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Structural refinement of nano $BaTiO_3$ powder using X-ray diffraction data

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Barium titanate ($BaTiO_3$) has been widely used in varios electronic applications such as multilayer capacitors, infrared detectors, thermistors, transducers and electro-optic devices. As the miniaturization of electronic devices increases, the effect of particle size on various properties has been become a very important factor to be considered. There have been many reports on the properties associated with particle size in the $BaTiO_3$ powders [1, 2].

When the primary particle size of $BaTiO_3$ is smaller than 1.0 μm, the dielectric constant markedly decreases due to the change of crystal system from tetragonal to cubic [3, 4]. In this way, the primary particle size has an important role in determining the properties of $BaTiO_3$. There is a critical primary particle size to transform from tetragonal to cubic phase at room temperature. The critical size depends on the synthesis method and varies from 25 to 200 nm [5]. It is necessary to determine the critical size for the various pareparation methods. A structural study of nano $BaTiO_3$ powders with around the critical size is essential to understand their properties at room temperature. However, the quantitative analysis about structural parameters such as lattice constants, atomic positions, and phase fraction, has not been carried out in sufficient detail. In this study, we described the structural refinement of nano $BaTiO_3$ powders using X-ray diffraction data.

The sample was prepared by the hydrothermal process using $TiCl_4$ and $Ba(OH)_2$ as precursors at 150 °C, and then washing, filtering and drying process were carried out. The primary particle size and shape of $BaTiO_3$ powders was observed by transmission electron microscopy (TEM). The X-ray diffraction data were measured at room temperature over scattering angle 15 °–130 ° at a 2θ step of 0.01° using Cu K_α radiations with graphite monochromator in reflection geometry. The General Structure Analysis System (GSAS) program was used to perform the structural refinement [6]. A pseudo-Voigt function was chosen as a profile function among profile ones in GSAS [7].

A TEM micrograph of $BaTiO_3$ powders is shown in Fig. 1. The primary particles of $BaTiO_3$ were well seperated. The overall shape of $BaTiO_3$ powders was nearly spherical. The average primary particle size was about 100 nm. It is well known that $BaTiO_3$ has four possible crystal structures, rhombohedral, orthorhomic, tetragonal and cubic, which depend on the transition temperature. Of them, the high temperature form is cubic and the stable crystal system at room temperature is tetragonal. However, as the particle size of $BaTiO_3$ decreases, the phase transformation depends not only on the temperature but also on the primary particle size. About the value of critical size occuring the phase transformation of $BaTiO_3$ at room temperature, it is very different from 25 to 200 nm and is dependent on the synthetic methods [5]. Uchino *et al.* observed that the powders prepared by hydrothermal method had the cubic phase at room temperature if the primary particle size was smaller than about 100 nm [8].

Consequently, we tried to perform the structural refinement of $BaTiO_3$ powders based on the cubic crystal system. In order to perform the structural refinement, a starting structural model that contains a reasonable approximation of the actual structure, is required. The starting structural model for the cubic crystal system was built with crystallographic data reported by Buttner *et al.* [9]. It was based on the Pm3m space group.

The zero-point shift was corrected by X-ray powder diffraction data of Si (640c:NIST) as a standard sample. It assumes that there is no defect for all atomic sites. The initial refinement was done by the unit-cell, the zero-point shift and background parameters. After a good match of peak positions was achieved, the peak profile parameters including the peak asymmetry were refined. The converged, weighted and profile R-factors, R_{wp} and R_p, were 9.24 and 6.99%, respectively. Also, the goodness-of-fit indicator, S $(=R_{wp}/R_e)$, was 1.74. The structural refinement patterns using X-ray powder diffraction data is shown in Fig. 2.

From the result of structural refinement based on the cubic phase, the synthesized $BaTiO_3$ powders might be completely composed of only cubic phase. However, if the size of particles is small enough to broaden the X-ray diffraction peaks, it is difficult to detect other phases except the cubic one in the synthesized $BaTiO_3$ powders due to the peak broadening. In addition, as shown in Fig. 1, there were particles above 100 nm size, although the number of such particles was small. These facts indicate that the tetragonal phase, which is stable at room temperature, may exist in the synthesized $BaTiO_3$ powders.

In order to confirm the possibility of the existence of tetragonal phase, we tried to do the structural refinement

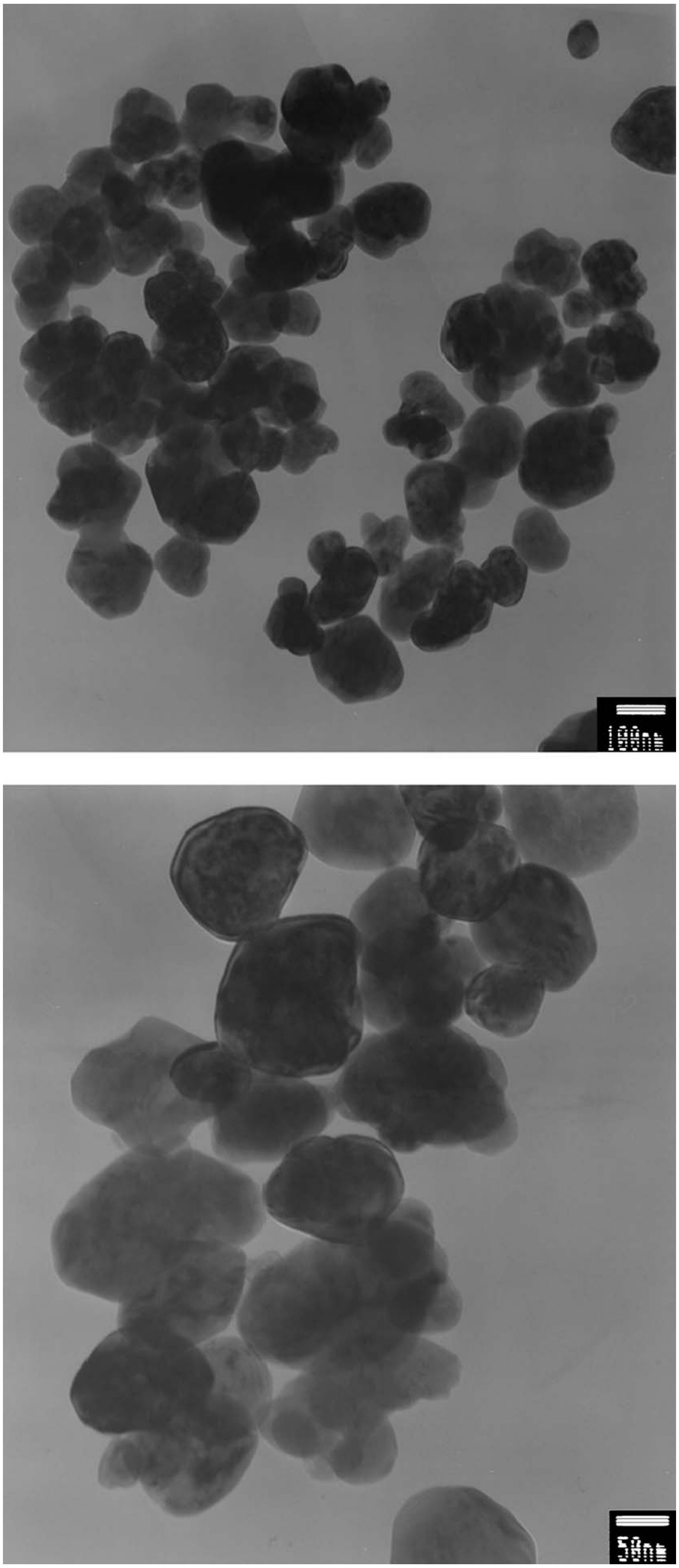

Figure 1 The transmission electron microscopy micrographs of $BaTiO_3$ powder synthesized by the hydrothermal processing.

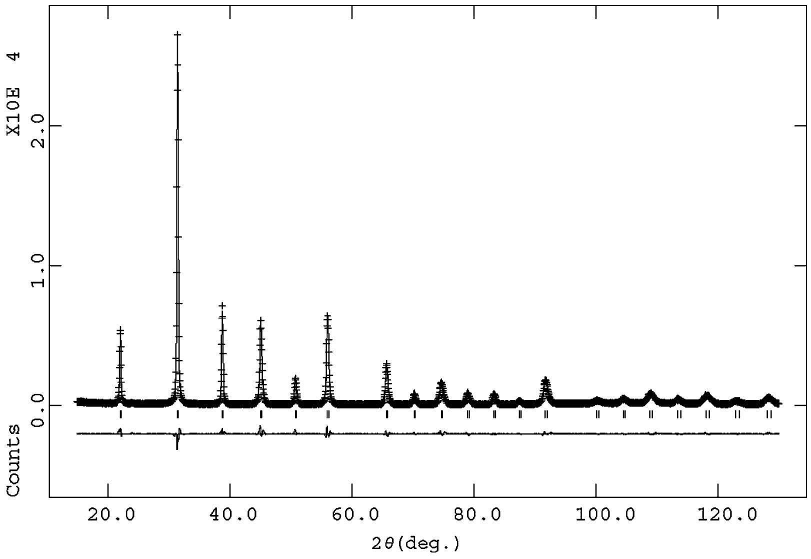

Figure 2 The structural refinement patterns of $BaTiO_3$ using X-ray powder diffraction data based on the cubic phase. Plus (+) marks represent the observed intensities, and the solid line is calculated ones. A difference (obs. – cal.) plot is shown beneath. Tick marks above the difference data indicate the reflection position.

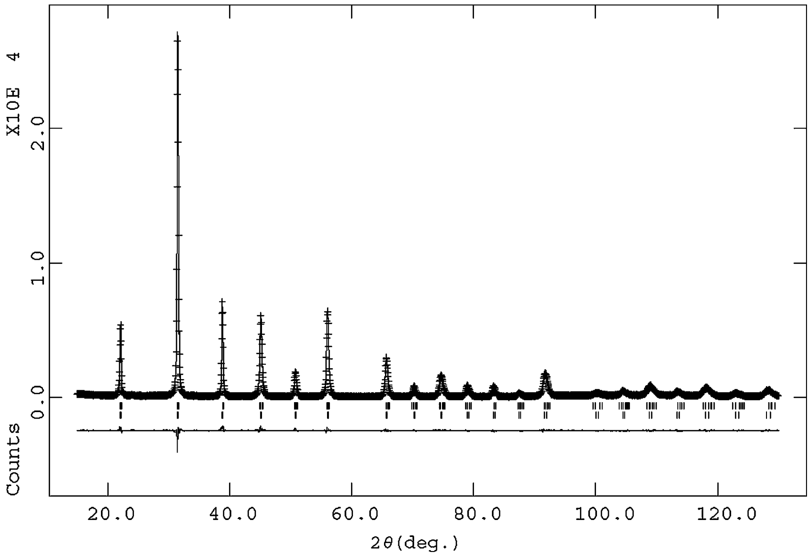

Figure 3 The structural refinement patterns of $BaTiO_3$ using X-ray powder diffraction data for a mixture of tetragonal and cubic phases. Plus (+) marks represent the observed intensities, and the solid line is calculated ones. A difference (obs. – cal.) plot is shown beneath. Tick marks above the difference data indicate the reflection position. The upper and lower tick marks above the difference data indicate the reflection position for tetragonal and cubic phases, respectively.

with the modified model which contains both tetragonal and cubic crystal systems. The crystallographic data for the tetragonal crystal system based on the P4*mm* was used [10].

The same structural refinement procedure was applied to the modified structural model. All R-factors for a mixture of cubic and tetragonal phases were lower than those for the only cubic model. Of R-factors, the final weighted R-factor, R_{wp}, was considerably decreased from 9.24 to 6.89%. The profile factor, R_{p}, was 4.93%. Also, the goodness-of-fit indicator, S $(= R_{\mathrm{wp}}/R_{\mathrm{e}})$, was decreased from 1.74 to 1.30. Fig. 3 and Table I show the structural refinement patterns of a mixture of cubic and tetragonal phases and the refined structural parameters, respectively. The mass fraction of cubic and tetragonal phases based on the refined scale factors for the two phases was 82.0 and 18.0%, respectively. The lattice parameters for each phase were a $(= b = c) = 4.0185(1)$ Å and a $(= b) = 4.0022(1)$ Å and $c = 4.0318(5)$ Å, respectively.

From the final weight R-factor and goodness-of-fit indicator for both models, it could be concluded that the two phases model was more suitable than the one phase as a model of $BaTiO_3$ with about 100 nm size at room temperature. Also, the structural refinement results suggest that the critical primary particle size of the hydrothermally synthesized $BaTiO_3$ powders, which can be transformed from tetragonal crystal system to cubic one at room temperature, may be around 100 nm. This approach may be useful to determine the structural parameters for the nano $BaTiO_3$ powders, such as mass fractions, lattice parameters, atomic coordinates and isotropic thermal parameters.

TABLE I Structural parameters for $BaTiO_3$ obtained from the structural refinement using X-ray powder diffraction data at room temperature

Atom	Site	x	y	z	g	$100 * U_{iso}/Å^2$
			Cubic phase			
Ba	1a	0.0	0.0	0.0	1.0	0.87(2)
Ti	1b	0.5	0.5	0.5	1.0	0.41(1)
O	3c	0.0	0.5	0.5	1.0	0.27(4)
			$a = b = c = 4.0185(1)$ Å			
			Tetragonal phase			
Ba	1a	0.0	0.0	0.0	1.0	0.20(3)
Ti	1b	0.5	0.5	0.537(2)	1.0	0.27(5)
O	1b	0.5	0.5	−0.037(4)	1.0	0.11(5)
O	2c	0.5	0.0	0.518(4)	1.0	0.68(7)
			$a = b = 4.0022(1)$ Å, $c = 4.0318(5)$ Å			
			Phase fraction			
	Cubic				Tetragonal	
	82%				18%	

The symbol, g, is the occupation factor. The numbers in parentheses are the estimated standard deviations of the last significant figure.

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