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THERMOANALYTICAL INVESTIGATION OF THE PHASE RELATION IN $BaBiO_{3-x}$

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ABSTRACT

The phase relation in $BaBiO_{3-x}$ has been studied at temperatures between 850 and 1225 K and at oxygen partial pressures from 1.85×10^1 to 1.01×10^5 Pa by thermogravimetric (TG) measurements and differential thermal analysis (DTA). Three phases, I, II and III, exist in the region of $0 \leqq x < 0.5$. Phase I is observed in the region of $0 \leqq x \leqq 0.05$. Phase II extends widely from $x = 0.085$ to $x = 0.328$ at 1100 K, and the homogeneous range becomes narrower with decreasing temperature. Phase III lies in the range $0.426 \leqq x < 0.5$. The DTA curves show the thermal anomaly due to the I–II phase transition. In the phase relation obtained by TG measurements, however, the phase transition is not, apparently, recognized above the oxygen partial pressure of 2.30×10^4 Pa.

INTRODUCTION

The valence of bismuth in $BaBiO_3$ with the perovskite structure has been in considerable argument. Nakamura et al. [1] have made ESR, magnetic susceptibility and electric resistivity measurements. They have concluded either that the valence is represented as $BaBi^{3+}_{0.5}Bi^{5+}_{0.5}O_3$ or that there is a filled Bi^{4+} band. In order to solve the problem, $BaBiO_3$ has been subjected to examinations of dielectric constant [2], IR spectra [3], X-ray photoelectron spectra [4] and crystal structure [5–7]. Although the examination of IR spectra [3] supports the state of Bi^{4+}–O^{2-}–Bi^{4+}, the other studies [2,4–7] provide the possibility of Bi^{3+}–O^{2-}–Bi^{5+}.

Since the finding of superconductivity in the $BaPbO_3$–$BaBiO_3$ system [8], much attention has been focused on the oxidation state of bismuth which may affect the conduction behavior [9]. The oxidation state is related to the deficiency of oxygen. Cox and Sleight [7] have reported that $BaBiO_3$ exhibits a reversible mass change above 925 K in air by thermogravimetry (TG). The phase relation in $BaBiO_{3-x}$ $(0 \leqq x < 0.5)$ has been first presented by Beyerlein et al. [10]. They found three nonstoichiometric phases by TG measurements. At the oxygen partial pressure (P_{O_2}) of 3.2×10^2 Pa, for

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example, phase I exists in the range $0 \leqq x \leqq 0.03$, phase II in the range $0.13 \leqq x \leqq 0.27$ and phase III in the range $0.42 \leqq x \leqq 0.45$. In their results, however, several points lie even in the two-phase regions, which is not acceptable in a thermodynamic equilibrium state. The nonstoichiometric range of phase II becomes narrower with decreasing temperature and is expected to form the line phase at $x = 0.19$. Chaillout and Remeika [11] have also reported the results of TG measurements, X-ray diffraction and electron diffraction. They have proposed that there exist other phases, $BaBiO_{2.97}$ and $BaBiO_{2.77}$, and that oxygen vacancies give rise to a superstructure in both phases. There are several discrepancies between the two studies mentioned above, and further studies are required to establish the phase relation in $BaBiO_{3-x}$.

In the present study, the phase relation in $BaBiO_{3-x}$ was examined by means of TG measurements and differential thermal analysis (DTA) at controlled oxygen partial pressures.

EXPERIMENTAL

Barium nitrate (99.9%, Wako Pure Chemical Industries Ltd.) and bismuth sesquioxide (99.99%, Rare Metallic Co., Ltd.) were mixed in the stoichiometric ratio of 2 : 1 and then pressed into a tablet (diameter, 20 mm; thickness, 10 mm) at 90 MPa. The tablet was heated in a platinum crucible at 860 K for 140 ks in air, and then melted at 1370 K for the complete formation of $BaBiO_{3-x}$. In order to obtain the fully oxidized sample ($x = 0$), it was annealed at 1000 K for 72 ks in air. The sample thus prepared exhibited a golden luster. The mass percentages of Ba and Bi in the specimen were determined, by a gravimetric method, as 34.83% and 53.05%, respectively, which were compared favorably with the calculated values of 34.83% and 53.00%. The X-ray powder pattern indicated a single phase with the perovskite structure.

The experimental setup for the TG measurements is shown in Fig. 1. The sample, of about 0.95 g, was accurately weighed in a platinum basket (9) and suspended from the thermobalance (5) (Sinku-Riko Inc., TGD-1500-2CH-S). The oxygen partial pressure is controlled by mixing Ar and O_2 for $P_{O_2} \geqq 2.0 \times 10^3$ Pa and Ar and Ar + O_2 (99 : 1) for $P_{O_2} \leqq 1.0 \times 10^3$ Pa, employing a gas mixer (2) connected to gas cylinders (1). The flow rate of the mixed gas is approximately 2.0×10^{-6} m^3 s^{-1}. The oxygen partial pressure in the mixed gas is monitored by oxygen sensors of calcia-stabilized zirconia (CSZ) (4) at the gas inlet and outlet of the thermobalance. Furthermore, the value of P_{O_2} is determined in situ by a small oxygen sensor of yttria-stabilized zirconia (YSZ) (7) placed near the sample. The Fe–FeO coexisting mixture is sealed in the YSZ sensor as a reference.

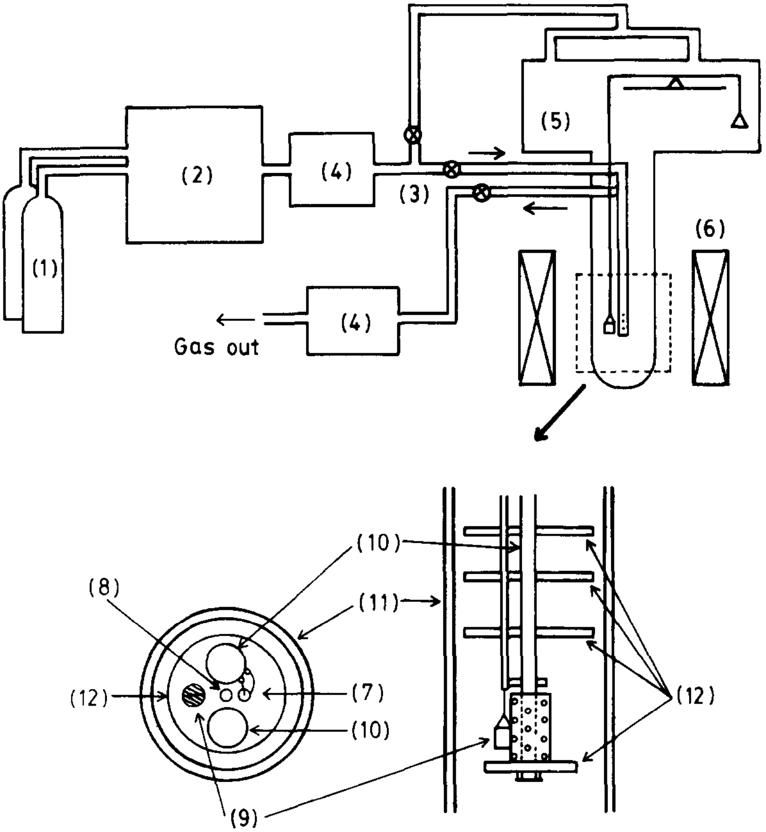

Fig. 1. Schematic diagram of the thermobalance: (1) gas cylinder, (2) gas mixer, (3) valve, (4) ZrO_2 oxygen sensor, (5) thermobalance, (6) furnace, (7) ZrO_2 oxygen sensor with Fe–FeO coexisting mixture as reference, (8) thermocouple R, (9) platinum basket, (10) alumina gas flow tube, (11) alumina tube, (12) alumina plate.

The measurements were made at temperatures of 850–1250 K and oxygen partial pressures of 1.85×10^1–1.01×10^5 Pa. The temperature was controlled within ± 1.0 K.

The nonstoichiometry, x, was determined from mass change using the following relation:

$$x = \frac{M_{BaBiO_3}}{M_O}\left(1 - \frac{m}{m\,*}\right) \tag{1}$$

where M_i is the molar mass of the species i, m the mass of the sample and m * the initial mass at 1000 K in air ($x = 0$).

The DTA experiments were carried out at various oxygen partial pressures by using a commercially available apparatus (Rigaku Denki Co. Ltd., M8075). The heating or cooling rate was 0.17 K s^{-1}. The oxygen partial pressure was determined by a CSZ oxygen sensor placed at the gas inlet of the apparatus. The gas flow rate was 1.67×10^{-6} m^3 s^{-1}.

RESULTS AND DISCUSSION

Figure 2 shows the phase relation in $BaBiO_{3-x}$ obtained in the present investigation. Along each isobar the value of x increases as the temperature increases. Above the oxygen partial pressure of 3.4×10^4 Pa, the value of x increases continuously with increasing temperature. The isobars at the oxygen partial pressures between 2.1×10^4 and 8.19×10^3 Pa have a horizontal portion suggesting the existence of a two-phase region. At the oxygen partial pressures below 3.4×10^3 Pa, two horizontal portions are observed in each isobar. This result indicates that there are three distinct phases in the region of x less than 0.5.

The time required for achievement of the equilibrium state depended on temperature and oxygen partial pressure. The time became longer with decreasing temperature and oxygen partial pressure. It took about 200 ks at

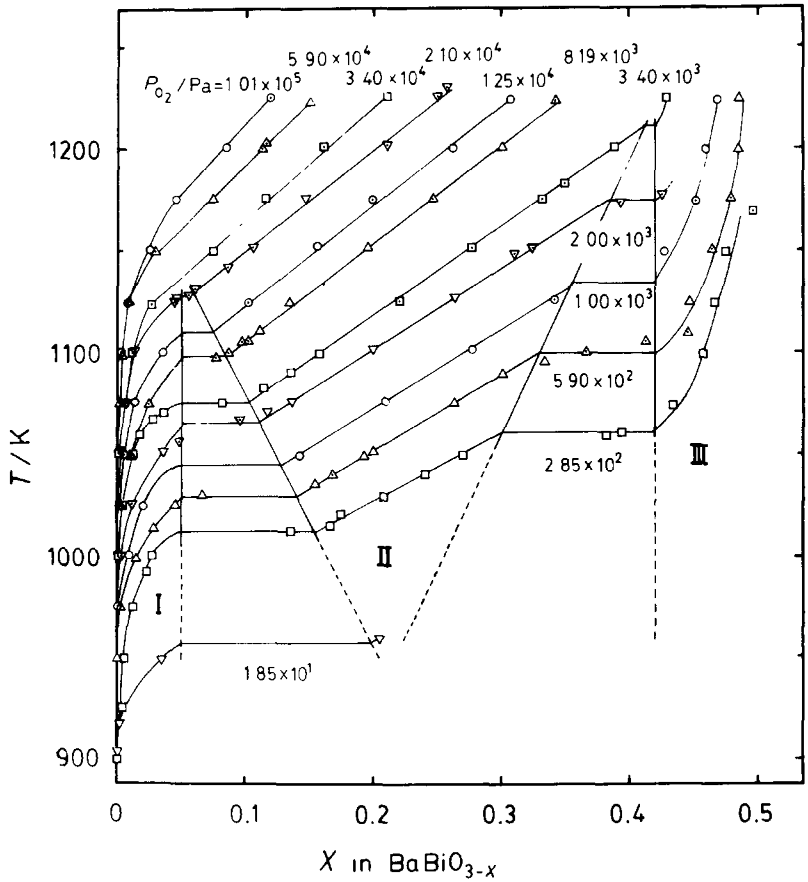

Fig. 2. Phase relation in $BaBiO_{3-x}$ obtained by TG measurements.

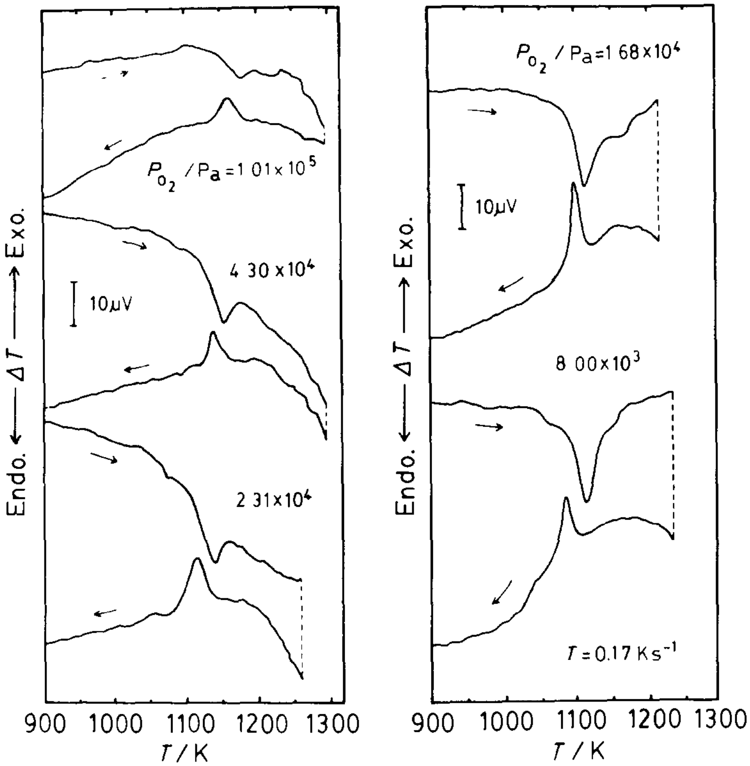

Fig. 3. DTA curves of $BaBiO_{3-x}$ at a heating (cooling) rate of 0.17 K s^{-1} at various oxygen partial pressures.

1060 K and $P_{O_2} = 2.85 \times 10^2$ Pa, while the equilibrium was attained within a few minutes at 1200 K and $P_{O_2} = 2.1 \times 10^4$ Pa. Several experimental points exist in the two-phase regions, which is not thermodynamically acceptable. This fact is attributed to the extremely slow reaction rate which provides undetectable mass changes even after rather long periods.

The three phases are denoted by I, II and III, according to Beyerlein et al. [10]. On the whole, the similarity is recognized between the result in the present study and that reported by Beyerlein et al. [10]. However, there are several discrepancies. The phase boundary of phase I exists at $x = 0.05$ in the present study, contrary to the value of $x = 0.03$ obtained by Beyerlein et al. [10]. In their result [10], the nonstoichiometric region of phase II becomes narrower with lowering temperature and converges on the line phase at $x = 0.19$. Chaillout and Remeika [11] have reported that a distinct phase exists at $x = 0.23$. The present result, however, suggests that the value of x is larger than 0.21.

Figure 3 presents DTA curves at various oxygen partial pressures. Endothermic peaks on heating and exothermic peaks on cooling are observed at

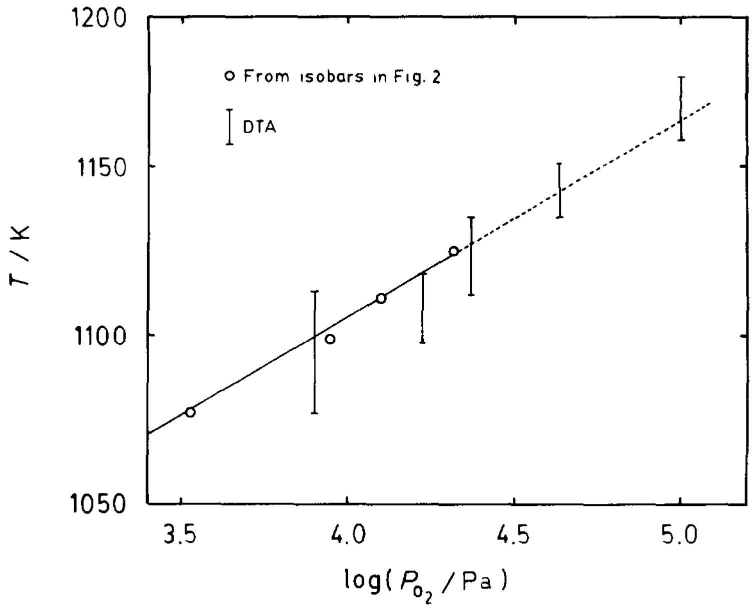

Fig. 4. Comparison of peak temperatures in DTA and the temperatures of the I–II phase transition obtained from TG measurements.

temperatures between 1050 and 1200 K. In DTA used in the present study, a phase transition terminates just before the top of peak [12,13]. The peak temperature on cooling is considerably lower than that on heating in each measurement. This hysteresis phenomenon indicates that the transition is of the first order. The peak area is enlarged as the oxygen partial pressure decreases, which corresponds to an increasing of the two-phase region (see Fig. 2). The DTA peaks are attributed to the I–II phase transition.

Figure 4 shows the peak temperatures in DTA as a function of oxygen partial pressure. The top and bottom of the bar denote the peak temperatures in heating and cooling runs, respectively. The open circles present the temperatures of the I–II phase transition obtained from isobars in Fig. 2. The temperatures agree fairly well, confirming that the DTA detects the thermal anomaly due to the I–II phase transition. Although the existence of the two-phase region of I and II is not clear at relatively higher oxygen partial pressures in Fig. 2, the DTA gives the clearly visible thermal anomaly as seen in Fig. 3. This result suggests that the two-phase region may extend at higher temperatures with an extremely narrow width, or that another phase transition may exist.

There still remain discrepancies among the results in the present study and the previous reports [10,11] where TG measurements were employed. However, the authors are continuously making efforts to establish the phase relation in $BaBiO_{3-x}$, employing coulometric titration as another approach.

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