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$Bi_2La_4O_9$: A Monoclinic Phase in the System Bi_2O_3–La_2O_3

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The binary system Bi_2O_3–La_2O_3 with $La_2O_3 \geq 50$ mole% has been investigated at 950–1000°C. The results revealed three compounds: $Bi_8La_{10}O_{27}$, $Bi_{2.4}La_{3.6}O_9$, and $Bi_2La_4O_9$. $Bi_{2.4}La_{3.6}O_9$ has a rhombohedral subcell with hexagonal lattice parameters $a = 3.96017(5)$ Å, $c = 9.9691(2)$ Å, and space group *R*3*m*. It is probably the same phase which was reported previously as $Bi_2La_4O_9$ (Refs. 5 and 6). $Bi_2La_4O_9$ has a monoclinic structure with the subcell lattice parameters $a = 6.8290(3)$ Å, $b = 3.9887(1)$ Å, $c = 4.0524(1)$ Å and $\beta = 125.094(3)°$ and subcell space group *C*2/*m*. Its average structure has been determined by X-ray powder diffraction and refined by the Rietveld method. The average structure can be described as an oxygen deficient fluorite structure of the δ-Bi_2O_3 type with La and Bi randomly distributed on the cation site. In addition, a superstructure has been observed by TEM. © 1996 Academic Press, Inc.

INTRODUCTION

The binary systems Bi_2O_3–Ln_2O_3 (*Ln* = rare earths) have been widely investigated, particularly for the Bi-rich regions, because δ-Bi_2O_3 and doped Bi_2O_3 with fluorite-like structures exhibit high ionic conductivity. In the system Bi_2O_3–La_2O_3, at least four compounds have been reported: a tetragonal phase $Bi_{1.92}La_{0.08}O_3$ (1), an fcc phase $Bi_{1.88}La_{0.12}O_3$ (δ-Bi_2O_3 type) (2), a rhombohedral phase $Bi_{0.7}La_{0.3}O_{1.5}$ (3), and an orthorhombic phase $Bi_8La_{10}O_{27}$ (4). Recently, Wolcyrz and co-workers (5, 6) reported a series of $Bi_3Ln_5O_{12}$-type phases (*Ln* = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, and Y). Among these, the La representive is exceptional in exhibiting a modified composition $BiLa_2O_{4.5} = Bi_2La_4O_9$. Its powder pattern was indexed on the basis of a rhombohedral subcell with the hexagonal lattice parameters $a = 3.963(1)$ Å, $c = 9.964(4)$ Å, and space group *R*3*m*. Some additional weak diffraction peaks were explained by the possible superstructure $a' = 8a = 31.672$ Å and $c' = 2c = 19.927$ Å (5, 6).

In the present study, $Bi_2La_4O_9$ was found to be a new phase with a monoclinic structure. We report here the synthesis and the average structure of this monoclinic phase.

EXPERIMENTAL

In the system Bi_2O_3–La_2O_3 samples with 50.0, 55.0, 57.5, 60.0, 62.5, 65.0, 66.7, and 80 mole% La_2O_3 were prepared by solid state reaction from mixtures of La_2O_3 (Fluka, 99.98%) and Bi_2O_3 (Heraeus, 99.999%). Before weighing, La_2O_3 was preheated at 1000°C for 12 h to remove the carbon dioxide and water it absorbs in air. The samples were mixed, ground, and preheated at 800°C for 12 h in air and then fired at 950–1000°C for 5–7 days. Additional annealings for 2 days with intermediate grindings were performed for some samples. The samples were finally quenched to room temperature in air. The weight loss, presumably due to Bi_2O_3 varporization during heating, was always less than 0.8% of the total sample weight.

Phase identification, determination of lattice parameters, and the Rietveld refinement were performed on an automated Norelco diffractometer using Ni filtered Cu*Kα* radiation at room temperature. All data were collected by step scanning with steps of 0.02° 2*θ*. An angular range from 10° to 70° and a measuring time of 1 s were generally applied for phase identification while 10° to 90° and ≥10s were used for the lattice parameter determinations. NBS SRM 640 Si was added as internal standard. The lattice parameters were calculated with the program NBS*AIDS 83(7). For the Rietveld refinement, the data were collected over an angular range of 25° to 135° with a measuring time of 14 s. A total of 5500 points and 96 independent

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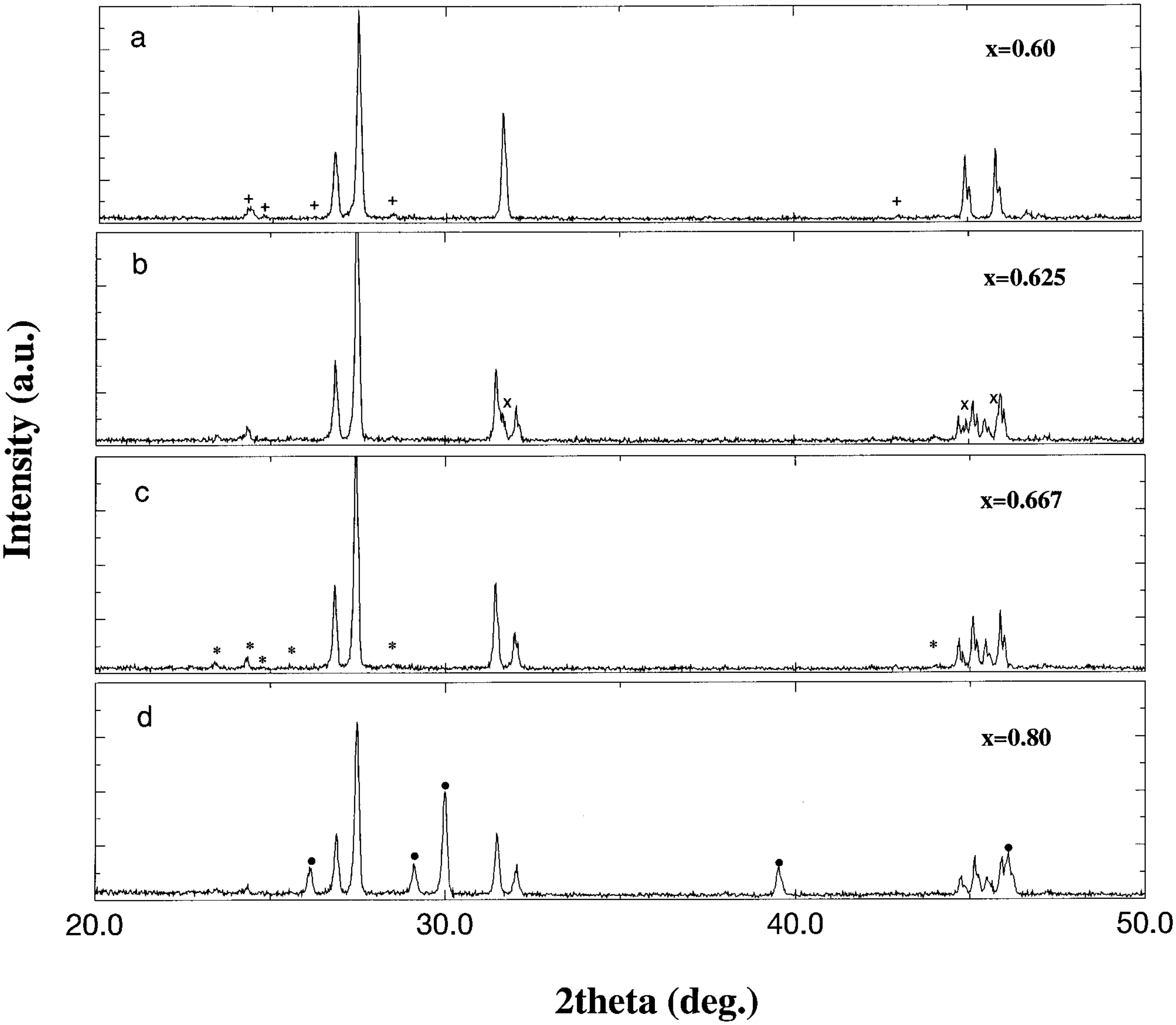

FIG. 1. The X-ray powder diffraction patterns of $Bi_{1-x}La_xO_{1.5}$. (a) $x = 0.60$, peaks marked by + are due to superstructure lines; (b) $x = 0.625$, peaks marked by x are due to $Bi_{2.4}La_{3.6}O_9$; (c) $x = 0.667$, peaks marked by * are due to superstructure lines; and (d) $x = 0.80$, the peaks marked by small dot are due to La_2O_3.

reflections were measured. The Rietveld refinement was carried out by using the computer program DBW3.2S(8).

RESULTS

For compositions with $La_2O_3 \geq 50$ mole%, X-ray powder diffraction (XRPD) measurements resulted in the existence of three compounds, namely $Bi_8La_{10}O_{27}$, $Bi_{2.4}La_{3.6}O_9$, and $Bi_2La_4O_9$. $Bi_8La_{10}O_{27}$ crystallizes in the space group *Immm* with $a = 12.083(4)$ Å, $b = 16.340(1)$ Å, and $c = 4.0989(2)$ Å. This is in good agreement with the previous data (4). The diffraction pattern of $Bi_{2.4}La_{3.6}O_9$ (Fig. 1a) agrees well with that reported for $Bi_2La_4O_9$ by Wolcyrz and co-workers (5, 6). Its main diffraction peaks can be indexed using a rhombohedral cell with hexagonal lattice parameters $a = 3.96017(5)$ Å and $c = 9.9691(2)$ Å. The observed conditions for reflections are $-h + k + l = 3n$ for hkl, $l = 3n$ for hhl, and $l = 3n$ for $00l$, resulting in the possible space groups $R\bar{3}m$ and $R3m$. $R3m$ is rather probable since it agrees with that of the closely related BiO (9). Some unindexed weak diffraction peaks (Fig. 1a) are due to the proposed superstructure $8a \times 2c$ (6). At 66.7 mole% La_2O_3, a new compound $Bi_2La_4O_9$ was found. Figure 1c shows its XRPD pattern. Although its composition is very close to $Bi_{2.4}La_{3.6}O_9$, it obviously is a different phase. Figure 1b shows the XRPD pattern for the sample with 62.5 mole% La_2O_3. It consists of the diffraction peaks of $Bi_{2.4}La_{3.6}O_9$ and $Bi_2La_4O_9$. This excludes that both are members of a solid solution series. Figure 1d shows the XRPD pattern for the sample with

TABLE 1
The Powder Data of $Bi_2La_4O_9$

d_{cal}	d_{obs}	I_{rel}(%)	*h k l*	d_{calc}	d_{obs}	I_{rel}(%)	*h k l*
	4.964	5	*		1.4353	2	*
	3.795	4	*	1.4212	1.4212	6	−2 2 2
	3.659	6	*	1.3969	1.3968	3	4 0 0
	3.594	4	*	1.3195	1.3194	2	−2 0 3
	3.474	4	*	1.3098	1.3099	3	1 1 2
3.3157	3.3154	35	0 0 1	1.3060	1.3059	3	−4 0 3
3.2464, 3.2453	3.2459	100	1 1 0, −2 0 1	1.2968	1.2968	3	2 2 1
2.8424	2.8423	35	−1 1 1	1.2935	1.2936	5	1 3 0
2.7938	2.7938	18	2 0 0	1.2839, 1.2837	1.2839	6	−4 2 1, −5 1 2
	2.0544	3	*	1.2791	1.2791	4	−3 1 3
2.0257	2.0255	12	−2 0 2	1.2749	1.2750	3	0 2 2
2.0084	2.0084	18	1 1 1	1.2633	1.2634	3	−1 3 1
1.9943	1.9944	12	0 2 0	1.2616	1.2616	3	3 1 1
1.9768	1.9767	20	−3 1 1	1.2587	1.2586	4	−4 2 2
1.7288	1.7287	9	−1 1 2	1.1726	1.1726	2	−1 1 3
1.7090, 1.7085	1.7086	18	0 2 1, −3 1 2	1.1541	1.1542	4	1 3 1
1.6991	1.6990	10	−2 2 1	1.1537	1.1537	4	−5 1 3
1.6876	1.6877	9	3 1 0	1.1480	1.1481	3	−3 3 1
1.6779	1.6778	6	−4 0 1	1.1441	1.1442	3	4 2 0
1.6579	1.6579	4	0 0 2	1.1380	1.1379	2	−6 0 2
1.6232, 1.6226	1.6231	10	2 2 0, −4 0 2	1.1004	1.1005	2	−2 2 3
	1.6093	3	*	1.0928, 1.0926	1.0926	3	−1 3 2, −4 2 3

Note. For the indexed subcell, the Smith/Snyder Figure of Merit $F(30) = 197.7(0.004, 38)$ (10). Reflections marked by * are due to the superstructure. (The data were submitted to ICDD for publication in the PDF.)

80.0 mole% La_2O_3. It contains the peaks of both $Bi_2La_4O_9$ and La_2O_3. This also demonstrates that $Bi_2La_4O_9$ coexists with La_2O_3 in the compositional range from $x = 66.7$ to 100 mole% La_2O_3. The observations clearly indicate that $Bi_2La_4O_9$ is a distinct compound with an individual structure.

$Bi_2La_4O_9$ is a stable compound. DTA results showed that it has no measurable phase transition up to 1100°C. The compound melts above 1350°C.

Like $Bi_{2.4}La_{3.6}O_9$, also $Bi_2La_4O_9$ exhibits some weak unindexed reflections (Fig. 1c). The main peaks can be indexed using a monoclinic subcell with lattice parameters

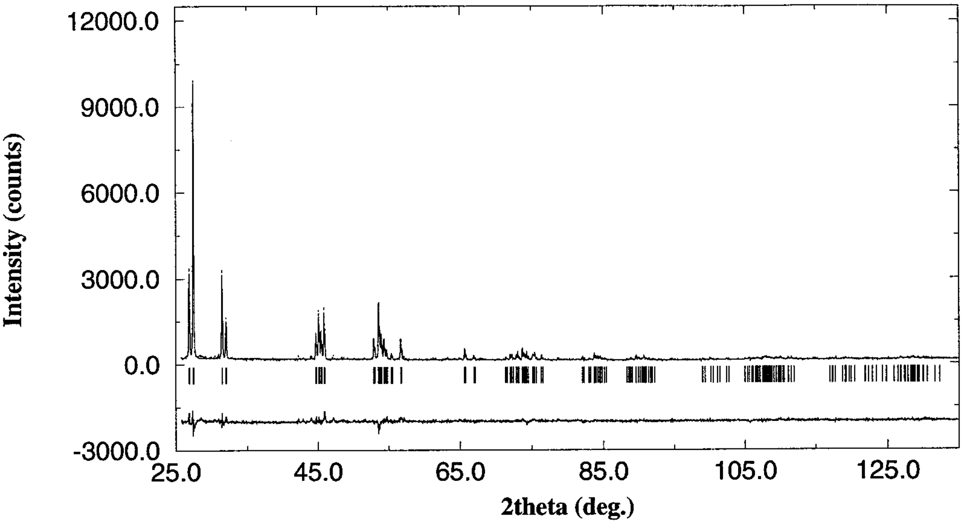

FIG. 2. The Rietveld refinement pattern of $Bi_2La_4O_9$. Small points represent the experimental values and solid lines the calculated pattern. The solid line at the bottom is the difference between the experimental and calculated values.

TABLE 2
$Bi_2La_4O_9$: Final Rietveld Refined Parameters from X-ray Powder Diffraction Data, $R_{Bragg} = 7.9\%$, $R_{wp} = 11.38\%$, $R_p = 8.66\%$, $R_{exp} = 6.73\%$

Atom	Site	x/a	y/b	z/c	$B(Å^2)$	Occupancy
La	2*a*	0	0	0	1.8(3)	0.667
Bi						0.333
O	4*i*	0.282(3)	0	0.741(4)	1.5(5)	0.75

Bond length Bi(La)–O: 2.46(2) × 2 2.35(1) × 3 2.67(2) × 3

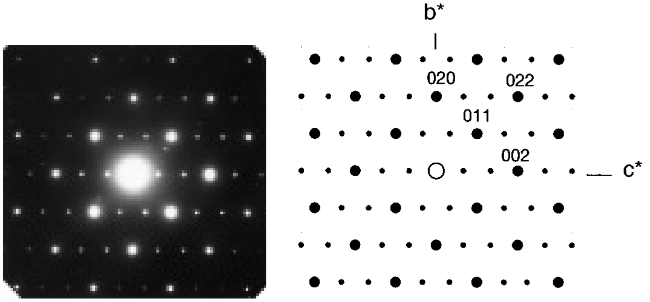

FIG. 4. Electron diffraction pattern of $Bi_2La_4O_9$. Indices refer to the body-centered cell. Electron beam is parallel to [100]. Superstructure along [001] with a period 3 × *c* (horizontal direction).

$a = 6.8290(3)$ Å, $b = 3.9887(1)$ Å, $c = 4.0524(1)$ Å, and $\beta = 125.094(3)°$. Table 1 presents its powder data. The observed condition for reflections allow for the space groups *C*2/*m*, *C*2, or *Cm*. The cell can be transformed to another setting with $a = 5.589$ Å, $b = 3.989$ Å, $c = 4.052$ Å, and $\beta = 91.30°$, corresponding to the space groups *I*2/*m*, *I*2, or *Im*. It is evident that the cell parameters of this body-centered cell are closely related to that of fluorite type δ-Bi_2O_3(fcc) by the relations $b \approx c \approx (\sqrt{2}/2)\ a_F$, $a \approx a_F$. Since the uninexed diffraction peaks are weak, the approximate crystal structure could be refined with the subcell.

Because of the apparent close relationship with the fluorite structure, calculations were performed with starting positional parameters according to those of the classical cubic fluorite. The subcell then should contain one $(Bi, La)_2O_3$. Starting with *C*2/*m*, the Bi and La atoms were put statistically on the site 2*a*(0, 0, 0) with the initial ratio La/Bi = 2.0. The oxygen atoms were set on the site 4*i*(*x*, 0, *z*) with $x = 0.25$ and $z = 0.75$. The occupancy factor for oxygen was set to 0.75, corresponding to 3 oxygen atoms in the cell. Under these conditions and with the isotropic thermal parameters fixed to 1 $Å^2$, the agreement factor of the initial refinement R_{wp} was 18.3%. Successive refinements of the positional parameters of oxygen and the isotropic thermal parameters lead to $R_{wp} = 11.3\%$, $R_p = 8.77\%$. At this stage refinement of the ratio Bi/La while keeping their isotropic thermal parameter fixed confirmed that the ratio Bi/La = 1:2. Attempts with space groups *C*2 and *Cm* only yielded larger agreement factors. Hence, the most probable space group is *C*2/*m*. The result of the final Rietveld refinement is plotted in Fig. 2. Table 2 gives the structural parameters of the final refinement. Figure 3 shows the average crystal structure of $Bi_2La_4O_9$.

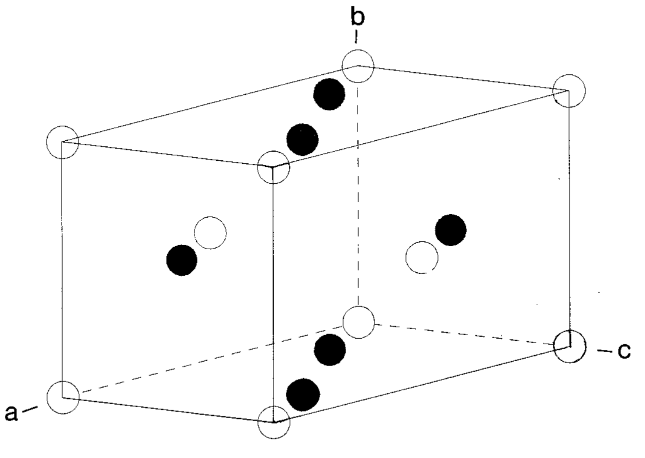

FIG. 3. The crystal structure for $Bi_2La_4O_9$. The open circles stand for La or Bi atoms and the filled circles for oxygen.

DISCUSSIONS

The bond lengths for Bi(La)–O range from 2.345 to 2.673 Å. These values are in good agreement with the known values. The average coordination number of the cations is 6 as in δ-Bi_2O_3. The polyhedron, however, is deformd due to some oxygen shift. The isothermal temperature factors *B* for (Bi, 2La) and O are 1.8(5) $Å^2$ and 1.5(5) $Å^2$, respectively. The values are rather large. Comparably large *B* values were observed for $Bi_{0.7}La_{0.3}O_{1.5}$ [*B*(La, Bi) = 0.91–1.35 $Å^2$, *B*(O) = 1.40–4.93 $Å^2$] (3) and $Bi_8La_{10}O_{27}$ [*B*(La, Bi) = 1.6–2.5 $Å^2$, *B*(O) = 1.9–6.3 Å] (4). The large *B* values in the present case may be attributed to ordering phenomena. It should be noted that the *B* values for La and Bi are larger than those for the light oxygen atoms. Hence, the ordering of the metal atoms is rather probable. Correspondingly, preliminary TEM investigations revealed the existence of a superstructure in $Bi_2La_4O_9$. Figure 4 shows the electron diffraction pattern along [100] of the body-centered cell. Strong spots originate from the average structure, while weak spots indicate a possible triple superstructure along [001] of the body-centered cell. However, no proper superstructure cell could be found so far which allows to index also all weak X-ray powder diffraction peaks. Further TEM investigations are needed.

In the present study, the hexagonal phase reported for $Bi_2La_4O_9$ by Horyń *et al.* (5) was also found, but for the slightly different composition $Bi_{2.4}La_{3.6}O_9$. This discrepancy may be due to the different syntheses conditions.

On the basis of our results, Wolcyrz *et al.* (private communication, 1996) did some reinvestigations and showed that $Bi_2La_4O_9$ converts from their hexagonal to our monoclinic structure by annealing it for 13 days at 900°C. This proves two polymorphic forms, of which the monoclinic structure is obviously the more stable one.

Finally, $Bi_2Nd_4O_9$ was also synthesized and found to be isostructural to the monoclinic $Bi_2La_4O_9$. Its lattice parameters are $a = 6.7066(3)$ Å, $b = 3.9002(2)$ Å $c = 3.9583(2)$ Å, and $\beta = 125.233(5)°$. Attempts to synthesize other isostructural compounds with further lanthanide ions failed, indicating that the structure is only stable with the largest cations La^{3+} and Nd^{3+}.

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