

Reinterpretation of the unit cell evolution of BaTiO₃

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Abstract

Reexamination of BaTiO₃ phase transitions by X-ray precession method has clarified that the crystal systems of the so-called three ferroelectric β -, γ - and δ -phases from high to low temperatures have crystal forms quite different from those obtained in the 1940s. In the γ -phase between 283 and 183 K, the crystal has a coherent hybrid structure composed of tetragonal and monoclinic forms sharing the tetragonal (101)_T lattice plane but it is different from another coherent hybrid structure in the room temperature β -phase which we have reported in a recent volume of Phys. Lett. A. In the δ -phase below 183 K, it reveals a tetragonal structure very close to a cubic system. The most notable aspect is that the orthogonal axes of the cubic unit cell of the α -phase are conserved in the form of tetragonal forms of all the phases. The unit cell evolution due to the phase transitions and the crystallographic relation are discussed.

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1. Introduction

Barium titanate (BaTiO₃) crystal is the typical ferroelectrics and has been most widely used as a functional material such as various kinds of transducers for more than half a century since the middle of the last century [1]. In these days, thin film and/or tiny single “crystal” are energetically studied in both fundamental and applied fields so that the commonly accepted data have been obtained using such small size of crystals less than 100 nm, which may lead to a conclusion of the nanoeffects [2]. Meanwhile some studies have been performed using the bulk crystals [3]. In the present Letter, it is aimed for the reexamination of structural phase transitions of the bulk BaTiO₃ single crystals studied in the 1940s.

BaTiO₃ is known to have four phases. They are conventionally called as “cubic”, “tetragonal”, “orthorhombic” and “rhombohedral” phases from high to low temperatures, undergoing

three phase transitions at approximately 403 K (T_1), 283 K (T_2) and 183 K (T_3). In the present Letter, however, we call them α -phase (P_α), β -phase (P_β), γ -phase (P_γ) and δ -phase (P_δ), respectively, by the reason of their notation.

In the latter half of the 1940s, many structural investigations have been made using X-ray and neutron diffractions in order to study the phase transition mechanism for the purpose of clarifying the origin of ferroelectricity [4–14]. Megaw [4–6] first engaged in the structural study of the phase transition at T_1 . According to her, the crystal has a cubic perovskite-type structure in P_α above T_1 and has a tetragonal structure in the room temperature phase P_β between T_1 and T_2 . Kay [7], Kay and Vousden [8] and Vousden [9] carried out the structural studies on the phase transitions below T_2 . According to them, it has an orthorhombic structure in the low temperature P_γ between T_2 and T_3 and has a rhombohedral structure in the lowest temperature P_δ below T_3 . These early crystal data, which were widely accepted, are summarized in Table 1.

On the other hand, Matthias and Hippel [11] took precession photographs of the crystal to investigate the origin of ferroelectricity and the domain formation mechanism. They pointed

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Table 1
Crystal data of BaTiO₃ of the four phases including the past data

Phase	T (K)	Crystal system	a (nm)	b (nm)	c (nm)	α (°)	β (°)	γ (°)	Z	c_T/a_T	V (nm ³)
Our previous X-ray data											
α^a	420	Cubic (C)	0.4010(10)						1		0.0645(4)
β^a	300	Tetragonal (T_β)	0.4009(10)		0.4048(10)				1	1.010	0.0651(5)
	300	Monoclinic (M_β)	0.4059(10)	0.4009(10)	0.5700(10)		135.33(10)		1		0.0652(4)
Present work											
γ	265	Tetragonal (T_γ)	0.4027(10)		0.3996(10)				1	0.992	0.0648(4)
	265	Monoclinic (M_γ)	0.3994(10)	0.4027(10)	0.5678(10)		134.77(10)		1		0.0648(7)
δ	90	Tetragonal (T_δ)	0.4011(10)		0.4008(10)				1	0.999	0.0645(4)
Representative earlier works											
$\alpha^{b,c}$	403	Cubic	0.4009						1		0.0640
$\beta^{b,c}$	293	Tetragonal	0.3994		0.4034				1	1.011	0.0643
γ^d	263	Orthorhombic	0.5682	0.5669	0.3990				2		0.1285
δ^e	105	Rhombohedral	0.4001			89.85			1		0.0640

^a Ref. [10]. ^{b,c} Refs. [4–6]. ^d Ref. [9]. ^e Ref. [14].

out that the $h_T 0 l_T$ tetragonal diffraction pattern of P_β is superposed on another composed of extra spots, which are not on a perfectly rectangular reciprocal lattice net but on a slightly oblique parallelepiped net. Both patterns, however, have common diffraction spots corresponding to the $\bar{h}_T 0 h_T$ tetragonal spots. Without analyzing such meaningful data, they simply interpreted it a twin plain, saying a direct lattice plane of which corresponded to these common spots. Rhodes [12,13] took X-ray oscillation photographs of the crystal in P_γ . He observed either single spots or double spots and in some case both having different intensities depending on samples. He stated that those patterns were possible to be explained if he assumed two crystal forms, i.e., a tetragonal and a monoclinic. Kay [7] took X-ray oscillation photographs at 90 K and concluded that BaTiO₃ had a tetragonal symmetry in P_δ . On the other hand, Jona and Pepinsky [14] took X-ray Weissenberg patterns of the crystal in P_δ and assumed a rhombohedral character. But they doubted their result, saying that a true symmetry of P_δ appeared to be lower, probably a monoclinic. Although all the researchers said that their results were not accurate having ambiguous points, those results have never been reexamined but were quite easily adopted to theoretical and experimental approaches [15–18].

Recently we succeeded in making precise simultaneous measurements of heat flux with the other physical properties such as the dielectric constant and the displacement current along the three cubic axes at each phase transition of BaTiO₃ crystals [19,20] and the ultrasonic resonance measurement at T_1 [21], using the “mK-stabilized cell” having the best temperature stability within ± 0.2 mK [22–24]. Samples used in these studies are from the same saucers as our previous X-ray diffraction study [10]. All the samples were grown by the top-seeded solution growth method. They were taken care neither to be affected by stress during the sample preparation nor to have any electric field applied on them before measurements. The heat flux measurements revealed that each phase transition is accompanied by complicated thermal anomalies. The most significant outcome of our study is finding two-step nature at the transition on cooling from P_α to P_β [19,20]. The result of the ultrasonic resonance passing through the transition point is correspondingly not so simple [21]. All the results strongly suggest there is a

possibility that BaTiO₃ single crystals have different structural series from those widely accepted hitherto so that they need to be reexamined by the better method looking three-dimensional reciprocal space exactly.

We started to make very precise X-ray diffraction studies by taking many precession photographs of BaTiO₃ single crystals. As for the crystal system of P_β , we reported very recently that BaTiO₃ single crystals reveal a notable feature [10]: different from the commonly accepted notion, BaTiO₃ changes its structure on cooling from the cubic to a coherent hybrid structure composed of tetragonal and monoclinic forms, having the tetragonal ($\bar{1}01$)_T lattice plane in common. Our crystal data of P_α and P_β are listed in Table 1.

Further reexamination of the two lower temperature phases, P_γ and P_δ , has followed. The crystals show excellent characteristic feature during the measurements with the rectangular cell axes being conserved fundamentally whenever the temperature is lowered from above T_1 to below T_3 and raised vice versa. Evolution and the crystallographic relation of the unit cell of all the phases will also be clarified in the later section. Throughout the Letter, cubic, tetragonal and monoclinic crystal systems are denoted respectively by suffixes C, T, and M of the Miller indices of X-ray diffraction and direct and/or reciprocal lattice vectors.

2. Experimental and results

BaTiO₃ crystals used in the present X-ray diffraction study are from the same saucers as our previous X-ray single crystal diffraction study [10] and the precise phase transition measurements [20]. They were cut in a nearly cubed shape with approximately 0.25 mm edge length. The sample crystals were either sealed inside thin-walled glass capillary tubes and/or fixed by epoxy resin on the top of a glass fiber having 0.2 mm diameter and mounted on a goniometer head. For the structural studies at lower temperatures below room temperature, the sample was cooled by a cold nitrogen gas flow-system. The sample temperature was kept within ± 0.5 K during the measurement.

X-ray diffraction patterns were taken by a precession camera (Enraf Nonius Company) combined with an imaging plate as a

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