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Evidence for a New Monoclinic Bi–La Oxide Solid Solution: Identification and Structural Relationship to the Rhombohedral Bi–Sr–O Type

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As a term of the Bi–Sr–O rhombohedral type $Bi_{1-y}La_yO_{1.5}$ solid solution, the $Bi_{17}La_4O_{31.5}$ mixed oxide (y no. 0.19) has been investigated. Air-quenching from the high temperature domain of the β_1 disordered form allows one to preserve at room temperature a metastable form of β_1. This form transforms exothermally on heating near 200°C to a new monoclinic phase. This transformation and the transition monoclinic phase → stable ordered rhombohedral β_2, which occurs at 445°C, are both irreversible on cooling for this composition. The $\beta_2 \rightarrow \beta_1$ transition occurs reversibly near 660°C, under usual dynamic conditions ($300^\circ\,h^{-1}$). The monoclinic cell lattice constants, $a = 9.492(2)$, $b = 7.951(2)$, $c = 7.028(2)$ Å, $\beta = 104.74(1)^\circ$, lead to $Z = 12$ for the unit formula $Bi_{0.81}La_{0.19}O_{1.5}$ and imply a disordered cationic sublattice. This mixed oxide appears as a term of a new variety of a wide solid solution (that will name ε hereafter). © 2000 Academic Press

Key Words: **bismuth lanthanum mixed oxide; phase transition; Bi–Sr–O rhombohedral type; metastable phase; monoclinic-hexagonal relationship; cationic layered structure.**

INTRODUCTION

The so-called Bi–Sr–O rhombohedral structural type, based on the crystal structure of $Bi_{0.851}Sr_{0.149}O_{1.425}$ (1) is observed for numerous Bi-based mixed oxide solid solutions with alkaline earth (2–4), as well as lanthanide or Y (5–8), alkaline earth + lead (9, 10), La + Ce + M_{II} (M_{II} = Ba, Pb), La + M_{VI} + M_{II} (M_{VI} = Mo, W; M_{II} = Ba, Pb) (11). Since the initial structure determination (1), many single-crystal studies, at room temperature, of the variety named β_2 have been carried out by X-ray diffraction (4, 12–14) or by neutron diffraction (15); investigations of powder samples of this phase have also been realized either by neutron diffraction (15, 16), by electron microscopy (17, 18), or by X-ray diffraction (19).

The structure consists of cationic slabs parallel to (001) faces of the hexagonal cell: in each slab, two Bi^{3+} layers sandwich a mixed Bi^{3+}/M^{n+} layer, and two oxygen sites, $O_{(1)}$ and $O_{(2)}$ are located. Complementary oxide ions ($O_{(3)}$) are distributed over one or two sites of the interslab space and are characterized by partial occupancy factors, thus ensuring interslab cohesion. A high-temperature form (β_1) with an hexagonal closely related structure is generally observed. The $\beta_2 \rightarrow \beta_1$ transition, which occurs in all cases with a fast increase of conductivity, is accompanied by a sudden enlargement of the cell parameters (7, 8, 12, 19), which can be attributed to a cationic disordering in the mixed layer and to the migration of the $O_{(2)}$ ions toward the interslab space. When reported, the evolution versus composition of the transition temperature and enthalpy, the isothermal conductivities and activation energies of β_2, and the expansion of c-cell parameter during transition, exhibit either maxima or minima values; for Bi_2O_3–MO systems, these extrema have been linked to the existence of one (M = Ca, Ba) or two (M = Sr) kinds of cationic ordering in the mixed sandwiched layers of the β_2 form, leading to one or two kinds of superstructure. Identification of triclinic supercells has been possible only by single-crystal investigation (18), because no X-ray line characteristic of a superstructure can be observed in powder X-ray diffraction patterns.

The presence of breaking points in the evolution of the cell parameters versus composition for the $Bi_{1-y}La_yO_{1.5}$ solid solution is likely to indicate the presence of such a superstructure for each corresponding composition range (11).

The drastic increase of the conductivity during the $\beta_2 \rightarrow \beta_1$ transition seems to indicate that the disordering of sandwiched cations occurs rapidly and entirely. The decrease of the conductivity of β_2, when the ceramics, initially quenched from β_1 high temperature domain, are annealed (12, 20), indicates that the cationic ordering is occurring slowly.

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This paper deals with the chronology of a sample investigation of the $Bi_{1-y}La_yO_{1.5}$ solid solution; it has been done in order to identify this ordering scheme and the related structural sequence.

EXPERIMENTAL

$Bi_{17}La_4O_{31.5}$ powder sample has been prepared by solid-state reaction of Bi_2O_3 and La_2O_3 oxides (purities of 99.9%); the reactants were prefired in air at 600 and 950°C, respectively, for dehydration and decarbonation. The composition was selected taking into account the anomalies previously observed for the cell parameter evolution (11). Stoichiometric proportions were accurately weighted and intimately ground in an agate mortar. The mixture was transferred into an alumina crucible and heated for successive 15-h treatments at 650, 800, and 850°C. Each thermal treatment was ended by an air quenching and followed by a regrinding. The purity of the hexagonal phase, checked by X-ray diffractometry using a Guinier de Wolff camera ($CuK\alpha$ radiation), characterized the end of the synthesis.

Further annealing thermal treatment was also realized on the sample, taking into account the results of the thermal behavior investigation of quenched material.

Powder diffraction data were obtained on a Siemens D5000 diffractometer using a Bragg Brentano geometry, with a back monochromatized $CuK\alpha$ radiation. Diffraction diagrams were scanned by steps of 0.02° (2θ) over the 15–80° angle range, with a counting time of 1.5 s per step. The sample was rotated at $3.14\ \mathrm{rad\,s^{-1}}$ during the data recording in order to minimize the orientation effects resulting from the material compactness. The positions of the peaks were determined by means of the software package DIFFRACT-AT from SOCABIM.

The sample thermal behavior has been investigated by two different techniques:

(1) X-ray thermodiffractometry using a Guinier Lenne camera (heating or cooling rate $\cong 10$–$20°\mathrm{h}^{-1}$). The sample was deposited on the sample holder (gold grid) using an ethanol slurry which yields upon evaporation, a regular layer of powdered compound.

(2) Thermal analysis was conducted on a Setaram 92-1600 apparatus. Analysis was performed using platinum crucibles, with heating or cooling rate $300°\mathrm{h}^{-1}$, temperature range 20–850°C.

RESULTS AND DISCUSSION

A careful examination of the lattice constants versus composition dependence for annealed samples (620°C for 3–7 days) of $Bi_{1-y}La_yO_{1.5}$ solid solution (11) has evidenced different linear domains with breaking points for y values close to 0.18, 0.275, and 0.333. The composition $y = 0.333$, evidently, corresponds to a particular layered structure with sandwiched cationic layers occupied only by lanthanum. The two other compositions are likely to correspond to the hypothetical cationic ordered phases, presumed from our previous investigation (19).

Taking into account the previous results obtained for the bismuth–strontium–oxide phase (12), which has indicated the formation of a supercell with sandwiched cationic layers containing 4 Bi/3 Sr, a careful examination of the sample corresponding to $y = 4/21$, no. 0.190, which corresponds to the occupancy of the mixed layers by 4 La/3 Bi, seems of interest to us.

Two complementary investigations were realized on the sample finally quenched from 850°C (β_1 domain), in order to interprete the particular lattice constants versus composition dependence observed for the annealed solid solution.

The cell parameters have been refined from 25 reflections. The results ($a = 4.008(1)$, $c = 27.77(1)$ Å) evidence a significant departure from the results obtained for the sample annealed at 620°C ($a = 4.0148(5)$, $c = 27.702(5)$ Å; β_2 domain). This difference between a quenched sample and an annealed sample implies that quenching β_1 leads to a disordered form of β_2 (or quenched β_1), which under further annealing at 620°C (3–7 days) transforms into ordered β_2.

X-ray diffraction pattern of the quenched sample has been recorded during a progressive heating ($\cong 18°\mathrm{h}^{-1}$) from 20 to 700°C (Fig. 1). Surprisingly, between 200 and 445°C, we observe the replacement of the characteristic pattern of the hexagonal phase by a new set of reflections. Over 445°C, a diffraction pattern analogous to the initial pattern is restored. At 660°C, the $\beta_2 \rightarrow \beta_1$ transition is evidenced by a small and sudden shift of the lines. The filiation between the new set of reflections and β_2 diffraction data, obtained at temperature below 200 and over 445°C, shows that a new structural form is obtained in a monoclinic system, closely related to the rhombohedral Bi–Sr–O

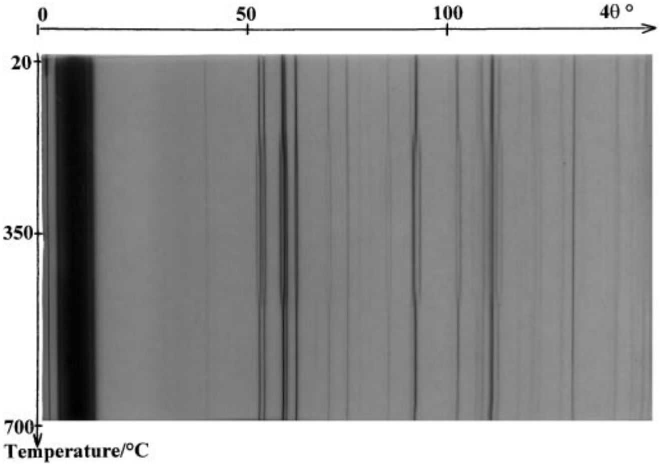

FIG. 1. Thermodiffraction pattern for the $Bi_{17}La_4O_{31.5}$ sample quenched from 800°C.

type structure. We can presume that somehow the layered organization is preserved. The metastable character of disordered β_2, at room temperature, which can be expected from the identified structural sequence, is confirmed by differential thermal analysis (Fig. 2). During the heating run, the DTA thermogram exhibits a broad exothermal effect in the 200–300°C temperature range and it is followed by an endothermal peak near 445°C, which characterizes the monoclinic → hexagonal structural transformation; contrary, to these two thermal effects, the endothermal peak which characterizes the $\beta_2 \rightarrow \beta_1$ transition at 660°C, is reversible during the sample cooling. The absence of $\beta_2 \rightarrow$ monoclinic transformation during cooling, confirms that β_2 is the stable phase at low temperature.

The monoclinic cell has been identified using a significant mass of disordered β_2, subsequently annealed at 300°C for 60 h. The room-temperature X-ray diffraction pattern has been recorded using a Siemens D5000 diffractometer. A monoclinic cell of this new phase has been identified from 21 reflections using the TREOR indexing program (21, 22) with figures of merit $M(20) = 11$ and $F(20) = 15$. From this solution, the lattice constants have been refined using 35 reflections: $a = 9.492(2)$, $b = 7.951(2)$, $c = 7.028(2)$ Å, $\beta = 104.74(1)°$. Table 1 lists the indexed powder X-ray diffraction pattern. The cell volume ratio: $\text{volume}_{\text{monoclinic cell}}/\text{volume}_{\text{hexagonal cell}} = 1.327 \cong 4/3$, implies 12 unit formula $Bi_{0.81}La_{0.19}O_{1.5}$ per monoclinic cell.

A relationship between the monoclinic lattice and the hexagonal cell of β_2 or β_1 form was easily understood from the crystal data comparison. Considering the crystallographic cell obtained for a quenched sample,

$$a_{\text{hex.}} = 4.0148(5), \quad c_{\text{hex.}} = 27.702(5)\ \text{Å},$$

$$b_{\text{mon. cell}}/a_{\text{hex. cell}} = 1.984 \cong 2, \quad c_{\text{mon. cell}}/a_{\text{hex. cell}} = 1.753 \cong \sqrt{3},$$

$$(a_{\text{mon. cell}} * \sin\beta)/c_{\text{hex. cell}} = 0.331 \cong \tfrac{1}{3},$$

$$(a_{\text{mon. cell}} * \cos\beta)/(a_{\text{hex. cell}} * \sqrt{3}) = -0.348 \cong -\tfrac{1}{3},$$

it appeared that the parameters of the monoclinic unit cell are related to those of the hexagonal cell of β_2 or β_1 according to

$$\left|\begin{matrix} a_{\text{mon.}} \\ b_{\text{mon.}} \\ c_{\text{mon.}} \end{matrix}\right| = \left|\begin{matrix} -\frac{2}{3} & -\frac{1}{3} & \frac{1}{3} \\ 0 & -2 & 0 \\ 2 & 1 & 0 \end{matrix}\right| * \left|\begin{matrix} a_{\text{hex.}} \\ b_{\text{hex.}} \\ c_{\text{hex.}} \end{matrix}\right|.$$

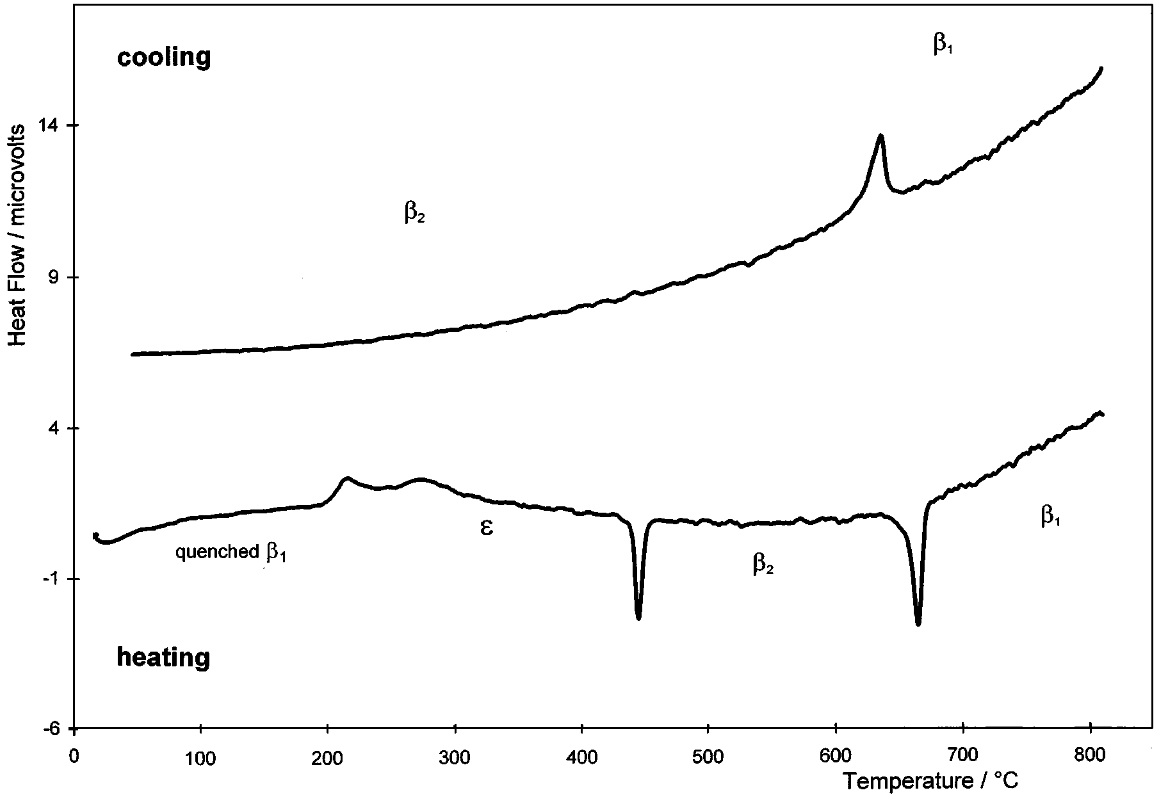

FIG. 2. DTA thermogram for the $Bi_{17}La_4O_{31.5}$ sample quenched from 800°C.

TABLE 1
Powder X-ray Diffraction Data for $Bi_{17}La_4O_{31.5}$—
ε Monoclinic Form

h	*k*	*l*	*d* (obs)	*d* (calc)	I/I_0 (%)
2	0	0	4.5911	4.5898	6
−1	0	2	3.4905	3.4890	18
0	2	1	3.4309	3.4316	36
0	0	2	3.3990	3.3984	16
−1	2	1	3.3576	3.3589	33
−2	0	2	3.1412	3.1398	64
1	2	1	3.0846	3.0869	100
3	0	0	3.0587	3.0599	70
1	0	2	2.9535	2.9519	38
−2	2	1	2.9336	2.9351	70
−3	0	2	2.6316	2.6310	6
2	2	1	2.5925	2.5933	10
−3	2	1	2.4461	2.4451	18
−4	0	2	2.1767	2.1758	6
3	2	1	2.1516	2.1507	9
−4	2	1	2.0317	2.0320	13
−1	2	3	2.0192	2.0183	44
3	3	0	2.0051	2.0033	15
4	2	0	1.9856	1.9875	28
−5	0	2	1.8201	1.8205	20
2	1	3	1.8040	1.8047	27
5	2	−1	1.7134	1.7129	24
4	2	−3	1.6899	1.6900	26
4	3	−2	1.6808	1.6817	49
5	2	0	1.6661	1.6668	24
1	4	2	1.6488	1.6488	12
4	2	2	1.5717	1.5714	5
4	1	−4	1.5400	1.5401	7
6	2	−1	1.4690	1.4693	8
6	3	−1	1.3582	1.3579	4
5	4	0	1.3492	1.3487	6
5	4	−2	1.3428	1.3425	10
6	0	2	1.2786	1.2786	11
3	5	−3	1.2659	1.2662	7
6	4	0	1.2124	1.2124	10

The corresponding relationship between the two cells is presented in Fig. 3. Each cross section corresponding to a bismuth or (bismuth/lanthanum) layer contains one cation for an hexagonal cell or four cations for the monoclinic cell. The cell cationic content (9.712 Bi + 2.286 La), would accordingly exhibit a statistical distribution over the different crystallographic sites, and therefore the sample corresponds to a term of a solid solution. Two ordered cationic structures are potentially possible in the composition range of the Bi–La–O (β_2/β_1) solid solution: $Bi_8(Bi_2La_2)O_{18}$ and $Bi_8(BiLa_3)O_{18}$ with, respectively, $y = 0.166$ and 0.25. These compositions are currently being investigated. The monoclinic structure is being determined and confirms the discovery of a new Bi–La–O phase that we will baptise ε.

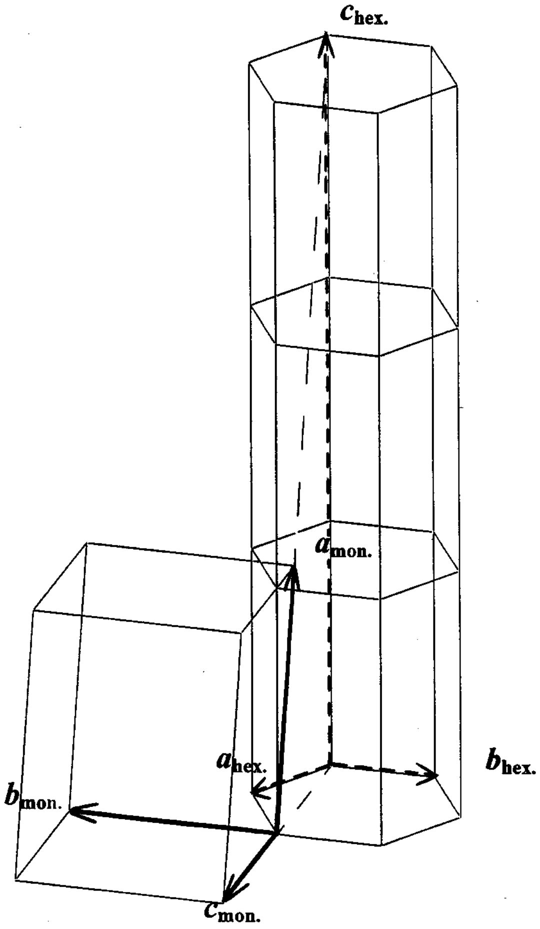

FIG. 3. Relationship between the hexagonal and the monoclinic cells.

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