

## 論文の内容の要旨

論文題目 超臨界水熱法の高度化に向けたナノ構造の計測および理論計算  
(Nanostructure measurements and theoretical calculation toward improvement of supercritical hydrothermal synthesis)

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### 1. Background

Nanometer-scale control over grain size is necessary for the realization and subsequent miniaturization of high-performance electronic devices. The use of nanoparticles enables the production of dense and thin sintered ceramics, which are expected to have applications in devices such as capacitors, sensors, fuel cells, and secondary cells. Nanoparticles can be obtained with a narrow size distribution using solution-based synthesis methods but not using conventional solid-state reaction methods. Various solution methods have recently been developed. Granulation methods strongly affect the particle size, morphology, and structure of materials, and the physical properties of materials synthesized using different methodologies differ, even if the same starting materials are used. Therefore, investigating synthetic methodology through a detailed characterization of the products is essential for the development of new nanomaterials.

Supercritical hydrothermal synthesis is a solution method that can be used to synthesize metal oxide nanoparticles with a narrow size distribution [1]. Nanoparticles can be obtained using supercritical water because of the acceleration of nucleation and the inhibition of ripening. High nucleation rates can be achieved through a high degree of supersaturation, and ripening can be suppressed via an extremely low solubility in supercritical water. A high degree of supersaturation can be obtained when the temperature of the water is increased rapidly from a normal temperature to a temperature above the critical temperature; the low kinetic viscosity of supercritical water enables rapid mixing of fluids with a continuous-flow reactor, which leads to a rapid increase in water temperature. Higher-crystallinity particles can be obtained compared to particles prepared via other solution methods because of the higher reaction temperature. The high crystallinity of the synthesized particles means that the calcination post-processing required for conventional solution methods can be simplified when supercritical hydrothermal methods are used to perform granulation.

A distinctive feature of supercritical hydrothermal synthesis is the rapid crystallization that occurs as a result of the high degree of supersaturation. Semi-stable-state or non-equilibrium-state materials can form during such rapid structural formation, and highly supersaturated conditions can affect structural and compositional factors other than the particle size. Structural analysis of nanoparticles formed in supercritical water and elucidation of the formation process of nanoparticles are necessary for further development of the technology. Particularly in the case of composite oxides, the nonstoichiometry and the deficient local structure become critical during the synthesis because different elements have different driving forces of crystallization as a consequence of their different solubility in water.

## 2. Method

All experiments were performed using a continuous-flow reactor. Starting solutions were simultaneously mixed with the base solution and heated distilled water using a cross-shaped component (SUS316; inner diameter: 1.3 mm). For *ex situ* experiments, the starting solution and base solution were introduced into the reactor at a flow rate of 10 g/min and heated distilled water was introduced at 80 g/min using a non-pulsation pump (NP-KX-500; Nihon Seimitsu Co., Ltd., Tokyo, Japan). The starting solution and the base solution were cooled just before the mixing point to prevent warming of the starting solutions via conductive heat transfer before mixing. The flow rates set a Reynolds number ( $Re$ ) of  $4 \times 10^4$  at the reactor, just after mixing. Kawasaki *et al.* investigated the relationship between particle size and  $Re$  and suggested that sufficient mixing was achieved at  $Re \geq 4 \times 10^4$ ; at these values, the mixing conditions did not affect the particle size because of kinetic control [2]. The temperature of the water was set at 400 °C, and the pressure was set at 30 MPa. The residence time was changed by the reactor volume from the mixing point to the point just before the cooling. After cooling, an HNO<sub>3</sub> solution was introduced using a flow rate of 5 g/min to reconcile the pH and thereby prevent the formation of carbonates in the recovered dispersion.

The recovered particles and filtrate were analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray absorption fine structure (XAFS). XAFS was conducted at beamline BL9C of the Photon Factory and beamline BL01B1 of SPring-8. *In situ* high-energy XRD for the continuous-flow reactor was conducted at beamline BL04B2 of SPring-8.

In addition to measurements, first-principles calculations based on density functional theory were performed to obtain structural information and to support the experimental data. Projector-augmented wave pseudopotentials were employed as implemented in the VASP code. The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof represented the exchange-correlation energy functional.

## 3. Results and Discussion

In chapter 3, supercritical hydrothermal synthesis of BaZrO<sub>3</sub> and its formation mechanism during the synthesis was investigated using a continuous-flow reactor. Monophasic, nanosized BaZrO<sub>3</sub> was successfully synthesized at a temperature and pressure of 400 °C and 30 MPa, respectively. The formation mechanism of BaZrO<sub>3</sub> was studied by examining the time dependence of size and composition using XRD, TEM, and inductively coupled plasma atomic emission spectroscopy (ICP). As a result of the time-resolved experiments, the following formation mechanism was revealed. At the first stage of the reaction (~0.1 s), a perovskite structure forms although it contains numerous Ba site defects. The particle size increases by coalescence during the middle stage (~1 s) and becomes constant at the last stage (1–10 s). Ba site defects are filled by the uptake of Ba with increasing time until the last stage (~10 s). Understanding this formation mechanism, i.e., the coalescence of nuclei and uptake of Ba, is necessary to enable the

development of a new methodology for controlling the size and composition of composite oxide nanoparticles.

In addition to the aforementioned *ex situ* experiments, *in situ* high-energy XRD measurements were conducted to elucidate the dynamics of barium zirconate ( $\text{BaZrO}_3$ ) nanoparticle formation in supercritical water. Time-resolved experiments with millisecond resolution were carried out using a continuous-flow reactor and high-energy XRD, which allows us to probe the sample in a stainless-steel tube. The size and structure of  $\text{BaZrO}_3$  in the early stage of crystallization under supercritical conditions (400 °C, 30 MPa) and on the order of milliseconds (46–66 ms) were successfully observed. An increase in the lattice parameter of  $\text{BaZrO}_3$  owing to a decrease in the number of defect sites in the time range was observed for the first time. As evident in Figure 1, first-principles calculation confirmed the relationship between Ba defects and the lattice parameter and supported the formation mechanism of  $\text{BaZrO}_3$  in which nuclei, consisting mainly of zirconium, absorb the barium ion in supercritical water during crystallization.

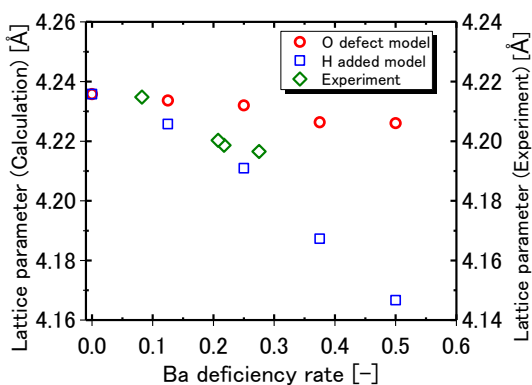


Figure 1 Lattice parameter of  $\text{BaZrO}_3$

In chapter 4, the formation of  $\text{Ba}_{1-x}\text{Sr}_x\text{ZrO}_3$  ( $0 \leq x \leq 1$ ) nanoparticles in supercritical water was discussed. B-site Zr in the perovskite structure is expected to play a dominant role in the nucleation stage because of the high nucleation rates associated with the substantially lower solubility of Zr compared to that of A-site ions (i.e., Zr precipitates faster, and A-site ions are taken up into the particle after the Zr nucleation). However, in this study, A-site Ba and Sr were observed to strongly influence the particle size, A-site deficiency rate, and surface–OH density of the nanoparticles. The differences in particle size suggested that the ripening or coalescence that occurred after the nucleation stage was dominant in determining the particle size, even under highly supersaturated conditions such as those in the supercritical hydrothermal synthesis. The unique nanostructure formed in the supercritical water was analyzed in detail; variables such as the A-site deficiency rate and the density of surface–OH groups were investigated. The existence of vacancies at the A-site was confirmed using XAFS, which revealed a highly defective structure, particularly in cases where the Ba content was high. The surface state of the nanoparticles was also studied using XPS and first-principles calculations, with the aim of understanding the differences in particle size and the effects of the A-site deficiencies; the amount of surface–OH groups corresponded to the A-site deficiency rate and exhibited an inverse relationship with the particle size.

In chapter 5, diffusion phenomena of A-site ions in A-site-deficient perovskite oxides were investigated by first-principles nudged elastic band calculations to elucidate the atomic behavior observed previously in supercritical hydrothermal synthesis. We found that the difference in diffusion models shows strongly influences the calculation results. Calculated diffusion barrier of barium atom in the bulk

barium deficient BaZrO<sub>3</sub> was as high as 3.409 eV, while the barrier of barium atom at the surface of barium deficient BaZrO<sub>3</sub> was determined to be 2.410 eV. By combining these results with thermal lattice expansion measurements via high-temperature XRD of BaZrO<sub>3</sub> nanoparticles synthesized in supercritical water, we demonstrated that lattice expansion could further lower the calculated energy barrier to 2.228 eV. For comparison, the diffusion barrier of Sr atoms in Sr-deficient SrZrO<sub>3</sub> was also studied and was determined to be 1.622 eV, which demonstrates that the diffusion of Sr atoms is much easier than that of Ba atoms. Our computation results support the A-site ion uptake phenomenon observed in the supercritical hydrothermal synthesis experiments and explains why BaZrO<sub>3</sub> has a much larger number of A-site vacancies than SrZrO<sub>3</sub>, as experimentally observed in the previous study.

In chapter 6, a characteristic nanostructure formed in supercritical water and surface state effects were discussed. The difference in nanostructure from the bulk structure was measured by XAFS. It was found that highly coordinated structure was maintained even at the nanoscale in the case of oxide nanoparticles synthesized in supercritical water. Structural stability in bulk and surface was investigated using XPS and high-temperature XRD. In the case of the surface structure of nanoparticles, cluster calculation was conducted using first-principles molecular dynamics simulation. Surface reconstruction was reproduced, and structural variance from the bulk structure was observed. The surface energy of the cluster after surface reconstruction was obtained, and different models of composite oxide were confirmed to possess different surface energies.

Particle-size variances, which have been observed in experiments involving supercritical hydrothermal synthesis was explained consistently using the surface energy of nanoparticles obtained in this study as showed in Figure 2. Furthermore, ion conductive property of the ceramics made of nanoparticles was evaluated, and improvement of device property by using nanoparticles was suggested.

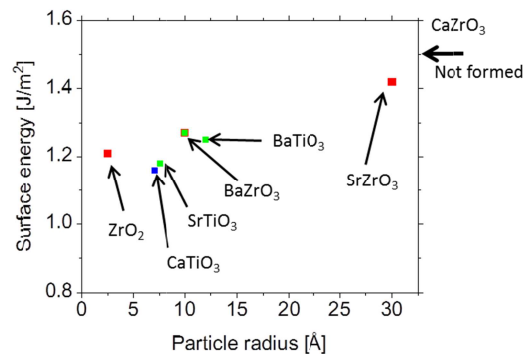


Figure 2 Surface energies and particle radius

#### 4. Conclusion

Highly supersaturated conditions provided by supercritical water was featured in this thesis. The formation of highly A-site-defective structure and the uptake of A-site ions were observed in the case of BaZrO<sub>3</sub>. This phenomenon was confirmed not only by *ex situ* experiments but also by *in situ* experiments. *In situ* measurements with millisecond time resolution were achieved for the first time. The A-site-deficient structure and A-site ion uptake were validated by various measurements and first-principles calculation. In addition, the formation of the A-site-deficient structure was found to play an important role in particle growth. First-principles calculation also indicated a surface state and surface energies of nanoparticles that can explain particle-size variances consistently.

References [1] T. Adschiri, *et al.*, J. Nanopart. Res., 2001, 3, 227–235. [2] S. I. Kawasaki, *et al.*, J. Supercrit. Fluids, 2010, 54, 96–102.