

Effect of water density on polymorph of BaTiO₃ nanoparticles synthesized under sub and supercritical water conditions

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Abstract

The effects of water density on polymorph of BaTiO₃ particles synthesized hydrothermally under sub and supercritical conditions have been studied. Experiments were performed within the temperature range of 300 to 420 °C and the pressure of 20 to 40 MPa using a flow reaction system. These conditions correspond to the water density of 0.15 to 0.70 g/cm³. Aqueous TiO₂ sols and Ba(OH)₂ solution were used as starting materials. Characterization of products was performed by powder X-ray diffraction, transmission electron microscopy and Raman spectroscopy. From the results, it has been found that the crystal phase of products depends not only on the temperature but also the pressure. The BaTiO₃ particles with tetragonal phase were obtained under the supercritical conditions, when the density of water was smaller than 0.5 g/cm³.

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1. Introduction

Barium titanate (BaTiO₃; BT) is widely used as electric ceramics materials. Fine particles or thin films of BT have been synthesized by sol–gel method [1–3], hydrothermal synthesis [4–15], and hydrothermal synthesis assisted by microwave process [16–18]. In the sol–gel route, non-crystalline BT precursors are made at first from titanium alkoxide and barium hydroxide by hydration, followed by heating at 800 °C to form BT particles or thin films. Those BT particles are usually polycrystalline or aggregates with an order of several micron meters. Hydrothermal synthesis is known to produce fine and crystalline metal oxide particles without post-heat treatment. Under highly basic conditions, BT particles can be obtained from Ba(OH)₂ and TiO₂ at a temperature of 80 to 230 °C by the hydrothermal treatment (e.g. [4,7]).

Although the BT particles produced by this method are larger than several 10 nm in diameter, the crystal phase is cubic, but does not have any ferroelectric property. Several researchers have reported the formation of cubic BT from the tetragonal one, due to the presence of the residual hydroxyl ions in the oxygen sublattice of BT [7,12]. The high temperature (1000 °C) is required to remove those residual hydroxyl ions.

In the previous studies we have described the hydrothermal synthesis electrode materials [19], phosphor [20], photocatalyst [21] and magnetic materials [22] of ultra fine particles under supercritical water. The advantage of hydrothermal synthesis in supercritical water is the ability to control the thermodynamic and transport properties of solvent (water), i.e. density and diffusivity, by changing the temperature and pressure. Especially, near the critical point of water (374 °C, 22.1 MPa), water density varied in a range of 0.1 to 0.5 g/cm³ continuously by changing temperatures and/or pressures. If hydrothermal reaction occurs under such a low water density condition, dehydration can be accelerated and so it is expected that the

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remained hydroxyl ions in the lattice of BT will reduce. Objective of this study is to reveal the effect of reaction temperature and pressure (i.e. water density) on crystal phase of BT via hydrothermal synthesis under supercritical water conditions.

2. Experiments

Titanium oxide sol (anatase: Ishihara Sangyo Kaisya, STS01) and barium hydroxide ($\text{Ba}(\text{OH})_2$: Wako Pure Chemical) were used as starting materials. Starting solutions were prepared by dissolving these materials into distilled water. Concentrations of titanium oxide sol solution and barium hydroxide were 0.1 M and 0.12 M, respectively.

Experiments were performed by a flow reaction phase. The detail procedure was described elsewhere [21]. The resultant particles were dried at 60 °C for 24 h. X-Ray diffraction method (XRD: RIGAKU model LINT 2000) and Raman spectroscopy (JASCO model NRS-2100) was used to study the crystal structure and phase. Morphologies and size of particles were observed by transmission electron microscopy (TEM: FEI; model TECNAI G20).

3. Results and discussion

In order to determine the appropriate solution condition for producing BT, we have conducted several preparatory experiments at temperature of 400 °C and 30 MPa of pressure. The Ba/Ti molar ratio was varied in range of 1 to 10 under various NaOH concentrations from 0.02 to 0.2 M. On our experimental conditions, BT was obtained from barium rich ($\text{Ba}/\text{Ti} > 1.2$) and basic ($\text{NaOH} > 0.1$ M). Therefore, we have fixed $\text{Ba}/\text{Ti} = 1.2$ in the starting solution for our entire study.

Table 1 shows experimental conditions discussed in this paper. As the volume of the reactor was fixed to 1.86 cm³, the reaction time was varied along with reaction temperature or pressure. We have confirmed that

Table 1
Experimental conditions and results

Temperature, °C	Pressure, MPa	Density of water, g/cm ³	Reaction time, s	Polymorph
300	30	0.751	5.11	Cubic BT
350	30	0.645	4.39	Cubic BT
380	30	0.588	4.00	Cubic BT
400	30	0.353	2.40	Tetragonal BT
420	30	0.203	1.38	Tetragonal BT
400	20	0.101	0.69	Tetragonal BT
400	25	0.166	1.13	Tetragonal BT
400	35	0.474	3.22	Tetragonal BT
400	40	0.524	3.56	Cubic BT

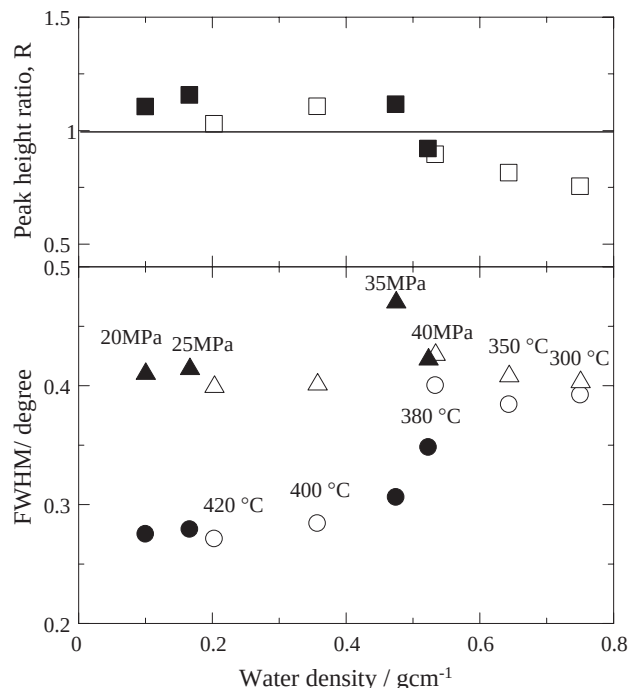


Fig. 1. Water density dependencies on the peak height ratio, R , and FWHM values of specific two peaks of the products. Symbols: Rectangles: FWHM_{200} (opened: 300 °C to 420 °C in 30 MPa, filled: 20 to 40 MPa at 400 °C), Circle: FWHM_{111} (opened, filled: same above), Square: R (opened, filled: same above).

there is no effect of the reaction time on BT polymorph focused in this study by other preparatory experiments.

The existence of cubic or tetragonal BT was confirmed by the presence of several doublets in the X-ray diffraction peaks, specific to the tetragonal BT. In the case of fine particles with several 10 nm in diameter, it is difficult to detect the doublet due to the peak broadening. So we evaluated the full widths at half maximum (FWHM) of two selected peaks, corresponding to a singlet (111) and doublet (200), (002) of the tetragonal BT. These FWHMs were named as FWHM_{111} and FWHM_{200} , respectively. When the FWHM_{200} was larger than the FWHM_{111} , the product was regarded as a tetragonal BaTiO_3 . The FWHM_{200} was thought to become larger than the FWHM_{111} , as there was a chance of overlapping between (200) and (002) doublet as a result of the phase transformation from cubic to tetragonal. In addition, we also evaluated the peak height ratio ($R = H_{111}/H_{200}$) of each peak. Compared to the standard peak pattern, the R value of cubic BT was smaller than 1, while that of tetragonal BT was greater than 1.

We have investigated the effects of the reaction temperature on the crystal phase by changing from 300 to 420 °C at the constant pressure of 30 MPa. According to XRD analyses, the product at 300 °C was the mixture of residual TiO_2 and BT. The samples obtained at 350 °C and above were single phase BaTiO_3 . In Fig. 1, both the R and the FWHMs of each peak of the products are plotted against the

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