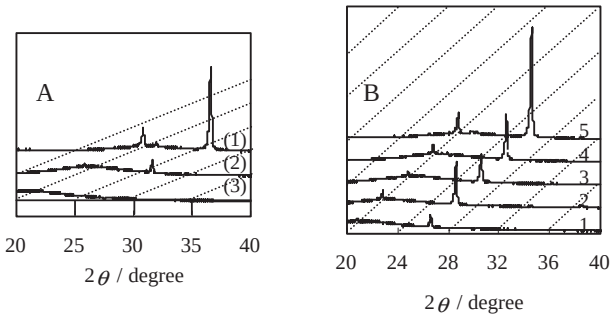

Figure 2. (A); XRD patterns of Homo-3C (1), Shell-3C (2), and Core-3C (3). The molar ratio of the 3 components is 100:2.5:2.5 for SiO_2:TiO_2:CaO. (B); XRD patterns of the Shell-3C after heat treatment for 1, 2, 3, 4, and 5 h described in the figure, respectively. All peaks are identified to α-quartz.

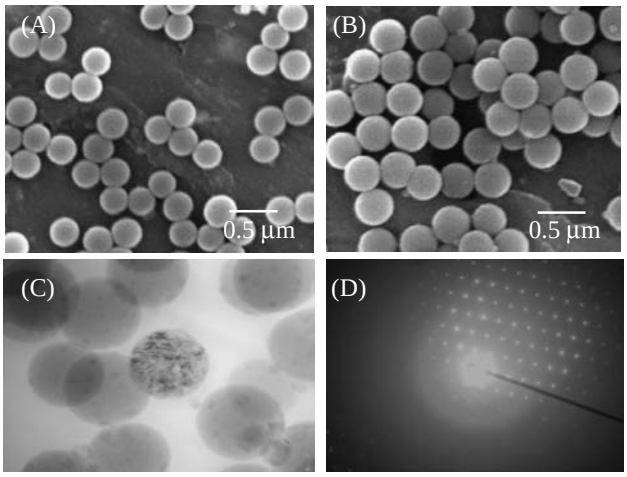

Figure 3. SEM images of silica particles (A) and Shell-3C (B). The photograph (C) is the bright-field image of TEM for Shell-3C after heat treatment of 1000 °C for 1 h. The crystallized particle is distinguished from amorphous particles. The photograph (D) is the electron diffraction pattern of the crystallized particle in the image (C).

temperature higher than 1100 °C, α-crystobalite coexisted with α-quartz (Figure 1). On the other hand, Core-3C was amorphous after the heat treatment (Figure 2a and Table 1). The XRD pattern of Shell-3C revealed weak peaks by the heat treatment as shown in Figure 2a. However, the crystallinity increased depending on the heating time (Figure 2b). These results suggest that the particle surface pays an important role in the crystallization by the heat treatment.

The shell layer of Shell-3C was confirmed by comparison of average particle before and after the coating procedure (Figures 3a and 3b). The thickness of the layer was estimated to be ca. 40 nm by the SEM images and this was in agreement with that based upon the amount of raw materials. According to the TEM image (Figure 3c), both amorphous and crystalline particles are observed. However, no particle in the course of crystallization in a particle was observed though it was expected. This result suggests that the nucleus grows at high speed after nucleation.

Table 1. Crystallinity of samples after heat treatment at 1000 °C for 1 h

Shape	Particle abbreviation	Crystallinity
	Homo-3C	quartz
	Shell-3C	quartz
	Core-3C	amorphous

Colorless and dark circles indicate silica and 3 components layer, respectively.

The crystallized particle in Figure 3c was determined to be a single crystal of α-quartz by the electron diffraction pattern (Figure 3d). The number of crystallized particles in TEM image increased apparently after being heated for 5 h as expected from XRD data.

The nucleus for quartz was estimated to be $CaTiO(SiO_4)$ because this was detected for samples containing SiO_2, TiO_2, and CaO in the molar ratio of 100:5:5. In conclusion, we succeeded in preparing spherical particles with α-quartz single crystal. Amorphous silica particles were prepared by the sol–gel process and then heated to crystallize at 1000 °C in the atmospheric pressure. This process may apply for the preparation of α-quartz single crystal with the shapes of fiber and film as well as particles.

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