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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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A series of compounds $Bi_2CaNb_2O_9 \cdot m NaNbO_3$ ($n=m+2$) were synthesized for $m=0$ to 8 in order to get the phases with $n>5$ which have so far been unknown. We have found from the investigations of x-ray diffraction and electron microscopic structure image that the phases with $n>5$ are present as micro-syntactic intergrowth. The origin of the intergrowth has been discussed.

§1. Introduction

Complex bismuth oxides with layered structure (CBOL) are generally described[1-3] as $Bi_2A_{n-1}B_nO_{3n+3}$ or $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ (where n = integer) which are constructed by the perovskite-like layers of $A_{n-1}B_nO_{3n+1}$ interleaved with each bismuth oxide sheet of Bi_2O_2, where A(-site ion) $=K^+$, Na^+, Ca^{2+}, Sr^{2+}, Pb^{2+}, Ba^{2+}, Bi^{3+}, La^{3+} etc, and B(-site ion) $=Cr^{3+}$, Fe^{3+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, Mo^{6+} etc. CBOL compounds usually belong to orthorhombic or pseudotetragonal system. Both Bi_2O_2 sheets and perovskite-like layers extend perpendicularly to the *c*-axis. The number of perovskite-like layers stacked between a pair of Bi_2O_2 sheets is equal to $n-1$.

No any CBOL compound with $n>5$ has so far been known. Ismailzade *et al*[4] reported the formation of $Bi_9Ti_3Fe_5O_{27}$ ($n=8$). But recently Hutchison *et al.*[5] have examined its structure image with a high-resolution electron microscope and found that the compound is composed of the inter-mixed phases $n=4$ and 5.

If *n*-value increases sufficiently, the stacked perovskite-like layers are to become thick. Based on this interest, we systematically synthesized a series of $Bi_2CaNb_2O_9$. $m NaNbO_3$ (where m = integer), which can be rewritten by (Bi_2O_2) $(CaNa_{n-2}Nb_nO_{3n+1})$, where the relation $n=m+2$ is valid if the compound is composed of a single phase n. It is known[6] that Na^+ is one of the most suitable ions for occupying the A-site. It is then expected that $NaNbO_3$, belonging to perovskite family, contributes to make the stacked perovskite-like layers thick. In the present paper, the compounds synthesized have been investigated by x-ray diffraction and electron microscopic observation. We have found that the phases with $n>5$ can be constructed involving even with $n=18$ and 30, as 'micro-syntactic intergrowth.'

§2. Experimental and Results

2.1 *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 in the pseudobinary system of $Bi_2CaNb_2O_9$–$NaNbO_3$ were synthesized respectively by heating preliminarily at 870°C for 2 hours and then at 1,080°C for 16 hours in a covered Pt crucible in air. $Bi_2CaNb_2O_9$ is one of CBOL and $NaNbO_3$ has a perovskite structure. Then, the mixture of them was heated at 1,170°C for 16 hours. The procedure of grinding and heating for the mixture was repeated more than five times to achieve the sufficiently homogeneous chemical composition.

For the convenience of description, we use the letter m to show a total composition on sample preparation while the letter n to show a real phase on synthesized compound. The sintered samples were prepared for $m=0$ to 8.

2.2 *Differential thermal analysis (DTA) and melting temperature*

DTA was made with a conventional equipment. All samples did not show any peak due to ferroelectric transition between room temperature and 960°C.

Melting temperature was measured by the direct observation method.[7] The samples had their melting temperatures between 1,301°C and 1,412°C. The former is the eutectic point at about 60 mol% $NaNbO_3$ in the pseudo-binary system. The latter is the melting temperature of $NaNbO_3$. The details of data will be reported in another paper.

2.3 *X-ray diffraction*

The powder samples were examined with an x-ray diffractometer using vanadium-filtered CrKα radiation. A Cr target was used to observe the low order of reflections and to separate doublet. The diffraction angles were calibrated by the external standard quartz powder.

The $m=0$ sample was composed of the single phase with $n=2$. For $3 \geq m \geq 1$, the sample was composed of two phases. For $m>3$, the sample was of multi-phases. These were identified from the observation of (0, 0, $2l$) reflections. For example, the $m=1$ sample was composed of $n=3$ (predominant) and $n=4$ phases, the $m=3$ sample was of $n=5$ (predominant) and $n=6$, and the $m=4$ sample was of $n=(5)$, 6, 7, (8) etc.

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 (belonging to orthorhombic system) were sharp. For $m>3$, most of peaks were weak and broad except the (0, 0, $2n$), (2, 0, 0) and (0, 2, 0) reflections. The lattice spacing of (0, 0, $2n$) reflection was about 4 Å irrespective of n-(or m-) value.

The lattice parameters, a, b and c, calculated from the (2, 0, 0), (0, 2, 0) and (0, 0, $2n$) reflections are shown in Table I.

2.4 *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.[8)]

Figure 1 shows the structure image of the $m=4$ sample. The incident beam is normal to the (1, 0, 0) plane, as noticed from the inserted diffraction pattern. The details of data was reported in the previous paper.[8)] In the figure, the narrow 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 ions. The layers between the Bi_2O_2 sheets are perovskite-like layers. The 'micro-syntactic intergrowth' frequently occurs; it means that the perovskite-like layers with a variety of thickness intergrow on unit-cell order of scale. The thickness of the layers corresponds mostly to that of $n=5$ and then $n=6$, and occasionally $n=18$ and 30 also.

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 ($n=2$ to 10).

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

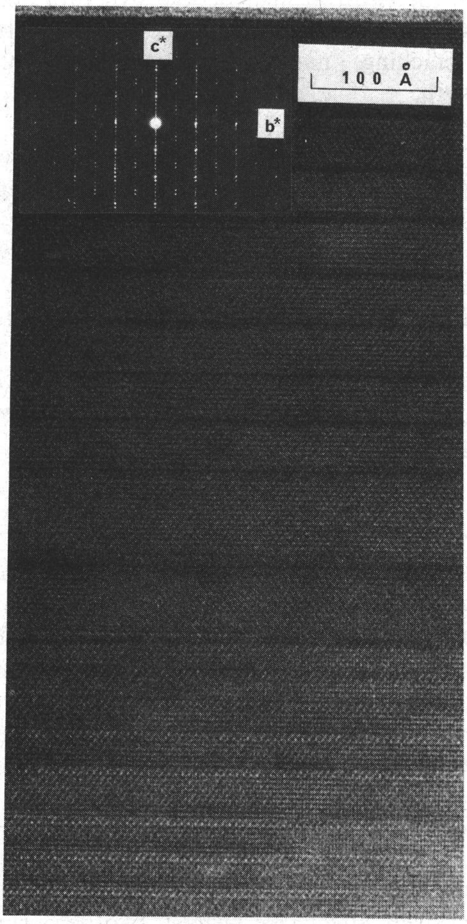

Fig. 1. Electron microscopic structure image in the sample with a nominal composition $Bi_2CaNb_2O_9 \cdot 4NaNbO_3$ ($m=4$), revealing a frequent microsyntactic intergrowth.

§3. Discussion

3.1 *Stacking of perovskite-like layers*

According to the observation of x-ray diffraction pattern, the (0, 0, 2*l*) reflections except 4 Å reflection became broad or diffused peak remarkably for the samples of $m>3$, while the (2, 0, 0) and (0, 2, 0) reflections were sharp irrespective of *m*-(or *n*-) value. The 4 Å sharp peak became stronger with increasing the value. These facts suggest that the structure of each perovskite-like subcell and its stacking within a pair of Bi_2O_2 sheets are kept with regular periodicity, and the thickness of the stacked subcells becomes thicker with increasing *m*-value, but that the regularity of stacking number for perovskite-like subcell is not kept as a whole.

This inspection from x-ray diffraction agrees with the electron microscopic structure image observed. The image elucidated the real picture of stacking, namely 'microsyntactic intergrowth.'

3.2 *Origin of the micro-syntactic intergrowth*

As noticed in Table I, the lattice parameters *a* and *b* increase with increasing *n*-value. Here, let us consider the perovskite-like layer, $[(CaNa_{n-2})Nb_nO_{3n+1}]^{2-}$. When *n*-value is sufficiently large, it approaches $[NaNbO_3]^0$. Supposing a perovskite structure of subcell, the nearest bond length between Na(Ca) and O, R_A, and that between Nb and O, R_B, can be shown[9] respectively by

$$R_A=\sqrt{a^2+b^2+4c_0}/4,\quad (c_0=3.95\ \text{Å}),$$

$$R_B=\sqrt{a^2+b^2}/4,$$

where c_0 corresponds to the perovskite subcell edge along the *c* direction. The results calculated using the data in Table I are shown in Fig. 2. The values of R_A and R_B increase remarkably with increasing *n*-value in the range $n\leq 5$, and the increasing rate becomes rather smaller in the range of *n* above 5. This characteristic of the curve may lead the following suggestion.

Since the number of perovskite-like layers between Bi_2O_2 sheets is 4 for the important point of $n=5$ on the curve, the Bi_2O_2 sheet intensively affects the nearest, two perovskite-like layers, through geometrical matching and electrostatic interaction. On the other hand, the perovskite-like layer located farther from the Bi_2O_2 sheet is little influenced. Then, additive perovskite-like layer can relatively easily be inserted to make the layers thick with rather arbitrary number of stacking. Then, the micro-syntactic intergrowth frequently occurs in the case of $m>3$.

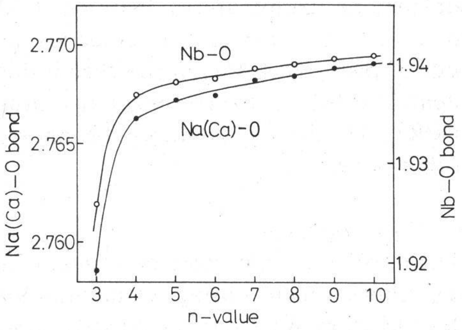

Fig. 2. Variation of the cation-oxygen bond lengths in $Bi_2CaNa_{n-2}Nb_nO_{3n+3}$ ($n=2$ to 10).

In other words, the micro-syntactic intergrowth suggests that the compounds are metastable, and that the phases with different *n*-value have the same order of magnitude in free energy one another.

The above mentions also may give a clue to the reason why no any regular structure of CBOL compound with $n>5$ has so far been known. R_A and R_B values vary depending on ionic radius and on ratio of ion content. The stability of CBOL due to geometrical factor, which closely reflects free energy, is under investigation.

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