Oxygen-Deficient and Ordered Perovskite-Type Solid–Solution System $Ba_{1+x}Bi_{1-x}O_y$ ($0 \leq x \leq 0.5$, $3.00 \geq y \geq 2.75$)

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A new oxygen-deficient and ordered perovskite-type solid–solution system $Ba_{1+x}Bi_{1-x}O_y$ ($0 \leq x \leq 0.5$, $3.00 \geq y \geq 2.75$) was synthesized, with the estimated ionic configuration $Ba(Ba_x^{2+}Bi_{3.5-1.5x-y}^{3+}Bi_{-3+0.5x+y}^{5+})(Bi_{0.5}^{5+})O_y$. The lattice parameters and mean valence of bismuth in the samples annealed in one atmosphere of oxygen at 773 K were determined by the powder X-ray diffraction method and iodometric titration method, respectively. Samples with the compositions $0 \leq x \leq 0.05$, $0.10 \leq x \leq 0.15$, $0.20 \leq x \leq 0.425$, $0.45 \leq x \leq 0.475$, and $0.475 < x \leq 0.50$ were found to be monoclinic, rhombohedral, cubic, tetragonal, and cubic, respectively. Oxygen deficiency was observed in the entire range of the composition; the ordering of the oxygen vacancies was confirmed in the range $X \geq 0.45$. © 1990 Academic Press, Inc.

1. Introduction

$BaBiO_3$ is an ordered perovskite-type compound with mixed (Bi^{3+}, Bi^{5+}) valency in the *B*-site (*1, 2*). With increasing temperature, many oxygen vacancies are introduced, accompanied by an increase in the trivalent ions (*3*). Therefore, it is of great interest to obtain a barium bismuth oxide with a perovskite structure whose Ba/Bi ratio differs from unity. For Ba/Bi < 1 we anticipate metallic conductivity originating from "electron doping" by replacement of Ba^{2+} ions with Bi^{3+} ions on the *A*-sites. For Ba/Bi > 1, on the other hand, we anticipate the replacement of bismuth ions by Ba^{2+} ions on the *B*-sites. In a brief study (*4*) of the phases of the system $Ba_{1-x}Bi_{1+x}O_y$ ($0 \leq x \leq 1$) a rhombohedral phase, different from the perovskite structure, has been reported for $x = 0.22$–0.29. Recently, the present authors (*5*) synthesized a new perovskite solid–solution system whose Ba/Bi ratio exceeds unity; the excess barium ions in $Ba_{1+x}Bi_{1-x}O_y$ ($0 \leq x \leq 0.33$) occupy the *B'*-site of the ordered perovskite $Ba_2(B')(B'')O_6$. No oxygen vacancy was assumed for the structure; the ionic configuration in the ordered perovskite was estimated to be $Ba_2(Ba_{2x}^{2+}Bi_{1-3x}^{3+}Bi_x^{5+})(Bi_1^{5+})O_6$, assuming pentavalency for bismuth ions in the *B''*-site.

In this paper, the phase relation in the $Ba_{1+x}Bi_{1-x}O_y$ system is examined for the range $-0.2 \leq x \leq 0.6$ and the oxygen deficiency and ionic distribution in the system

are discussed, based on the mean valence of bismuth ions as determined by the iodometric titration method.

2. Experimental

A $Ba_{1+x}Bi_{1-x}O_y$ ($-0.20 \leq x \leq 0.60$) sample was synthesized by a solid state reaction from a stoichiometric mixture of $BaCO_3$ or $Ba(NO_3)_2$ of 99.9% purity and Bi_2O_3 of 99.99% purity. The metal content in $BaCO_3$, $Ba(NO_3)_2$, and Bi_2O_3 were determined by titration using EDTA. Samples with the composition of $0.05 \leq x \leq 0.60$ were prepared by mixing and grinding $BaCO_3$ and Bi_2O_3 powders for 1 hr in an agate mortar with ethanol. After drying, the mixture was pressed into a pellet 15 mm in diameter and 2 mm in thickness at a pressure of 80 MPa/m^2. These pellets were calcined at 1073 K for 18 hr, then heated at 1073 K for 12 hr, at 1173 K for 18 hr, and at 1273 K for 4 hr, with intermediate pulverization and pelletization. Samples with the composition $0.45 \leq x \leq 0.50$ were heated at 1273 K for 48 hr, cooled to 773 K, maintained at that temperature for 12 hr ($0 < x \leq 0.425$) or 48 hr ($0.45 < x \leq 0.50$), then furnace-cooled. Samples in the range $-0.20 \leq x \leq 0$ were prepared by mixing powders of $Ba(NO_3)_2$ and Bi_2O_3, pressing these into pellets, and calcining at 923 K for 1 hr. The samples were heated at 1023 K for 6 hr and reheated at 1073 K for 24 hr with intermediate pulverization and pelletization. The samples were cooled to 773 K, kept at that temperature for 24 hr, 673 K for 12 hr, 573 K for 12 hr, and then furnace-cooled. All $Ba_{1+x}Bi_{1-x}O_y$ samples were heated in a flow of oxygen gas. Metal compositions of the samples analyzed by a titration technique revealed that the cation ratio was invariant during the heat treatments at high temperatures. The mean valence of bismuth ions was determined by the iodometric method. From the metal composition and the mean valence of bismuth ions, the oxygen content y was then calculated.

The samples were characterized by powder X-ray diffraction method at room temperature using a Rigaku horizontal $\theta-\theta$ scanning diffractometer with a curved graphite monochromator for $2\theta = 5-120°$, using a Cu target X-ray tube at 40 kV and 25 mA. To avoid possible overlap errors, nonoverlapping peaks higher than $2\theta = 80°$ were used to determine the unit cell dimensions. Silicon powder was used as an internal standard.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns for some $Ba_{1+x}Bi_{1-x}O_y$ samples. Table I summarizes the results of lattice parameter and oxygen content y determined by the iodometric titration. X-ray diffraction patterns for almost all samples, except for $x = 0.45$ and 0.475, indicated a pseudocubic perovskite structure. Samples with the compositions $x = 0.45$ and 0.475 exhibited a tetragonal structure. Superlattice lines due
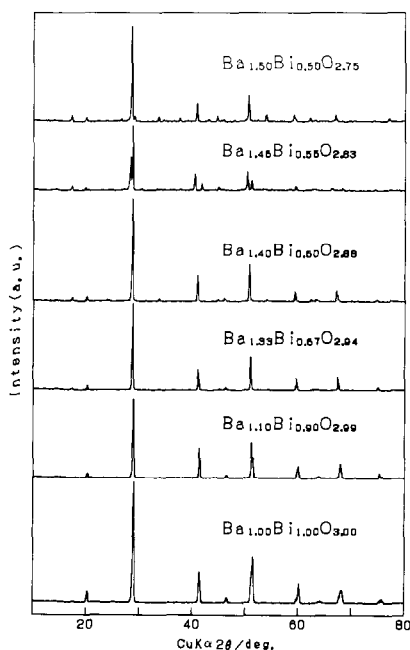

FIG. 1. X-ray diffraction patterns for $Ba_{1+x}Bi_{1-x}O_y$.

TABLE I

LATTICE CONSTANT AND OXYGEN CONTENT OF $Ba_{1+x}Bi_{1-x}O_y$

X	Lattice constant (nm)	Oxygen content (y)
0.00	Monoclinic $a = 0.6185 \pm 0.0001$ $b = 0.6139 \pm 0.0001$ $c = 0.8670 \pm 0.0002$ $\beta = 90.17°$	3.000
0.05	Monoclinic $a = 0.6186 \pm 0.0002$ $b = 0.6148 \pm 0.0007$ $c = 0.8686 \pm 0.0002$ $\beta = 90.00°$	2.998
0.10	Rhombohedral $a = 0.8730 \pm 0.0001$ $\alpha = 90.24°$	2.994
0.15	Rhombohedral $a = 0.8730 \pm 0.0001$ $\alpha = 90.13°$	2.989
0.20	Cubic $a = 0.8743 \pm 0.0001$	2.984
0.25	Cubic $a = 0.8754 \pm 0.0002$	2.972
0.30	Cubic $a = 0.8766 \pm 0.00008$	2.970
0.33	Cubic $a = 0.8776 \pm 0.0001$	2.950
0.40	Cubic $a = 0.8802 \pm 0.0003$	2.880
0.425	Cubic $a = 0.8817 \pm 0.0004$	2.862
0.45	Tetragonal $a = b = 0.8925 \pm 0.0006$ $c = 1.7303 \pm 0.0018$	2.825
0.475	Tetragonal $a = b = 0.8917 \pm 0.0006$ $c = 1.7344 \pm 0.0011$	2.788
0.50	Cubic $a = 3.0587 \pm 0.0008$	2.753

to a superstructure were observed for samples with $0.10 \leq x \leq 0.50$. These additional lines were assigned to reflections from the 1 : 1 ordered structure in the B-sites (NaCl-type arrangement of the B-site ions). Additional lines observed for the samples with $x \geq 0.45$ were assigned to reflections from a superstructure involving a regular arrangement of oxygen vacancies. The growth of superlattice lines with increasing x is due to an increase in the number of Ba^{2+} ions in the B'-site of $Ba_2(B')(B'')O_6$. Samples with the compositions $x > 0.50$ or $x < 0$, respectively, were found to be in the perovskite phase containing an additional BaO- or Bi_2O_3-rich phase. In Fig. 2, the increasing perovskite parameter $\bar{a}$ (cube root of the perovskite unit) indicates an expanding unit cell as the Ba content increases. The $\bar{a}$ value shows a maximum at $x = 0.475$, then decreases as $x \to 0.50$. The ionic radii (6) of Ba^{2+}, Bi^{3+}, and Bi^{5+} ions at the six-coordination site are 0.135, 0.103, and 0.076 nm, respectively. Therefore, the replacement of bismuth by barium increases, thereby expanding the perovskite unit. Figure 3 shows that the mean valence of bismuth reaches 5.0 at $x = 0.425$. Based on these results, we
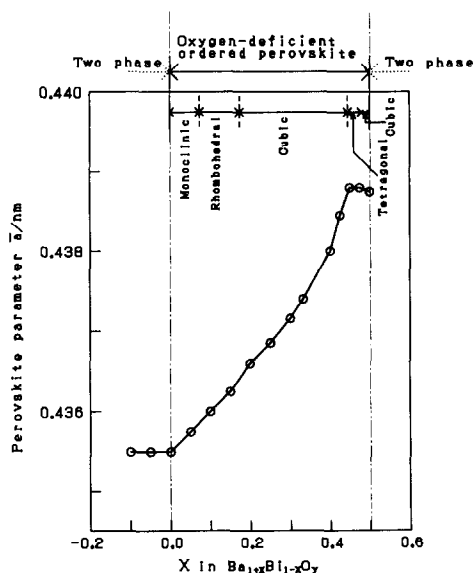

FIG. 2. Perovskite parameter $\bar{a}$ vs x. Symmetries of the lattice are given in the upper horizontal axis.
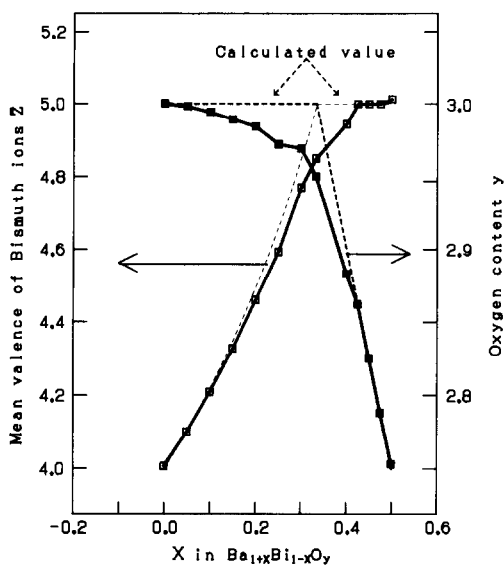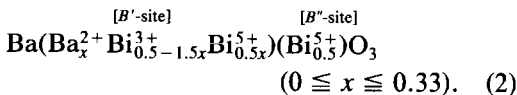
FIG. 3. Mean valence of bismuth ions $\bar{z}$ and oxygen content y vs x. The broken lines represent the calculated values based on processes [1] and [2].

resolve the replacement reaction of Bi^{3+} by Ba^{2+} into two elementary processes which satisfy the electroneutrality conditions.

Process [1]. In process [1] which is formally applied to the range $x \leqq 0.33$, the diminution of positive charge in the replacement of Bi^{3+} by Ba^{2+} ions is compensated by the increase in the valence of remaining Bi ions from $+3$ to $+5$. The replacement reaction is represented by
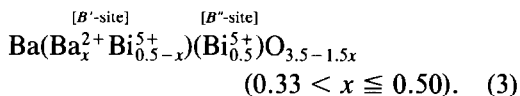
$$2Ba + (3Bi^{3+})_{B'\text{-site}} \rightarrow$$
$$(2Ba^{2+} + Bi^{5+})_{B'\text{-site}} + 2Bi. \quad (1)$$
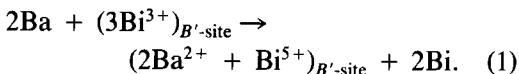
Assuming perfect ordering of bismuth ions on B'- and B''-sites, the ionic configuration can be represented by

$$\overset{[B'\text{-site}]}{Ba(Ba_x^{2+} Bi_{0.5-1.5x}^{3+} Bi_{0.5x}^{5+})} \overset{[B''\text{-site}]}{(Bi_{0.5}^{5+})O_3}$$
$$(0 \leqq x \leqq 0.33). \quad (2)$$

Process [2]. In process [2], formally applicable to the range $x > 0.33$, the diminution of positive charges is compensated by the formation of oxygen vacancies, keeping the

valence of all bismuth ions at $+5$. Then the ionic configuration can now be represented by

$$\overset{[B'\text{-site}]}{Ba(Ba_x^{2+} Bi_{0.5-x}^{5+})} \overset{[B''\text{-site}]}{(Bi_{0.5}^{5+})O_{3.5-1.5x}}$$
$$(0.33 < x \leqq 0.50). \quad (3)$$

The mean valence of bismuth ions and oxygen content in these elementary processes are plotted in Fig. 3. There is good agreement between the calculated and experimental values, except for the range $x = 0.33$–0.40; this supports the proposed charge compensation model based on these two elementary processes.

However, oxygen vacancies are also introduced by the following equilibrium reaction

$$(Bi_{Bi^{5+}}^{5+})^x + (O_{O^{2-}}^{2-})^x = (Bi_{Bi^{5+}}^{3+})^{2-}$$
$$+ (V_{O^{2-}})^{2+} + 1/2O_2(g). \quad (4)$$
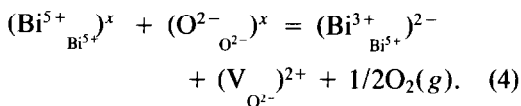
The difference between the experimental and the calculated values in Fig. 3 is due to the formation of oxygen vacancies in the above reaction. Therefore, the overall ionic configuration can be represented as
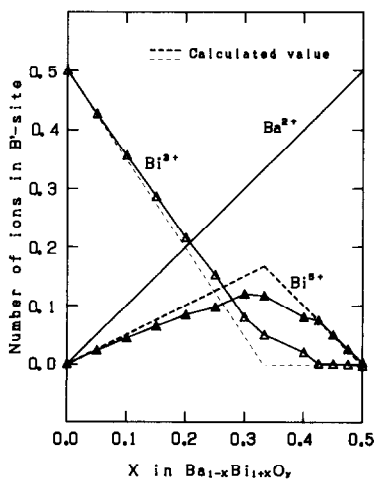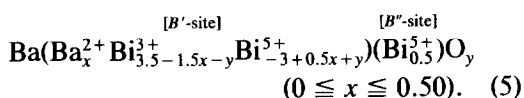

FIG. 4. Numbers of ions in the B'-site vs x. The broken lines represent the calculated values based on processes [1] and [2].

$$Ba(\overset{[B'\text{-site}]}{Ba_x^{2+} Bi_{3.5-1.5x-y}^{3+} Bi_{-3+0.5x+y}^{5+}})(\overset{[B''\text{-site}]}{Bi_{0.5}^{5+}})O_y$$

$$(0 \leqq x \leqq 0.50). \quad (5)$$

The Ba^{2+}, Bi^{3+}, and Bi^{5+} ions in the B'-site were calculated from Eq. (5) using the oxygen content y in Table I. Figure 4 indicates that the numbers of Bi^{3+} and Bi^{5+} ions change linearly in the range $x \leqq 0.33$ where the oxygen deficiency is small. The broken lines in Fig. 4 represent calculated values based on the two mechanisms proposed above. Reasonably good agreement was observed between the two calculated values. The oxygen content reaches 2.75 at the composition $x = 0.5$, as shown in Fig. 3, and the ionic configuration of the sample at that composition is $Ba_2(Ba_1^{2+})(Bi_1^{5+})O_{5.5}$. Barium ions occupy the B-site because it is well known that Ba^{2+} ion can enter the B-sites which also contain smaller hexavalent cations, such as Re^{6+} (7) (0.055 nm), Os^{6+} (7) (0.0545 nm), and U^{6+} (8) (0.073 nm). The ionic radius of Bi^{5+} (0.076 nm) is comparable to that of U^{6+}. The changes of the lattice symmetry from cubic to tetragonal to cubic and the superlattice lines due to the oxygen vacancies in the range $x > 0.425$ suggest a change in the arrangement of oxygen vacancies with composition. The sequence of changes in lattice symmetry with composition should be interpreted in terms based on the lattice energy, and the exact arrangement of the oxygen vacancies should be investigated by neutron diffraction.

Acknowledgment

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