

# Discovery of new phase and analysis of phase relationships in BaBiO<sub>3</sub> with thermal analyses

Makoto Yamaguchi, Fumikazu Takeuchi, Takuya Hashimoto\*

*Department of Integrated Sciences in Physics and Biology, College of Humanities and Sciences, Nihon University,  
3-8-1 Sakurajousui, Setagaya-ku, Tokyo 156-8550, Japan*

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## Abstract

Structural phase transition of BaBiO<sub>3</sub> was investigated by using thermal analyses such as dilatometry, differential scanning calorimetry (DSC) and quantitative differential thermal analysis (DTA). First order phase transition, corresponding to so far reported structural one from monoclinic- to rhombohedral-distorted perovskite, was detected at 160 °C both in thermal expansion and DSC for the first time. Two kinds of phase transitions were also detected for the first time at 520 and 620 °C with dilatometry and quantitative DTA, respectively. High-temperature X-ray diffraction measurement revealed that crystal structure more than 620 °C was face centered cubic perovskite with ordered arrangement of Bi<sup>3+</sup> and Bi<sup>5+</sup>. In 520–620 °C, X-ray diffraction peaks which indicated existence of superstructure were observed, which had been already proposed by electron diffraction measurement.

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**Keywords:** BaBiO<sub>3</sub>; Phase transition; Dilatometry; DSC; Quantitative DTA

## 1. Introduction

BaBiO<sub>3</sub> attracts much interest as a mother phase of superconducting oxides, such as BaPb<sub>1-x</sub>Bi<sub>x</sub>O<sub>3</sub> [1] and Ba<sub>1-x</sub>K<sub>x</sub>BiO<sub>3</sub> [2]. Since formal valence of Bi in BaBiO<sub>3</sub> is 4+, i.e., electronic configuration of Bi is 6s<sup>1</sup>, metallic conduction behavior could be expected. However, semiconducting electric conduction has been reported in BaBiO<sub>3</sub> [3–5]. It has been reported that this contradiction could be explained from a viewpoint of crystal structure. Cox and Sleight carried out neutron diffraction measurement and concluded that crystal structure of BaBiO<sub>3</sub> was monoclinic-distorted perovskite with two kinds of Bi site, i.e., “Bi<sup>3+</sup>” and “Bi<sup>5+</sup>” [6]. They attributed semiconducting temperature dependence of electrical conductivity to generation of energy gap due to this charge disproportion, so-called charge density wave (CDW).

Thus, it is concluded that crystal structure of BaBiO<sub>3</sub> affects electrical conduction behavior and that the electrical property might be controlled by variation of crystal structure. One of the probable methods to control the crystal structure is partial cation substitution. Hashimoto et al. insisted that CDW gap was collapsed and large amount of conduction electron was generated by structural variation from monoclinic to orthorhombic or cubic, containing single Bi site, with partial substitution of Pb for Bi or K for Ba site [5].

Another probable method for control of crystal structure is utilization of phase transition by temperature. However, variation of crystal structure of BaBiO<sub>3</sub> has not been understood enough. So far, temperature dependence of crystal structure of BaBiO<sub>3</sub> has been investigated by neutron diffraction measurement. Cox and Sleight reported that the crystal structure of BaBiO<sub>3</sub> changed from monoclinic distorted perovskite to rhombohedral one at about 130 °C and that the rhombohedral one varied to ideal cubic perovskite at about 470 °C [7]. However, their proposed cubic structure showed contradiction with semiconducting property of BaBiO<sub>3</sub> more

\* Corresponding author. Tel.: +81 3 3329 1151x5516;  
fax: +81 3 5317 9432.

E-mail address: [takuya@chs.nihon-u.ac.jp](mailto:takuya@chs.nihon-u.ac.jp) (T. Hashimoto).

than 470 °C. Pei et al. carried out neutron diffraction measurement with high sensitivity and concluded that crystal structure of BaBiO<sub>3</sub> more than 600 °C was cubic with alternative three-dimensional arrangements of large BiO<sub>6</sub> octahedron and small one, which resulted in as twice lattice constant as ideal cubic perovskite one [8]. Their proposed structure showed agreement with semiconducting electrical conduction behavior, however, phase transition temperature from monoclinic to cubic was not clarified.

For the measurement of phase transition temperature, thermal analyses such as dilatometry, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are more appropriate than diffraction measurement since they are carried out with continuous temperature variation. However, results of thermal analyses of BaBiO<sub>3</sub> have not been reported except DTA work by Cox and Sleight [7], in which DTA curve was not described.

In this study, we have succeeded in detection of three kinds of phase transition in BaBiO<sub>3</sub> at 160, 520 and 620 °C with thermal analyses for the first time. Each phase was analyzed by high-temperature X-ray diffraction measurement. In particular, it was revealed that crystal structure of BaBiO<sub>3</sub> between 520–620 °C was perovskite with superstructure, which had been also proposed by electron diffraction measurement [9].

## 2. Experimental

BaBiO<sub>3</sub> ceramic specimen was prepared by solid state reaction method. The nominal composition of powdery BaCO<sub>3</sub> (Furuuchi Kagaku, 99.9%) and Bi<sub>2</sub>O<sub>3</sub> (Furuuchi Kagaku, 99.9%) was mixed in ethanol with Al<sub>2</sub>O<sub>3</sub> mortar. The obtained mixture was calcined in air at 720 °C for 8 h followed by pressing into disc shape pellet. The disc was sintered at 800 °C for 18 h followed by cooling at a rate of 200 °C/h in air. The sample was confirmed to be a single phase monoclinic distorted perovskite with  $a = 6.188 \text{ \AA}$ ,  $b = 6.141 \text{ \AA}$ ,  $c = 8.675 \text{ \AA}$  and  $\beta = 90.16^\circ$  by X-ray diffraction measurement, showing agreement with preceding study [5]. The apparent sintering density calculated from weight and volume of the specimen was more than 90%.

Phase transition behavior in air was analyzed with dilatometry (Rigaku Co. Ltd.: TMA8310), DSC (Rigaku Co. Ltd.: DSC8230) and quantitative DTA (Rigaku Co. Ltd.: DSC8270). Dilatometry was carried out using the cylindrical specimen with 4 mm diameter and 15 mm height. SiO<sub>2</sub> was employed for material of reference, stage and push rod. The measurement was carried out both in heating and cooling procedure with rate of 10 °C/min at temperature range from 25–750 °C. DSC was performed at temperatures from 25 to 500 °C using 20 mg of powdery BaBiO<sub>3</sub> sealed in Al pan. Quantitative DTA was measured for 20 mg of powdery specimen set in Pt pan. The measurement temperature was 25–800 °C. In both measurements, Al<sub>2</sub>O<sub>3</sub> was employed as a reference and heating and cooling rate was 10 °C/min.

Crystal structures at various temperatures were estimated with high-temperature X-ray diffraction apparatus (Cu K $\alpha$ , 50 kV, 250 mA; Rigaku Co. Ltd.: RINT-2500). The measurement was performed both in heating and cooling procedure at temperature range of 30–750 °C.

## 3. Results and discussion

### 3.1. Thermal analyses of BaBiO<sub>3</sub>

Fig. 1 shows the results of thermal expansion, expansion coefficient calculated from the thermal expansion, quantitative DTA and DSC measured at heating procedure. At 160 °C, peak corresponding to abrupt increase of volume ( $\Delta V$ ) and endothermic one were observed in expansion coefficient and DSC, respectively. The temperature of these peaks showed agreement with so far reported structural phase transition from monoclinic-distorted to rhombohedral-distorted perovskite [7], which will be also reported in the next section. Variation of enthalpy,  $\Delta H$ , calculated from the peak area in DSC curve was about 25 J/mol, which was about one order smaller than that of similar structural phase transition of LaGaO<sub>3</sub> [10] or LaCrO<sub>3</sub> [11]. We suspect that the  $\Delta H$  is so small that the endothermic peak could not be detected by our quantitative DTA with lower sensitivity and that detection of the phase transition in BaBiO<sub>3</sub> with DSC or DTA measurement has not been reported so far.

In curves of expansion coefficient, base-line shift was observed at 520 °C. The shift indicates existence of second order phase transition. It was suspected that variation of specific heat,  $\Delta C_p$ , at 520 °C was too small to observe the transition in quantitative DTA.

Another phase transition was observed at 620 °C in quantitative DTA curve; however, anomaly was not detected in

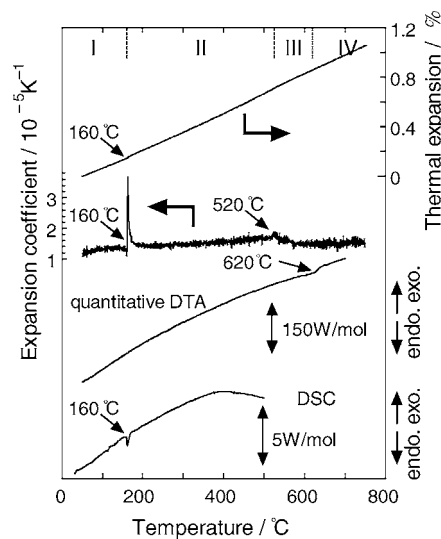


Fig. 1. Results of thermal analyses of BaBiO<sub>3</sub>. Phase transition temperature proposed in this study was depicted by dotted line on upper axis.

expansion coefficient at the temperature. This suggested that variation of expansion coefficient at 620 °C was less than  $1.0 \times 10^{-6} \text{ K}^{-1}$  that was detection limit of the dilatometry. The characteristics of the phase transition at 620 °C will be discussed in Section 3.3.

Thermal analyses carried out in this study indicated that there were four phases in BaBiO<sub>3</sub> denoted as I–IV in Fig. 1. So far, it has been reported that crystal system of BaBiO<sub>3</sub> changed from monoclinic to rhombohedral at 130 °C [7] and from rhombohedral to cubic at 470 °C [7] or 600 °C [8]. However, our results indicated existence of phase other than monoclinic, rhombohedral nor cubic one, depicted as III in Fig. 1. Analysis of crystal structure by high-temperature X-ray diffraction was carried out and the results were presented in the following section.

### 3.2. X-ray diffraction measurement of BaBiO<sub>3</sub> at high temperatures

In order to clarify the crystal structure of each phase in BaBiO<sub>3</sub>, X-ray diffraction patterns were measured at 30, 200, 600 and 700 °C in a series. After 1h interval since the temperature reached to the measurement level, the diffraction measurement was performed. Fig. 2 shows the results. In order to identify the crystal symmetry, not only diffraction patterns depicted in Fig. 2(c) but also splitting of the particular peaks shown in Fig. 2(a) and (b) were analyzed.

Triplet peaks and doublet ones were observed in  $2\theta$  range of 74–77° and 89–91° at 30 °C, respectively, suggesting that crystal structure of phase I was monoclinic. Monoclinic symmetry of phase I could be confirmed since all peaks in the diffraction pattern depicted in Fig. 2(c) could successfully indexed as monoclinic symmetry.

In the diffraction pattern of phase II, i.e. BaBiO<sub>3</sub> at 200 °C, doublet peaks was observed in  $2\theta$  range of 74–77°, however, peak splitting was not detected in  $2\theta$  range of 89–91°. This suggested rhombohedral symmetry, which was also confirmed from identification of all the diffraction peaks depicted

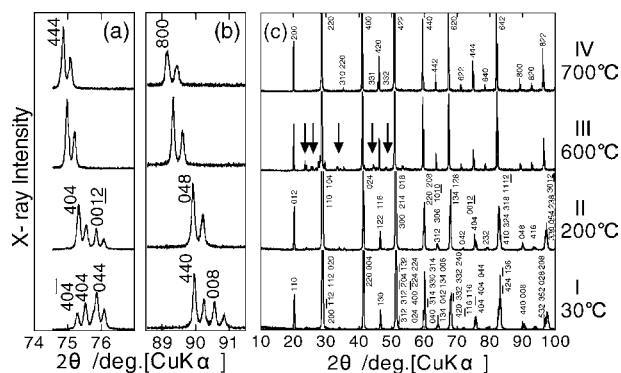


Fig. 2. X-ray diffraction peaks of BaBiO<sub>3</sub> at various temperatures in  $2\theta$  range of (a) 74–77° and (b) 89–91°. Whole diffraction patterns were shown in (c). Diffraction peaks and patterns were indexed as monoclinic, rhombohedral and cubic with  $a = 2a_p$  at 30, 600 and 700 °C, respectively. Arrows indicate diffraction peaks which could not be indexed as cubic symmetry.

in Fig. 2(c). These observed crystal symmetry agreed well with preceding studies [7,8].

At 700 °C, where phase IV was stable, peak splitting was not observed neither in 74° <  $2\theta$  < 77° nor 89° <  $2\theta$  < 91° and all the diffraction peaks could be indexed as cubic with lattice constant of  $2a_p$ , where  $a_p$  was lattice constant of ideal cubic perovskite, indicating that crystal symmetry of phase IV was cubic as Pei et al. reported [8]. At 600 °C, single peak was detected in  $2\theta$  range of both 74–77° and 89–91°, however, diffraction peaks which could not be identified by cubic symmetry was observed as arrows in Fig. 2(c). It can be concluded that the crystal symmetry of BaBiO<sub>3</sub> at 600 °C differ from that at 700 °C, showing agreement with the result of thermal analyses.

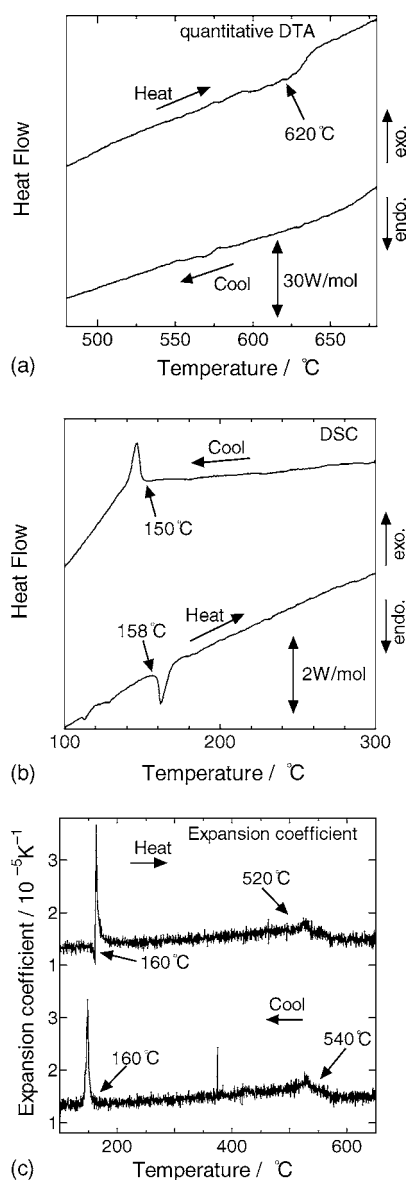


Fig. 3. Results of (a) quantitative DTA, (b) DSC and (c) expansion coefficient of BaBiO<sub>3</sub> at heating and cooling procedure. Temperature scanning rate was 10 °C/min.

### 3.3. Characteristics of phase III—new phase in BaBiO<sub>3</sub>

Fig. 3 shows the results of (a) quantitative DTA, (b) DSC and (c) expansion coefficient measured at both heating and cooling procedure. It was confirmed that phase transition between monoclinic phase (phase I) and rhombohedral one (phase II) was reversible at scanning rate of 10 °C/min since both DSC signal and peak of expansion coefficient at about 160 °C were observed in both heating and cooling procedure. Phase transition between III and IV was irreversible at a rate of 10 °C/min since signal at 620 °C observed in quantitative DTA at heating procedure disappeared at cooling process. This suggested that transition from phase III to phase IV was first order and that phase III could not be generated during this cooling process. Therefore, variation of expansion coefficient at 540 °C during cooling procedure could be identified as transition from phase IV to phase II, whereas that at 520 °C during heating procedure as transition from phase II to phase III.

Fig. 4(a) shows X-ray diffraction patterns of BaBiO<sub>3</sub> at various temperatures. At first, X-ray diffraction measurement was performed at 750 °C and phase IV was confirmed. Then temperature was decreased to 550 °C. After 1 h interval, diffraction pattern was recorded and peaks corresponding to the phase III were observed. Similarly, X-ray diffraction measurement was carried out at 200 and 30 °C. From X-ray diffraction patterns thus obtained, it was revealed that phase III existed even at 200 and 30 °C, indicating that phase III did not decompose at temperatures lower than 200 °C. Phase III transformed to phase IV at 750 °C as Fig. 4(b) shows. From the discussion on quantitative DTA depicted in Fig. 3(a), it was suspected that phase III could not generate at cooling rate of 10 °C/min. Fig. 4(b) shows the X-ray diffraction patterns of BaBiO<sub>3</sub> at 200 and 30 °C. The measured sample was cooled from 750 °C at a cooling rate of 10 °C/min. No peak corresponding to phase III was observed, showing correspondence with quantitative DTA shown in Fig. 3(a).

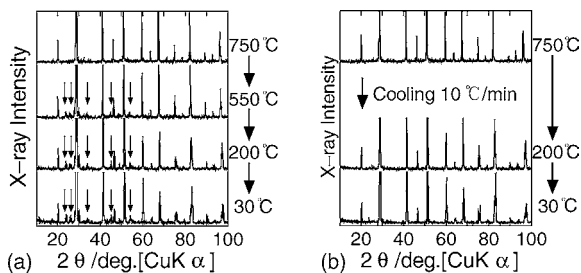


Fig. 4. (a) High-temperature X-ray diffraction patterns at cooling procedure. Prior to diffraction measurement, the sample was kept at the measurement temperatures for 1 h. (b) High-temperature X-ray diffraction patterns at cooling procedure. The specimen at 30 °C depicted in (a) was heated at 750 °C and the diffraction measurement was carried out. After the measurement, the temperature was decreased to 200 °C at cooling rate of 10 °C/min, then diffraction pattern was obtained. Similarly, diffraction pattern at 30 °C was measured. The peaks indicating existence of phase III was only observed in diffraction patterns depicted in (a).

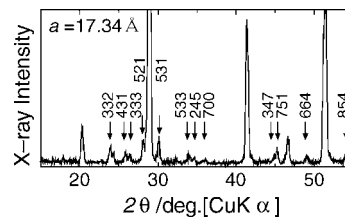


Fig. 5. X-ray diffraction patterns of BaBiO<sub>3</sub> at 30 °C depicted in Fig. 4(a). The peaks represented by arrows could be indexed assuming superstructure with  $a \sim 4a_p$  ( $\sim 17.34$  Å).

It was concluded that phase III has not been reported so far although it could be remained to room temperature since slow cooling, which was not employed for ordinary preparation process, was necessary to remain phase III to room temperature. Chaillout and Remeika reported that BaBiO<sub>3</sub> with  $\sim 4a_p$  (17.34 Å) superstructure was occasionally observed by electron diffraction [9]. Fig. 5 shows X-ray diffraction pattern depicted in Fig. 4(a) at 30 °C. Peaks indicated by arrows in Fig. 4(a) could be indexed assuming superstructure with  $\sim 4a_p$ . Therefore, we suspect that phase III is cubic perovskite with some superstructure as was already reported by electron diffraction [9].

## 4. Conclusion

Thermal analyses revealed that there are three kinds of phase transition in BaBiO<sub>3</sub>. First order structural phase transition with  $\Delta H$  of about 25 J/mol was observed at 160 °C. The second order one and another first order one were observed at 520 and 620 °C, respectively. At 160 °C, monoclinic-distorted perovskite structure varied to rhombohedral-distorted one. At more than 620 °C, diffraction pattern of BaBiO<sub>3</sub> could be explained as cubic with lattice constant of  $2a_p$ . The crystal system of BaBiO<sub>3</sub> at 520–620 °C was regarded as cubic with some superstructures. This phase could be remained to room temperature by slow cooling during the temperature between 520 and 620 °C.

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