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Structure Transformations in $BiLa_2O_{4.5+\delta}$

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DEDICATED TO PROFESSOR JAN KLAMUT ON THE OCCASION OF HIS 60TH BIRTHDAY

Formation of the fluorite-related binary oxide $Bi_{1+x}La_{2-x}O_{3-1.5x+((1+x)/2)\cdot\bar{V}_{Bi}}$ has been studied under various temperature and oxygen pressure conditions. The phase covers a certain compositional interval within the Bi_2O_3–Bi_2O_5–La_2O_3 ternary system, being defined by the substitution parameter $0 \le x < 1/8$ and the average valency of Bi ions $3 \le \bar{V}_{Bi} < 5$. Within this domain of homogeneity the phase can exhibit three different but closely related polymorphic forms, namely rhombohedral, monoclinic, and triclinic. Only the monoclinic form is stable in air in the whole temperature range. The rhombohedral form transforms to the monoclinic form, most efficiently for $x = 0$. This structure transformation is irreversible and becomes noticeable in air at and above 900°C. The new triclinic form (space group $P\bar{1}$, $a = 3.921(1)$ Å, $b = 4.024(1)$ Å, $c = 5.623(1)$ Å, $\alpha = 87.62(1)°$, $\beta = 90.32(1)°$, $\gamma = 90.09(1)°$) develops from the monoclinic form when the latter is oxidized to the level given by $\bar{V}_{Bi} \ge +4$. This process is fully reversible. Oxidation of the rhombohedral form preserves its structure type and seems not to induce any structure transformation. As in the case of the monoclinic form, the process is accompanied by an effective increase of $\bar{V}_{Bi}$ above +4. Both oxidized forms are stable in air but not higher than up to 300–350°C. Above this temperature they release oxygen with a maximum speed at ca. 400°C and retransform back to the appropriate starting structures. © 1997 Academic Press

INTRODUCTION

A series of $Bi_3RE_5O_{12}$-type phases (RE = Y, La, and lanthanides) has been recently reported (1). The compounds are stable in air at 900°C and exhibit a comparatively wide compositional interval centered around the 3:5:12 stoichiometry. An exception is the La member of the series with its composition localized at 66.6 at.% La ($BiLa_2O_{4.5}$) rather than at 62.5 at.% La ($Bi_3RE_5O_{12}$).

Characteristic features of the series are:

1. trivalent state of Bi ions;
2. rhombohedral symmetry with a subcell in the $R\bar{3}m$ space group (2) showing evident signs of a superstructure with $8a_h \times 8a_h \times 2c_h$-type multiplication of the fluorite-related unit cell (a_h and c_h, the subcell parameters in hexagonal setting);
3. low molecular content of the subcell (three molecules of $MeO_{1.5}$ type) suggesting a random distribution of Bi and RE on the only cation positions and consequently the $Bi(RE_{2-x}Bi_x)O_{4.5}$-type general formula ($x = 1/8$) occurring within the 3:5:12 stoichiometry;
4. oxygen deficiency resulting in an overall oxygen content of 4.5 instead of 5 (or even 5.5). The deficiency has been proved with some easy oxidizable REs, such as Pr and Tb (1), the presence of which causes the oxygen content, even under sintering conditions in air, to reach five oxygen atoms in the unit cell.

In light of these features, an exceptional position of the phase $BiLa_2O_{4.5}$ within the $Bi_3RE_5O_{12}$-type series seems to be reasonably justified. Nevertheless, according to the results of X-ray and electron diffraction studies performed on the samples synthesized in air, the crystal structure of this compound does not require an ordered occupation of the Bi and La positions (2). That is why the compound is able to exist in a certain compositional interval (ca. 62.5–66.6 at.% La) given by the formula $Bi_{1+x}La_{2-x}O_{4.5}$ ($0 \le x \le 1/8$) rather than by $BiLa_2O_{4.5}$.

Recently, a paper on the crystal structure of a monoclinic form of $Bi_2La_4O_9$ obtained in air at ca. 1000°C has been published (3). According to it, the appropriate stoichiometry of the rhombohedral $BiLa_2O_{4.5}$ should be $Bi_2La_3O_{7.5}$ (60 at.% La) or $Bi(La_{1.8}Bi_{0.2})O_{4.5}$ if based on the subcell given in (1, 2). Both phases are considered in (3) as close neighbors existing in the binary Bi_2O_3–La_2O_3 system.

The aim of this work was to clarify the problem outlined above and to evaluate possible relations between the rhombohedral and monoclinic phases. We assumed that both structures might be some polymorphic forms of the same phase, with the structure transformation based on the reordering of the metal atoms, taking place at temperature between 950–1000°C.

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EXPERIMENTAL

Samples were prepared by solid state reaction of appropriate mixtures of $4N$ Johnson–Mathey La_2O_3 (freshly preheated overnight at 1000°C) and Bi_2O_3. The following compositions within the interval of 60–66.6 at.% La were made: $Bi_2La_3O_{7.5}$, $Bi_{1.875}La_{3.125}O_{7.5}$, $Bi_{1.800}La_{3.200}O_{7.5}$, and $Bi_{1.667}La_{3.333}O_{7.5} \equiv BiLa_2O_{4.5}$.

The first stage of the synthesis was performed at 800°C for 24 h to avoid the undesired melting of Bi_2O_3. Then, the mixtures were pelletized and fired in air at 900°C for 5 days with intermediate grinding. Finally, they were quenched in air on a copper plate to room temperature.

Phase analyses of the final products with subsequent determination of the lattice parameters were performed using DRON-3 and/or SIEMENS D5000 X-ray powder diffractometers (Cu$K\alpha$ radiation with Si or Cu as internal standards). Then, a subsequent sintering in air at 1000°C for 2 days was applied and the phase composition was determined again in the same manner.

A somewhat different procedure was applied to the sample of exact 1:2 stoichiometry ($BiLa_2O_{4.5}$), denoted below as sample A. As all the remaining samples, it was synthesized at 900°C resulting in the rhombohedral structure. Then, its total amount was divided into several portions, each subjected to further sintering and thermal treatment (cp. scheme in Fig. 1), namely:

1. To long-term (14 days) annealing in air at 900°C, accompanied by a periodic X-ray analysis performed after every 24 h. The aim of this treatment was to evaluate the thermal stability of the rhombohedral form and its possible changes vs time.
2. To sintering at 1000°C for 2 days to transform the rhombohedral form to the monoclinic one according to (3). The final product of this treatment is denoted sample B.

Both forms (A and B) were subjected to oxidation in pure oxygen of normal and elevated pressure at ca. 400 bar, the latter in a high pressure furnace by Morris Research. This was done to see to what extent they were able to bound extra oxygen at various temperatures. In the text, samples resulting from the oxidation at normal pressure and at 300°C for 24 h are denoted A^n and B^n while those oxidized at elevated pressure and at 750°C for 12 h are denoted A^h and B^h.

The temperature of normal pressure oxidation (300°C) was intentionally chosen with respect to the TG results which proved it as an optimal for oxygen uptake. The temperature of high-pressure oxidation (750°C) was chosen to avoid the possible transformation of the rhombohedral form (A) to the monoclinic form (B) noticed during long-term thermal treatment described in item 1 of the Experimental section.

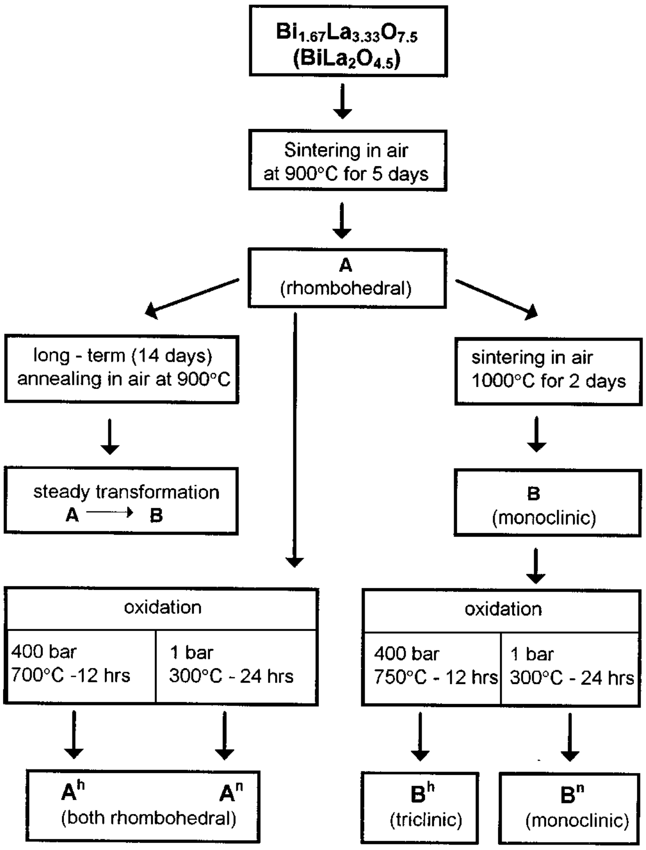

FIG. 1. Thermal treatment applied to the $BiLa_2O_{4.5}$ samples of exact 1:2 stoichiometry.

All single-phase samples of 1:2 stoichiometry were subjected to iodometric titration, in order to determine the average valency of the Bi ions, and to density measurements. The appropriate procedures have been described in (4). Additionally, thermogravimetric (TG) and differential thermal analysis (DTA) curves were collected with a Linseis L-81 thermobalance.

RESULTS AND DISCUSSION

According to our results, under sintering in air at 900°C, the Bi_2O_3–La_2O_3 binary system does not contain the monoclinic $BiLa_2O_{4.5} \equiv Bi_2La_4O_9$ phase. In the $Bi_2La_3O_{7.5}$ and $Bi_{1.875}La_{3.125}O_{7.5}$ samples we have identified the rhombohedral phase with traces of $Bi_8La_{10}O_{27}$ (5) (Fig. 2). The rhombohedral phase appears as a single phase in the $Bi_{1.8}La_{3.2}O_{7.5}$ and $BiLa_2O_{4.5}$ samples, which is in full agreement with our previous results (1). In this light, the rhombohedral structure should be described by the formula $Bi_{1+x}La_{2-x}O_{4.5}$ with $0 \leq x < 0.125$ at 900°C.

At 1000°C, the only single-phase sample of the rhombohedral structure is $Bi_{1.875}La_{3.125}O_{7.5}$ (Fig. 3). The sample $Bi_2La_3O_{7.5}$ remains two-phase as at 900°C while sample B, i.e., $Bi_{1.667}La_{3.333}O_{7.5} \equiv BiLa_2O_{4.5}$, represents

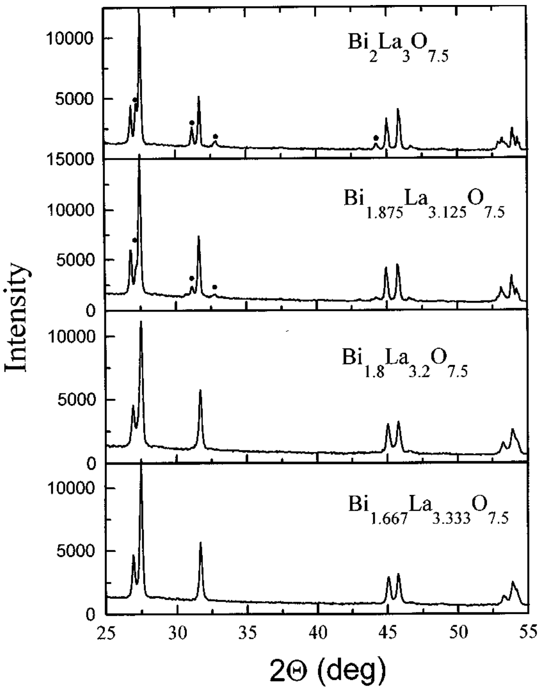

FIG. 2. X-ray powder diffraction diagrams of samples in the system Bi_2O_3–La_2O_3 (60–66.6 at.% La) at 900°C in air. The major phase present corresponds to the rhombohedral form of $Bi_{1+x}La_{2-x}O_{4.5}$. Dark spots indicate traces of $Bi_8La_{10}O_{27}$.

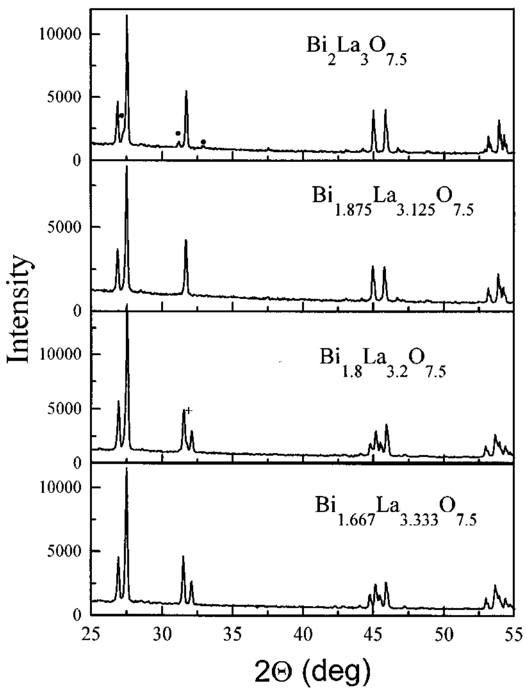

FIG. 3. X-ray powder diffraction diagrams of the same series as in Fig. 2 taken after sintering in air at 1000°C. Dark spots indicate traces of $Bi_8La_{10}O_{27}$ while the cross denotes a weak peak of the rhombohedral form of $Bi_{1+x}La_{2-x}O_{4.5}$. The pure monoclinic form of this phase is seen in $Bi_{1.667}La_{3.333}O_{7.5} \equiv BiLa_2O_{4.5}$.

fully the monoclinic phase in agreement with the results reported in (3). The phase composition of the intermediate sample $Bi_{1.8}La_{3.2}O_{7.5}$ is somewhat surprising. Admittedly, this sample is composed, as expected, of both phases. Nevertheless, the amount of the rhombohedral phase in it is too small. The only explanation of this fact seems to be a polymorphic transformation from rhombohedral to monoclinic structure, the kinectics of which would strongly depend on the sample composition.

Long-term Annealing in Air

To prove that the monoclinic structure develops from the rhombohedral structure (most efficiently at the preferential composition 1:2) as a result of a polymorphic transformation taking place at a certain temperature between 900 and 1000°C, a long-term annealing of the rhombohedral phase of this "preferential" composition (sample A) has been performed in air. It revealed indeed that the transformation takes place at 900°C (Fig. 4). However, at this temperature it proceeds slowly and it is practically undetectable until the eighth day. This low speed indicates a diffusional nature of the transformation, probably connected with reordering of the metal atoms. A possibility for an ordering of Bi and La ions in monoclinic $BiLa_2O_{4.5}$ is also suggested in (3). Such an ordering seems to be easy since, as evident from (2, 3), both structures are very closely related.

At temperatures higher than 900°C the transformation accelerates effectively and at 1000°C it becomes difficult to record vs time. The character of the transformation taking place in the 1:2 sample was derived from the tests performed on samples with more than 33.3 at.% Bi. It occurred that such samples require higher temperatures and longer annealing to undergo complete transformation. In this light, the two-phase state of the $Bi_{1.8}La_{3.2}O_{7.5}$ sample mentioned earlier (Fig. 3) with the surprisingly low content of the rhombohedral phase may as well be a result of too short (2 days) firing at 1000°C.

Interesting to note is that the transformation has been found to be irreversible; i.e., the monoclinic form does not retransform back to the rhombohedral form in air below 900°C. This proves indirectly a reordering of the Bi and La ions rather than an uptake or loss of oxygen. In the latter case the process should be reversible. The last possibility, namely a variation of the overall oxygen content as the main reason for the transformation, has been denied based on the TG curves obtained for both structure forms. The results of the iodometric titration applied to samples A and B have also definitively excluded the structure transformation to be activated by a loss of extra oxygen present in the

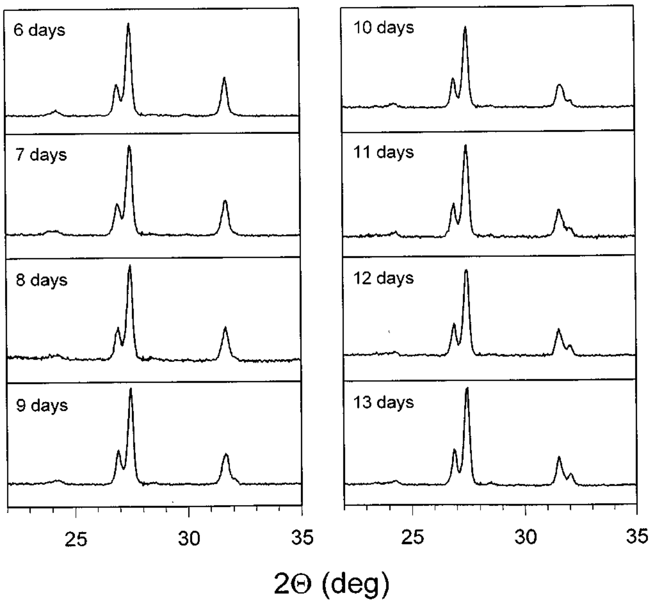

FIG. 4. X-ray diffraction diagrams of $BiLa_2O_{4.5}$ illustrating transformation of the rhombohedral form to the monoclinic form vs time at 900°C in air.

rhombohedral form. As seen in Table 1 (samples A and B), the average valency of Bi ions in both structure forms is almost the same and close to + 3. Admittedly, a higher than normal average valency of Bi ions (ca. 3.4) was occasionally detected in some preliminary tests of the rhombohedral form, but those referred to the unquenched samples, left in the furnace for a slow cooling in air to room temperature. This very important feature has inspired us to undertake work on a possible effect of oxygen pressure on the stability of both forms at elevated temperatures.

Oxidation in Pure Oxygen

As expected, oxidation of the rhombohedral and the monoclinic polymorphs of $BiLa_2O_{4.5}$ under elevated oxygen pressure (400 bar, 750°C) has revealed an essential uptake of an extra oxygen. According to the results of iodometric titration (samples A^h and B^h in Table 1) both forms show an increase of the average valency of Bi ions which evidently exceeds + 4. This leads to an increase in the overall oxygen index and, as a consequence, leads to the formula $BiLa_2O_{4.5+\delta}$. Moreover, as evidenced by X-ray diffraction, incorporation of the extra oxygen causes the monoclinic form to undergo a structure transformation (sample B^h in Fig. 5). On the first glance it looks as if the new form would correspond exactly to the rhombohedral polymorph of sample A (Fig. 2) or its oxidized equivalent A^h. Note that oxidation of sample A (sample A^h in Fig. 5) has resulted in a clear change in the unit cell parameters and in density of the phase (cp. appropriate values in Table 1). A slight increase in the half-widths of the diffraction profiles observed for the A^h sample may admittedly indicate a subtle structure distortion. However, this is very difficult to prove at this stage of the investigations.

The TG analysis was applied to the oxidized samples A^h and B^h (Fig. 6). Note that the original TG data (loss of sample weight) have been recalculated and expressed in terms of sample oxygen index. This was done based on the results of the iodometric titration performed on freshly

TABLE 1
Crystallographical Parameters of $BiLa_2O_y$ Synthesized in Air at 900°C (A) and at 1000°C (B) and at 400 bar of Oxygen at 750°C (A^h and B^h)

Specification	A	A^h	B	B^h
Crystallographic system	Rhombohedral	Rhombohedral (?)	Monoclinic	Triclinic
Space group	$R3m$	$R3m$	$C2/m$	$P\bar{1}$
Lattice parameters for the subcell (Å)	$a_h = 3.959$	$a_h = 3.927$	$a = 6.828$	$a = 3.921$
	$c_h = 9.926$	$c_h = 9.945$	$b = 3.992$	$b = 4.024$
			$c = 4.052$	$c = 5.623$
			$\beta = 125.10$	$\alpha = 87.62$
				$\beta = 90.32$
				$\gamma = 90.09$
Unit cell volume (Å)	134.73	132.81	90.36	88.64
Lattice parameters for the superstructure cell	$A = 8 \cdot a_h$	$A = 8 \cdot a_h$	?	?
	$C = 2 \cdot c_h$	$C = 2 \cdot c_h$		
Average valency of Bi ions $\bar{V}_{Bi}$	3.06	4.34	3.01	4.10
Overall oxygen index y	4.53	5.17	4.50	5.05
Number of $MeO_{1.5-\Delta}$ formal molecules in unit subcell[a]	3	3	2	2
Observed density (g/cm^3)	6.71	7.11	6.79	7.04
Calculated density (g/cm^3)	6.895	7.123	6.848	7.092

[a] Me = at.% Bi + at.% La. $\Delta = y/3 - 1.5$. y, oxygen index in the formula $BiLa_2O_y$.

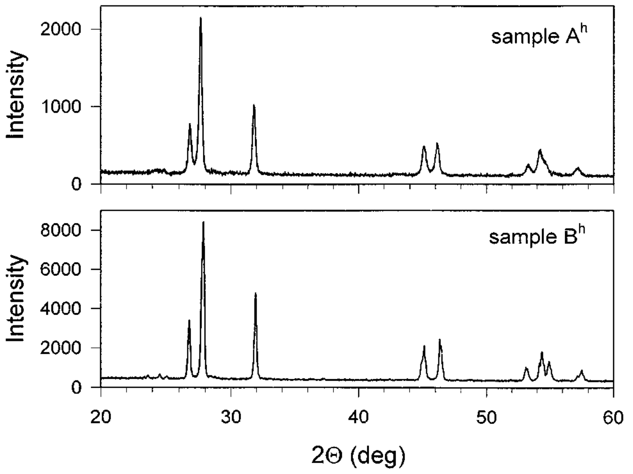

FIG. 5. X-ray diffraction diagrams of $BiLa_2O_{4.5+\delta}$ samples A^h and B^h after oxidation in pure oxygen at 400 bar and 750°C for 12 h.

prepared samples A^h and B^h as well as on the final products of TG analysis collected at 900°C. Due to this procedure, sample weight losses caused by the release of humidity could be precisely extracted.

In the case of identity of A^h and B^h crystal structures, the TG analyses should result in mutually identical curves. Moreover, depending on the upper limit of temperature applied, the final products of the TG analysis should be also the same, confirming the presence of either rhombohedral structures typical for sample A or the monoclinic structures typical for sample B. The latter result would occur due to the structure transformation which, as indicated earlier, happens to the rhombohedral form in air above 900°C.

Surprisingly, the TG curves of the A^h and B^h samples (Fig. 6) do not confirm the supposition given above. They differ too much to consider the observed release of oxygen as taking place in structurally identical phases. First, the oxidized rhombohedral form (A^h) exhibits evidently a higher level of oxidation than that of the oxidized monoclinic form (B^h). Second, it releases oxygen in a different way than the B^h sample. From its two-step shaped TG curve we may conclude a much higher affinity to oxygen exhibited by the rhombohedral form. Note that even at 700°C this structure form preserves the average valency of the Bi ions as high as 3.3.

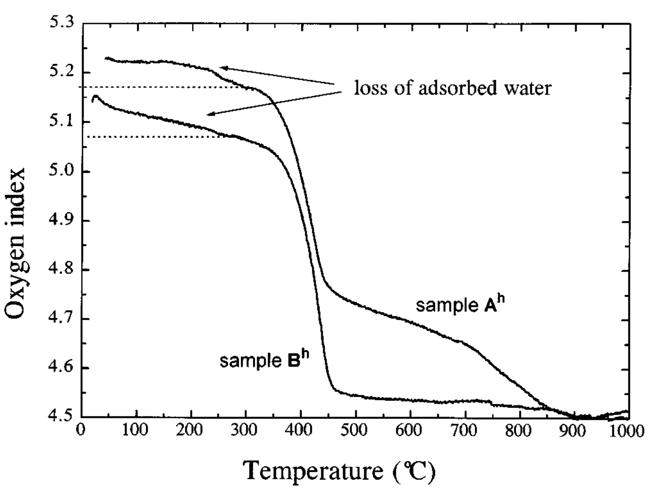

FIG. 6. Thermogravimetric curves of the $BiLa_2O_{4.5+\delta}$ samples A^h and B^h when they were heated in air with 5°C/min.

This feature has been fully confirmed in separate oxidation tests of both A and B samples performed at normal oxygen pressure at 300°C. The iodometric titration of the A^n and B^n samples obtained in the treatment mentioned above has revealed a high susceptibility for oxidation of the rhombohedral form ($\bar{V}_{Bi} = 3.40$) and a negligible one of the monoclinic form ($\bar{V}_{Bi} = 3.04$).

Apart from the TG curves, from which some essential differences in the crystal structures of the oxidized forms of $BiLa_2O_{4.5}$ have been deduced, X-ray diffraction diagrams of the products resulting from TG analysis (performed in air at 600 and 900°C) have indirectly proved the same feature. Those collected from either partly or fully deoxidized B^h sample exhibited the monoclinic starting structure. The rhombohedral form (sample A^h) was found to be insensitive to a structure transformation when exposed to deoxidization.

Crystal Structure of the Triclinic $BiLa_2O_{4.5+\delta}$

A direct proof confirming different structures of the oxidized forms of $BiLa_2O_{4.5}$ formed in the A^h and B^h samples was obtained via careful analysis of the X-ray diffraction diagrams. In Fig. 7, in the case of the B^h sample, a subtle splitting of the diffraction profiles is seen. The diffraction pattern of the A^h sample is free of such an effect. Preliminary simulations of X-ray powder diffraction diagrams have shown a possible triclinic distortion of the monoclinic structure reported in (3) for $BiLa_2O_{4.5}$. Lattice parameters for such a cell would be $a = 6.778$ Å, $b = 3.921$ Å, $c = 4.025$ Å, $\alpha = 90.14°$, $\beta = 124.05°$, and $\gamma = 90.18°$. This unit cell can be transformed to the equivalent one applying the transformation matrix

$$\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 1 \end{pmatrix}.$$

A new unit cell, closely related to the fluorite one, with lattice parameters $a \approx b \approx 4$ Å, $c \approx 5.6$ Å, and $\alpha \approx \beta \approx \gamma \approx 90°$ was accepted for the triclinic structure and applied in the successive Rietveld refinement using the Full Prof program (6) in space group $P\bar{1}$. The experimental and

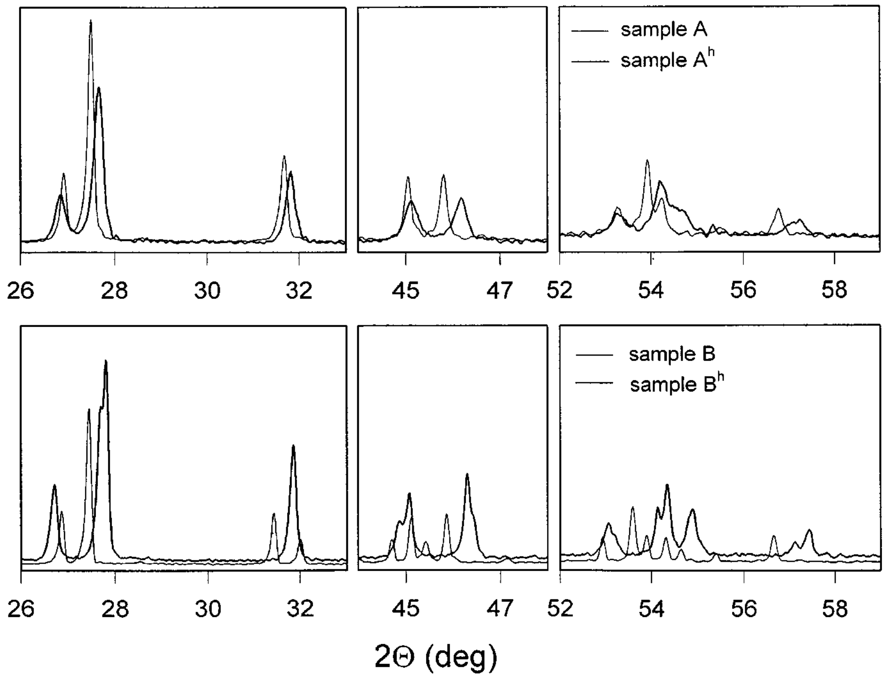

FIG. 7. A comparison of some selected ranges from X-ray diffraction diagrams of the samples A, B, A^h, and B^h. Note: for higher clarity, all diagrams in this figure were exceptionally subjected to a conventional stripping procedure eliminating Cu$K\alpha_2$ radiation.

calculated X-ray diffraction diagrams are shown in Fig. 8, whereas all refined structural parameters are collected in Table 2. Attempts to refine the structure in space group $P1$ have not resulted in a better fit, thus justifying the accepted $P\bar{1}$ symmetry. Additionally, a standard indexation procedure for all registered and well resolved peaks of the triclinic form was performed giving the lattice parameters $a = 3.921(1)$ Å, $b = 4.024(1)$ Å, $c = 5.623(1)$ Å, $\alpha = 87.62(1)°$,

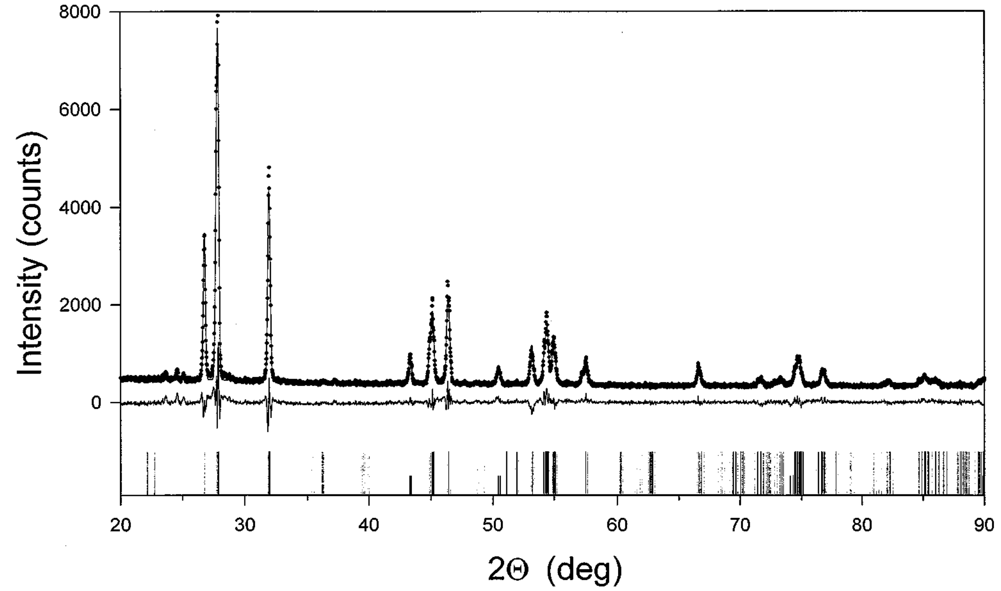

FIG. 8. Results of the Rietveld refinement of the triclinic form of $BiLa_2O_{4.5+\delta}$ (sample B^h). Dots in the upper diagram denote experimental data; full line, the Rietveld fit. Below, the differential diagram and peak positions are shown. Several short sticks denote copper peaks from sample holder. This phase was taken into account in the refinement as a second phase.

TABLE 2
Final Results of the Rietveld Refinement of the Triclinic $BiLa_2O_{4.5+\delta}$ (B^h Sample)

Atom	Wyckoff position	x	y	z	B (Å^2)	Occupancy
La(1)	1(*a*)	0	0	0	1.0	0.667
Bi(1)	1(*a*)	0	0	0	1.0	0.333
La(2)	1(*h*)	0.5	0.5	0.5	1.0	0.667
Bi(2)	1(*h*)	0.5	0.5	0.5	1.0	0.333
O(1)	2(*i*)	0.07(1)	0.35(1)	0.24(1)	1.5	0.779(6)
O(2)	2(*i*)	0.50(2)	0.01(2)	0.77(1)	1.5	0.779(6)

$R_p = 6.57\%$, $R_{wp} = 8.53\%$, $R_{Bragg} = 8.51\%$, $R_{exp} = 4.50\%$

Bond lengths

La/Bi(1)–O 2.04, 2.30, 2.34 2.85 Å (all × 2)

La/Bi(2)–O 2.44, 2.48, 2.54 2.66 Å (all × 2)

Note. Space group $P\bar{1}$; $a = 3.920(1)$ Å, $b = 4.023(1)$ Å, $c = 5.628(1)$ Å, $\alpha = 87.63(1)°$, $\beta = 90.29(1)°$, $\gamma = 90.09(1)°$.

TABLE 3
The Powder Data of the Triclinic $BiLa_2O_{4.5+\delta}$

d_{calc}	d_{obs}	$2\Theta_{obs}$	I_{rel} (%)	hkl
—	3.7506	23.703	4.2	*
—	3.6105	24.637	4.8	*
—	3.5385	25.146	3.5	*
3.3354	3.3353	26.706	38.6	0 1 1
3.2238	3.2227	27.657	74.6	1 0 −1
3.2069	3.2072	27.793	100.0	1 0 1
2.8089	2.8072	31.852	56.6	1 −1 0, 0 0 2
2.0198	2.0188	44.859	12.5	1 −1 −2
2.0101	2.0102	45.062	23.1	1 1 2, 0 2 0
1.9606	1.9599	46.286	27.6	1 1 −2, 2 0 0
1.9543	1.9551	46.405	23.1	1 −1 2
1.7251	1.7250	53.044	9.0	0 1 3, 1 −2 −1
1.7208	1.7209	53.181	8.4	1 2 1
1.6935	1.6929	54.132	12.2	1 0 −3
1.6869	1.6875	54.318	19.0	2 1 1, 1 2 −1
1.6743	1.6744	54.777	9.7	2 1 −1
1.6712	1.6711	54.896	12.9	2 −1 1, 0 1 −3
1.6119	1.6116	57.104	3.9	2 0 −2
1.6035	1.6029	57.443	7.7	2 0 2, 0 2 −2
1.4045	1.4043	66.529	5.8	0 0 4, 2 −2 0
1.3201	1.3200	71.403	1.9	1 −2 −3
1.3159	1.3159	71.658	2.6	1 2 3, 0 3 1
1.2988	1.2992	72.728	2.3	2 −1 −3
1.2914	1.2919	73.204	2.3	2 1 3, 0 3 −1
1.2731	1.2736	74.426	5.1	1 −1 −4, 2 −2 2
1.2715	1.2717	74.562	7.7	3 0 1, 1 2 −3
1.2686	1.2687	74.766	7.7	1 −3 0, 1 1 −4
1.2425	1.2428	76.600	5.5	2 2 −2, 3 1 0
1.2399	1.2396	76.838	4.5	1 −1 4, 2 −2 2
1.1744	1.1743	81.984	1.9	0 2 4, 1 −3 −2
1.1719	1.1721	82.171	1.9	1 3 2
1.1448	1.1445	84.600	1.9	2 0 −4, 3 −1 −2
1.1395	1.1393	85.076	3.2	3 1 2, 1 3 −2
1.1331	1.1331	85.654	1.9	3 1 −2
1.1295	1.1297	85.976	2.3	0 2 −4, 3 −1 2
1.0939	1.0939	89.526	1.9	2 −3 −1, 0 1 5
1.0913	1.0909	89.832	2.3	2 3 1

Note. $a = 3.921(1)$ Å, $b = 4.024(1)$ Å, $c = 5.623(1)$ Å, $\alpha = 87.62(1)°$, $\beta = 90.32(1)°$, $\gamma = 90.09(1)°$. For the indexed cell, the Smith/Snyder figures of merit are $F_{20} = 22.87$ (0.011, 81), $F_{34} = 21.99$ (0.011, 144). Reflections marked by * are due to superstructure.

$\beta = 90.32(1)°$, and $\gamma = 90.09(1)°$. Full data are presented in Table 3.

The triclinic $BiLa_2O_{4.5+\delta}$ has a distorted fluorite-type crystal structure (Fig. 9). Similarly to the rhombohedral and monoclinic forms, metal atomic positions in this structure are also commonly occupied by Bi and La ions. Very weak traces of superstructure observed as unindexed peaks in the diffraction pattern (cf. Table 3) indicate the existence of a weak ordering effect. The low symmetry of the discussed phase, the noticeable unit cell distortion, and the distinct shifts of the oxygen atoms cause some changes in the La(Bi)–O distances. As a result, the triclinic form exhibits two types of MeO_8 polyhedra with clearly different bond lengths (cp. Table 2). Note that according to (2) and (3) the rhombohedral and the monoclinic forms are characterized by only one type of highly oxygen-deficient MeO_8 polyhedra.

CONCLUSIONS

The most essential data concerning the $BiLa_2O_y$ phase can be summarized as follows:

1. The phase exhibits variable composition and its domain is defined by a variable ratio of Bi/La within the interval $0.5 \leq Bi/La < 0.6$ ($66.6 \leq$ at.% La < 62.5). This leads to a general formula $Bi_{1+x}La_{2-x}O_y$, with $0 \leq x < 1/8$.

2. The oxygen content of the phase appears to be variable and dependent on the average valency of the Bi ions ($\bar{V}_{Bi}$). This permits for a more precise specification of the formula given above, namely $Bi_{1+x}La_{2-x}O_{3-1.5x+((1+x)/2)\cdot\bar{V}_{Bi}}$, with $0 \leq x < 1/8$ and $3 \leq \bar{V}_{Bi} \leq 5$.

3. Under suitable temperature and oxygen pressure, the overall oxygen content can in principle reach a level of 5.625 or, at least, 5.5 (dependent on the Bi/La ratio) provided that $\bar{V}_{Bi} = 5$. Our tests performed on samples with Bi/La = 0.5 ($x = 0$) at 750°C under 400 bar of oxygen have permitted the oxygen level to reach 5.17, determined by $\bar{V}_{Bi} = 4.34$.

4. Within the domain of existence given in 1, the phase can exist in three, closely related crystallographic forms, namely rhombohedral (space group $R3m$) (2), monoclinic (space group $C2/m$) (3), and triclinic (space group $P\bar{1}$).

5. Mutual relation between the first two forms is such that the monoclinic form irreversibly develops from the rhombohedral form when the latter is heated in air at and above 900°C. The process probably consists of a

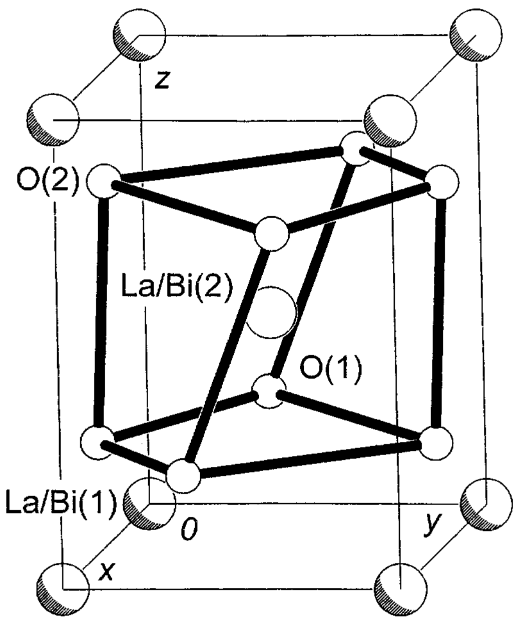

FIG. 9. The crystal structure of the triclinic $BiLa_2O_{4.5+\delta}$ (La/Bi(2) – O polyhedron is shown).

temperature-activated reordering of the Bi and La ions. It has been found that for a given temperature, the transformation proceeds most effectively at the exact 1 : 2 stoichiometry (66.6 at.% La). Samples of the rhombohedral form with higher Bi content exhibit steadily decreased sensitivity for the transformation and require either a higher temperature or a longer annealing for its complete occurrence. The average valency of the Bi ions in the monoclinic form never exceeds +3, whereas in the rhombohedral form (not quenched) it can vary in the range $3 \leq \bar{V}_{Bi} < 5$. In air, the rhombohedral form can exhibit $\bar{V}_{Bi}$ close to +3.5.

6. The triclinic form develops from the monoclinic form with oxidation under moderate conditions (750°C, 400 bar O_2). This fully reversible process seems to consist of a further reordering of the structure (probably the oxygen sublattice) caused by the amount of oxygen incorporated into the structure. Oxidation of the rhombohedral form seems not to induce any structure transformation.

7. At 300°C and under normal pressure of oxygen, only the rhombohedral form undergoes oxidation with $\bar{V}_{Bi} \approx 3.5$ as in air. The monoclinic form remains intact.

8. Both oxidized forms are stable when heated in air up to the temperature of ca. 300–350°C. Above this level they release oxygen with the maximum speed at ca. 400°C and retransform back to their starting structures.

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