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High n-Value Phases in the Complex Bismuth Oxides with Layered Structure, $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$

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Complex bismuth oxides with layered structure are prepared with a series of compositions in the system $Bi_2CaNb_2O_9$–$NaNbO_3$. It is found by X-ray powder diffraction that each compound is composed of more than two phases, which are described by a formula $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$, e.g., in the sample with the nominal composition $Bi_2CaNb_2O_9 \cdot 8NaNbO_3$, the phases with $n = 6$ to 8 appear predominantly. These phases are closely intergrown to each other. Moreover, high-resolution electron microscopy reveals that microsyntactic intergrowth frequently occurs in the phases with $n > 5$. The occurrence of the latter intergrowth is explained in terms of the bond length obtained.

Introduction

Complex bismuth oxides with layered structure, generally described as $Bi_2M_{n-1}R_nO_{3n+3}$ or $(Bi_2O_2)^{2+}(M_{n-1}R_nO_{3n-1})^{2-}$, are constructed by the perovskite-type layers of $M_{n-1}R_nO_{3n+1}$ and the bismuth oxide sheets of Bi_2O_2. Both the layers and sheets extend two-dimensionally normal to the c axis. M and R are cations belonging to particular species, respectively (*1–3*). The stacking number of perovskite-type subcells in the layers is equal to $n - 1$.

Complex bismuth oxides with layered structure have so far been reported limited for $n \leq 5$ except that made by Ismailzade *et al.* (*4*), i.e., $Bi_9Ti_3Fe_5O_{27}$ ($n = 8$). It is however not clear whether the compound is composed of the single phase with $n = 8$ or not, because the spacings of low order $(0, 0, l)$ reflections are not shown in their diffraction data. In fact, Hutchison *et al.* (*5*) examined the compound with the same nominal composition by lattice imaging electron microscopy and found the lattice fringes almost from $n = 4$ and $n = 5$, mixed randomly.

It is very interesting to investigate the possibility of the formation of complex bismuth oxides with $n > 5$. In the previous paper (*6*), we have tested the possibility using the system $Bi_2CaNb_2O_9$–$NaNbO_3$; the symmetry of $Bi_2CaNb_2O_9$ ($n = 2$) is orthorhombic and $NaNbO_3$ has an orthorhombic perovskite structure with lattice parameters $a = 5.557$, $b = 5.512$, and $c = 4 \times 3.885$ Å (*7*). It is known (*8*) that Na^{1+} is one of the most suitable ion for taking the A site in the perovskite-type layer. It has then been expected that $NaNbO_3$ contributes to make thick the perovskite-type layers. High-resolution electron microscopy has however made clear that no single phase is formed in the compound, $Bi_2CaNb_2O_9 \cdot 4NaNbO_3$; several phases are intergrown and, moreover, finer inter-

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growth on a unit-cell scale, i.e., microsyntactic intergrowth, occurs with mixed phases frequently.

In the present paper we examine a series of compounds, $Bi_2CaNb_2O_9 \cdot m NaNbO_3$ ($m = 0$ to 8), mainly by X-ray diffraction. The dependence of the manner in the intergrowth on the m-value is made clear and the reason is discussed in terms of the bond length together with referring to tolerance factor.

Experimental

Sample preparation. The starting chemical reagents were Bi_2O_3, Nb_2O_5, $CaCO_3$, and Na_2CO_3 which are all 99.9% in purity. First, the end members, $Bi_2CaNb_2O_9$ and $NaNbO_3$, were synthesized, respectively, by heating preliminarily at 870°C for 2 hr and then at 1080°C for 16 hr. They were identified by X-ray diffractometry. The mixture of them was heated at 1170°C in a Pt crucible with a cap. The mechanochemical treatment (i.e., grinding and heating) of the mixture was repeated more than five times to get the sufficient homogeneity in chemical composition. For the convenience of description in the following sections, we use the letter m to show the total chemical composition, i.e., the nominal composition on the preparation. It then follows that $n = m + 2$ if the sample is prepared with a single phase. The samples are prepared for $m = 0$ to 8.

X-ray diffraction. The powder samples were examined with an X-ray diffractometer using vanadium-filtered Cr$K\alpha$ radiation. A Cr target was used to observe the reflections of larger lattice spacings and to separate reflection doublet. The diffraction angles were calibrated by the external standard of quartz powder.

Electron microscopic observation. Electron diffraction and structure image were examined by 1 MV high-resolution electron microscopy. The method of observation is as reported in the previous paper (*6*).

Experimental Results

X-Ray Diffraction

It is known from the X-ray diffraction that, for $m \leq 3$, the sample was composed of two or three phases, while, for $m > 3$, the sample was of three or more phases. For example, the $m = 1$ sample was of $n = 3$ (predominant) and $n = 4$ phases. The $m = 3$ sample was of $n = 5$, 6 and 7 phases with similar quantity. In the $m = 8$ sample, the $n = 6$, 7 and 8 phases were equally predominant and the $n = 10$ phase was contained as a minor component.

For $m \leq 3$, many diffraction peaks such as $(0, 0, 2l)$, $(1, 1, 0)$, $(1, 1, 2l + 1)$, $(2, 0, 0)$, and $(0, 2, 0)$ reflections were sharp. For $m > 3$, most reflections were weak and broad except the $(0, 0, 2n)$, $(2, 0, 0)$, and $(0, 2, 0)$ reflections. The lattice spacing of $(0, 0, 2n)$ reflections is about 4 Å irrespective of the n-value. But the precise measurement revealed that it became slightly smaller with increasing the n-value, i.e., 4.150 Å ($n = 2$), 4.100 ($n = 3$), 4.065 ($n = 4$), 4.042 ($n = 5$), 4.029 ($n = 6$), . . . , and 4.001 ($n = 10$). The intensity of these reflections became stronger with the n-value. The difference of the spacings, Δc, is nearly constant, 3.95 Å ($= c_0$) irrespective of n-value.

The lattice parameters, a, b, and c, calculated from the $(2, 0, 0)$, $(0, 2, 0)$ and $(0, 0,$

TABLE I

Lattice Parameters of a, b, and c in the Orthorhombic $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$ and the Difference, Δc, between Adjoining Phases

n	a	b	c	Δc
2	5.476	5.435	24.90	7.90
3	5.491	5.452	32.80	7.85
4	5.496	5.461	40.65	7.85
5	5.498	5.466	48.50	7.90
6	5.500	5.466	56.40	7.92
7	5.504	5.468	64.32	7.99
8	5.504	5.470	72.31	7.90
9	5.506	5.471	80.21	7.81
10	5.507	5.472	88.02	

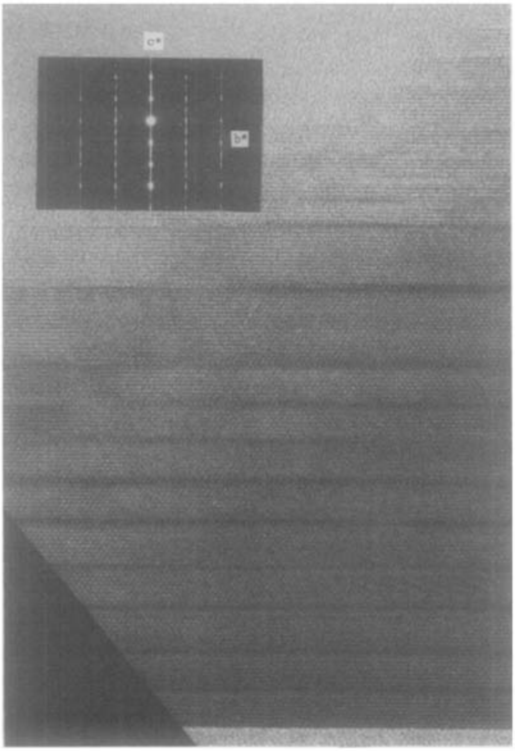

FIG. 1. Electron microscopic structure image in the sample with a nominal composition $Bi_2CaNb_2O_9 \cdot 4NaNbO_3$ ($m = 4$), revealing a frequent microsyntactic intergrowth.

$2n$) reflections, respectively, are shown in Table I.

Structure Image

Figure 1 shows the electron microscope image of the $m = 4$ sample. The incident electron beam is normal to the (1, 0, 0) plane, as noticed from the inserted diffraction pattern. According to the previous paper (*6*), the image contrast is interpreted as follows: the nallow dark bands normal to the c direction correspond to the Bi_2O_2 sheets. Bi ions are projected to form pairs. They show dark contrast since they are heavy. The layers between these sheets are perovskite-type layers. The microsyntactic intergrowth frequently occurs; the perovskite-type layers with a variety of thickness intergrow on a unit-cell scale. The thickness of layers corresponds mostly to that of $n = 6$ and occasionally of $n = 18$.

Discussion

Tolerance Factor, t

In order to discuss the stability of complex bismuth oxide with layered structure, let us first consider the tolerance factor, t,

$$t = (r_A + 1.40)/2^{1/2}(r_B + 1.40),$$

where r_A and r_B are the ionic radii of A and B site ions (*8*), respectively, in the perovskite unit-cell, and the radius of O^{2-} is 1.40 Å. If there are more than two ionic species, the radius should be averaged taking the content ratio into consideration.

The t-values calculated for a series of compounds, $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$, are shown in Table II. It is noticed that they increase with n. The difference, Δt, between the t-values of adjoining compounds is also presented in the table. It is clear that the Δt's are relatively larger in $n \leq 5$ while they are very small in $n > 5$. This may be related to that the microsyntactic intergrowth occurs in the sample of $n > 5$, as will be made clear through the discussion of bond length.

TABLE II

TOLERANCE FACTOR, t, AND THE DIFFERENCE, Δt, BETWEEN ADJOINING PHASES, $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$

m	n	t	Δt
0	2	0.8735	
1	3	0.8804	0.0069
2	4	0.8827	0.0023
3	5	0.8839	0.0012
4	6	0.8846	0.0007
5	7	0.8850	0.0004
6	8	0.8854	0.0004
7	9	0.8856	0.0002
8	10	0.8858	0.0002

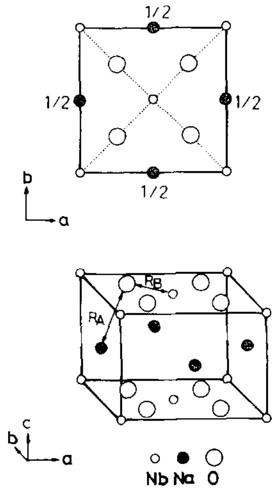

FIG. 2. Idealized atomic arrangement in the unit cell of the orthorhombic perovskite $NaNbO_3$.

Origin of the Microsyntactic Intergrowth

As noted in Table I, the lattice parameters a and b increase remarkably with increasing n-value within the range $n \leq 5$. The increasing rate becomes small and almost constant for $n > 5$. In order to discuss the meaning, let us consider the structure in the perovskite-type layer, $[(CaNa_{n-2})NB_nO_{3n+1}]^{2-}$. When n is sufficiently large, it approaches $[NaNbO_3]^0$. Referring to Fig. 2, the bond length between Na(Ca) and O, R_A, and that between Nb and O, R_B, are represented respectively as,

$$R_A = (a^2 + b^2 + 4c_0)^{1/2}/\ 4,$$
$$R_B = (a^2 + b^2)^{1/2}/\ 4,$$

where c_0 = 3.95 Å. The results calculated using the data in Table I are shown in Fig. 3. The values of R_A and R_B increase remarkably with increasing n-value in the range $n \leq 5$. But they increase rather slowly in the range $n > 5$. This might suggest that, since the number of perovskite-type subcells between the Bi_2O_2 sheets is 4 for the case n = 5, the Bi_2O_2 sheet intensively affects the nearest, two perovskite-type subcells, through the geometrical matching and electrostatic interaction. On the other hand, the perovskite-type subcells located farther from the Bi_2O_2 sheet are little influenced. Then, it may be said that additive perovskite-type subcells can relatively easily be inserted in the layer. This may be reason why the microsyntactic intergrowth frequently occurs in the case of $n > 5$.

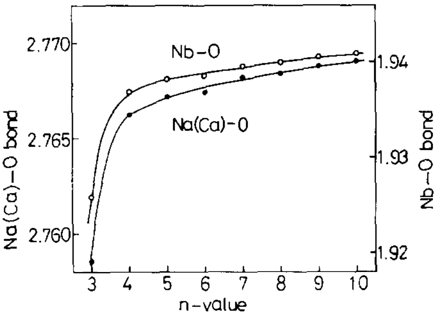

FIG. 3. Variation of the cation–oxygen bond lengths in $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$ (n = 2 to 10).

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