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An Oxygen Deficient Fluorite with a Tunnel Structure: $Bi_8La_{10}O_{27}$

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A new lanthanum bismuth oxide, $Bi_8La_{10}O_{27}$, has been synthesized. It crystallizes in the *Immm* space group with the following parameters: $a = 12.079$ (2) Å, $b = 16.348$ (4) Å, $c = 4.0988$ (5) Å. Its structure was determined from powder X-ray and neutron diffraction data. It can be described as an oxygen deficient fluorite superstructure ($a \approx 3a_F/\sqrt{2}$, $b \approx 3a_F$, $c \approx a_F/\sqrt{2}$) in which bismuth and lanthanum, as well as oxygen vacancies, are ordered. The structure consists of fully occupied (110) or ($\bar{1}10$) lanthanum planes (La) which alternate with mixed $\{^{\mathrm{Bi}}_{\mathrm{La}}\}$ planes and fully occupied oxygen planes (A) which alternate with two sorts of oxygen deficient (110) or ($\bar{1}10$) planes (B and C) according to the sequence $-[\ \mathrm{La}\ A\ B\ \{^{\mathrm{Bi}}_{\mathrm{La}}\}\ C\ C\ \{^{\mathrm{Bi}}_{\mathrm{La}}\}\ B\ A\ [-$. The anionic distribution determines tunnels where the bismuth ions are located, forming diamond-shaped based tunnels. The coordination of bismuth and lanthanum is discussed. The high thermal factor of some oxygen atoms suggests that this oxide exhibits ionic conductivity.

Undoped and doped Bi_2O_3 materials with fluorite-type crystal structure have been intensively studied for their high ionic conduction properties (*1–15*). For pure Bi_2O_3, the ionic superconductive form (called δ) is stable above 1002 K (6). It can be stablized at lower temperature by addition of divalent, trivalent, pentavalent, and hexavalent ions (*4, 5, 7–15*). For instance, in the system Bi_2O_3– Ln_2O_3, the solid solution $Bi_{1-x}Ln_xO_{1.5}$ can be observed at room temperature with the fluorite-type structure for Ln = Sm ($0.1 \leq x \leq 0.4$), Dy ($0.20 \leq x \leq 0.40$), Er ($0.20 \leq x \leq 0.30$), Yb ($0.10 \leq x \leq 0.40$) (*11*) and Y($0.25 \leq x \leq 0.42$) (*10*). When lanthanum is substituted for bismuth, only rhombohedral phases are observed up to $x = 0.50$ (*11*). A recent structural study by single crystal X ray diffraction and powder neutron diffraction of the oxide $Bi_{0.7}La_{0.3}O_{1.5}$ (*16*) has shown that the structure of this oxide of rhombohedral symmetry (parameters of the hexagonal cell: $a = 4.040$ Å, $c = 27.557$ Å) can be described as a regular stacking along the **c** axis of identical $M_3O_{4.143}$ fluorite-like sheets with extra oxygens partially filling delocalized sites within vacant octahedra of the interlayer space. This confirms that even if no composition with the fluorite structure was reported in the system with lanthanum, the structure of the rhombohedral form remains closely related to the latter. This suggests the possible existence in the Bi_2O_3–La_2O_3 system of microphases closely related to the fluorite structure. We report here the synthesis and structure of a new oxide $Bi_8La_{10}O_{27}$, an ordered member of the oxygen deficient fluorite series $Bi_{1-x}La_xO_{1.5}$, corresponding to $x = 0.55$

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Experimental

The Bi_2O_3–La_2O_3 system was investigated by solid state reaction in air between bismuth and lanthanum sesquioxides. Adequate mixtures of these oxides were intimately ground and heated in a platinum crucible at 950–1000°C for 24 hr and then quenched down to room temperature.

Cell parameters were fitted from X-ray and neutron powder diffraction data which were collected by means of a Philips diffractometer (CuK_α radiation) and the multicounter diffractometer 3t2, installed at the Orphee reactor in Saclay (λ = 1.2269 Å), respectively. For structural studies, integrated intensities measured from X-ray diffraction pattern were introduced in the refinement computer program Maryse (*17*). Neutron data were collected by step scanning over an angular range of $6° < 2\Theta < 115°$, in increments of 0.05° (2 Θ). The Bragg reflections were used to refine the crystal structure with the profile refinement computer program DBW 3.2 (18). The diffraction lengths used were 0.8533 (Bi), 0.827 (La), and 0.5805 (0) ($\times 10^{-12}$ cm).

The electron diffraction observations were performed on a Jeol 120CX electron microscope fitted with a side entry goniometer (±60°).

Results

For $x = 0.55$, a new compound was obtained. It was a pale yellow colored powder. Attempts to obtain single crystals were unsuccessful because of the decomposition which occurs above 1100°C. The electron diffraction investigation revealed an orthorhombic symmetry with cell parameters closely related to the one of fluorite cubic cell (a_F) by the relations: $a \approx 3\ a_F \sqrt{2}/2$, $b \approx 3a_F$, $c \approx a_F \sqrt{2}/2$ whose refinements from X-ray powder data led to the values: a = 12.079 (2) Å, b = 16.348 (4) Å, c = 4.0988 (5) Å. The observed conditions of reflection: $h\ k\ l$, $h + k + l = 2n$ involved an I space group. It appeared that the unit cell of this oxide is a superstructure of the cubic fluorite cell, which could result from the ordering of lanthanum and bismuth and (or) of oxygen vacancies with regard to the cubic fluorite. Owing to the relative values of the X-ray scattering factors and neutron diffusion lengths of the different elements, the complete structural study could only be solved using both X-ray and neutron data.

X-Ray Diffraction

This study was performed in the *Immm* space group using the first 43 integrated intensities of the powder diffraction pattern, i.e., 89 $h\ k\ l$. Because of the apparent close relationships with the fluorite structure, calculations were performed with starting positional parameters corresponding to those of the classical cubic fluorite. The distribution of Bi^{3+} and La^{3+} ions over the 2(a), 4(e), 4(g), and (8n) sites of the *Immm* group was chosen considering the ratio Bi/La = 8/10. No oxygen vacancies were assumed in the first step. For these conditions and with global isotropic thermal parameters fixed at 1 Å^2, the discrepancy factor was R_i = 21.5%. Successive refinements of all the variable positional parameters and of the B factors of metallic ions confirmed that bismuth and lanthanum were located on 4(e) + 4(g), and 2(a) + 8(n) sites, respectively. In a second step, occupancy factors of oxygen in the different sites were refined leading to an occupancy of the $O_{(3)}$ site close to zero. $\tau_{O(3)}$ was then fixed to zero and new refinement cycles were performed with x, y, and B(Bi, La) as variables which led to R_i = 7.1% for the parameters given in Table I. At this stage, 32 oxygen atoms per unit cell instead of 27 atoms imposed by the charge balance were located; although $\tau_{O(6)}$ had shown a significant deviation from 1 during occupancy refinements, calculations were stopped and the structure was then studied with neutron data.

TABLE I

$Bi_8La_{10}O_{27}$: FIND REFINED PARAMETERS FROM X-RAY POWDER PATTERN DATA

Atom	Site	x/a	y/b	z/c	B(Å^x)	τ
$Bi_{(1)}$	4(e)	0.3158 (56)	0	0	1.3 (7)	1
$Bi_{(2)}$	4(g)	0	0.3394 (27)	0	1.1 (7)	1
$La_{(1)}$	8(n)	0.3492 (53)	0.3203 (17)	0	1.2 (8)	1
$La_{(2)}$	2(a)	0	0	0	1.6 (9)	1
$O_{(1)}$	4(h)	0	0.063 (10)	½	1	1
$O_{(2)}$	4(h)	0	0.241 (11)	½	1	1
$O_{(3)}$	4(h)	0	5/12	½		0
$O_{(4)}$	8(n)	0.228 (12)	0.073 (9)	0	1	1
$O_{(5)}$	8(n)	0.161 (17)	0.260 (9)	0	1	1
$O_{(6)}$	8(n)	0.154 (15)	0.439 (7)	0	1	1

Neutron Diffraction

The neutron diffraction pattern was studied in the range 10–110° (2Θ). A characteristic of this pattern was that we observed a rapid decrease of the peak intensities as Θ increases. Such a feature was previously reported by P.D. Battle *et al.* (*10*) for $Bi_{0.6}Y_{0.4}O_{1.5}$, who attributed this phenomenon to a disordered nature of the material. Profile analysis was performed; it confirmed the absence of oxygen in the $O_{(3)}$ site. Moreover the $O_{(6)}$ site was found to be not completely filled with an occupancy factor close to 0.34. Considering the number of oxygen atoms per unit cell, $\tau_{O(6)}$ was then fixed as 0.375. Refinements of the positional parameters and of the isotropic thermal factors for all the atoms led to the values contained in Table II and to the discrepancy factors: $R_p = 0.051$, $R_{wp} = 0.068$, $R_i = 0.094$. Experimental, calculated, and difference diffraction patterns are plotted in Fig. 1. From Table II, it appears that all the B factors exhibit high values, in agreement with the remark concerning the characteristic of the neutron diffraction pattern. However they are not higher than those obtained for $Bi_{0.7}La_{0.3}O_{1.5}$ (16) ($B_{(Bi,La)}$ = 1.6–2.5 Å^2 and $B_{(O)}$ = 1.9–6.3 Å^2). Fourier maps at the level of $O_{(4)}$ (B = 2.58 Å^2) and $O_{(6)}$ (B = 4.93 Å) were calculated to detect eventual anisotropic vibrations or a splitting of the atomic positions, but they did not reveal any significant features. This is in agreement with the results of calculations with anisotropic thermal parameters or delocalization of the oxygens on more general positions, which did not give any significant decrease of the R factors.

On the other hand, calculations performed in a less symmetrical space group such as *I2mm* or *Im2m*, to detect an eventual higher degree of order in the oxygen distribution, do not lead to a decrease of the different R values in spite of the increase of the variables (16 independent atoms in *Im2m* instead of 9). Moreover, one of these groups, *I2mm*, leads to a twofold coordination of one-half of the $Bi_{(1)}$ site and for the other half to a fourfold coordination with a very short O–O distance of 1.81 Å along the b axis (see next section) which is unlikely. The result is that, if *Im2m* cannot be excluded, *Immm* remains the most probable space group.

Description of the Structure and Discussion

$Bi_8La_{10}O_{27}$ appears as a superstructure of the cubic fluorite, characterized by a complete ordering of bismuth and lanthanum

TABLE II

$Bi_8La_{10}O_{27}$: FINAL REFINED PARAMETERS FROM NEUTRON POWDER PATTERN DATA: $R_p = 0.051$, $R_{wp} = 0.068$, $R_i = 0.094$

Atom	x/a	y/b	z/c	B(Å^2)	τ
$Bi_{(1)}$	0.3110 (6)	0	0	0.97 (14)	1
$Bi_{(2)}$	0	0.3316 (4)	0	0.71 (12)	1
$La_{(1)}$	0.3430 (5)	0.3225 (3)	0	1.35 (10)	1
$La_{(2)}$	0	0	0	1.32 (22)	1
$O_{(1)}$	0	0.0916 (9)	½	1.71 (21)	1
$O_{(2)}$	0	0.2776 (7)	½	1.33 (19)	1
$O_{(3)}$					0
$O_{(4)}$	0.1878 (8)	0.0864	0	2.58 (18)	1
$O_{(5)}$	0.1541 (6)	0.2647 (5)	0	1.40 (13)	1
$O_{(6)}$	0.1672 (28)	0.4446 (17)	0	4.93 (67)	0.375

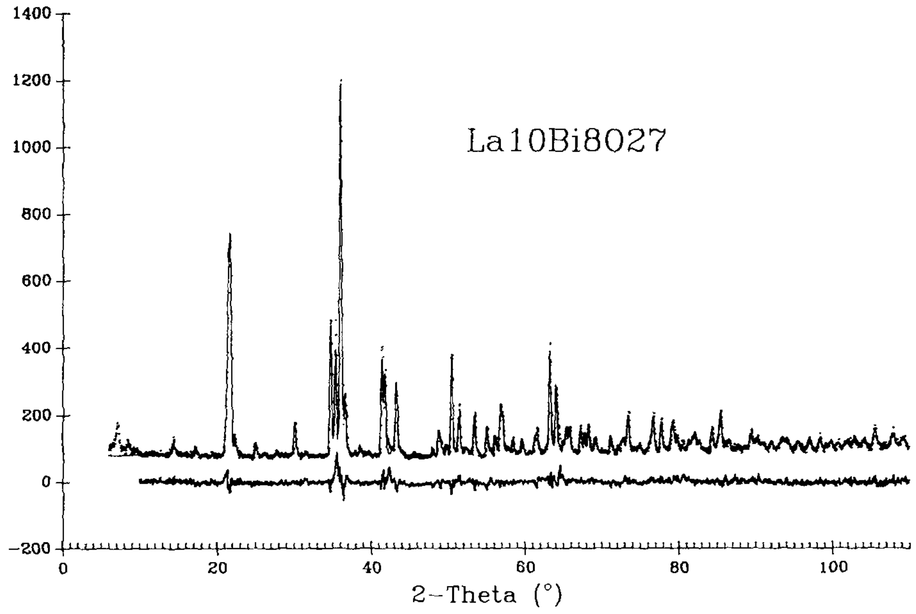

FIG. 1. Experimental, calculed, and difference neutron powder diffraction patterns for $Bi_8La_{10}O_{27}$.

cations, and a partial ordering of the oxygen vacancies. The projection of the structure on the (001) plane (Fig. 2) shows that one plane (110) or ($\bar{1}$10) out of three is completely occupied by lanthanum, whereas the two other planes are mixed, i.e., contain one-third lanthanum and two-thirds bismuth. In those latter planes, the Bi^{3+} and La^{3+} ions are themselves ordered, one La^{3+} cation alterning with two Bi^{3+} cations along one [110] or [$\bar{1}$10] row. As a consequence the bismuth atoms form diamond-shaped based prisms running along **c**.

In the same way two consecutive (110) or (1$\bar{1}$0) oxygen planes out of six are fully occupied (labeled A), whereas the four next consecutive oxygen planes are deficient (labeled B and C). Two sorts of oxygen deficient planes are observed: in the B planes two oxygens alternate with one partially occupied anionic position along the direction [110] or [$\bar{1}$10], whereas in the *C* planes the [110] rows can be described by the sequence -[*F E P* [-, in which *F*, *E*, *P* correspond to fully occupied, empty, and partially occupied anionic sites, respectively. These oxygen planes are stacked according to the sequence [*A B C C B A* [. The lanthanum planes are sandwiched by the fully occupied oxygen planes (*A*), whereas the oxygen deficient planes are adjacent to the mixed planes containing bismuth in agreement with the stereoactivity of the $6s^2$ lone pair of Bi^{3+}, which can play the role of an anion.

Thus the stacking sequence is -[La *A B* $\langle{}^{\mathrm{La}}_{\mathrm{Bi}}\rangle$ *C C* $\langle{}^{\mathrm{La}}_{\mathrm{Bi}}\rangle$ *B A* [-. This semiordered distribution of the oxygen vacancies leads to the formation of tunnels running along **c** (Fig. 2) where the bismuth prisms are located. In those tunnels the bismuth cations are located close to the oxygen walls. It is worth pointing out that no oxygen is located inside these prisms, leaving a free space where the $6s^2$ lone pairs of the Bi^{3+} cations can extend.

The interatomic *M*–O distances (Table III) are close to those usually observed in

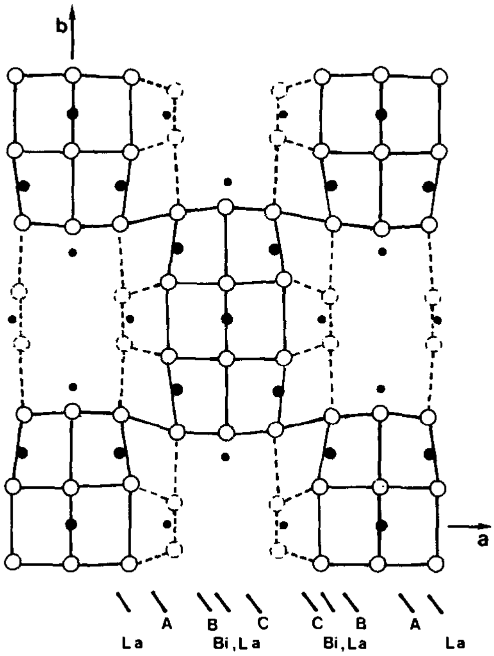

FIG. 2. Projection on to the (001) plane of the structure of $Bi_8La_{10}O_{27}$. Bismuth, lanthanum, and oxygen are schematized by small black circles, large black circles, and open circles, respectively; open circles with dashed line represent the partially occupied $O_{(6)}$ site. Succession of (110) planes is given as an example.

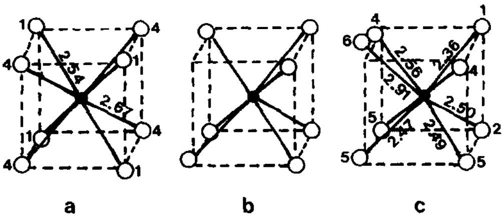

FIG. 3. Oxygen environment for $La_{(2)}$ (a) and $La_{(1)}$ sites (b and c).

lanthanum or bismuth oxides. Two different coordination polyhedra are observed for lanthanum. $La_{(2)}$ exhibits the classical eightfold coordination of the fluorite compounds (Fig. 3a); however, the La O_8 polyhedra are distorted since $La_{(2)}$–$O_{(1)}$ and $La_{(2)}$–$O_{(3)}$ distances differ by about 0.13 Å and $O_{(1)}$–$O_{(1)}$ and $O_{(4)}$–$O_{(4)}$ distances along **b** are 2.99 and 2.82 Å, respectively. The fact that only 3/8 of the $O_{(6)}$ sites are occupied leads, for lanthanum in $La_{(1)}$ sites, to a sevenfold or an eightfold coordination in accordance with the nonoccupation or the occupation of the $O_{(6)}$ site (Figs. 3b and 3c). Here again the polyhedron is distorted with regard to the cubic coordination in the fluorites. Distances ranging from 2.36 to 2.56 Å are observed and the $La_{(1)}$–$O_{(6)}$ distance is particularly long: 2.91 Å. Such a sevenfold coordination derived from the cubic one by elimination of an oxygen has already been observed in $Bi_{0.7}La_{0.3}O_{1.5}$(*16*).

TABLE III

$Bi_8La_{10}O_{27}$: INTERATOMIC *M*–O DISTANCES (IN Å)

$Bi_{(1)}$–$O_{(4)}$	2.05 (1) × 2	$La_{(1)}$–$O_{(1)}$	2.36 (1) × 1
$Bi_{(1)}$–$O_{(6)}$	2.25 (1) × 4	$La_{(1)}$–$O_{(2)}$	2.504 (9) × 1
$Bi_{(2)}$–$O_{(2)}$	2.230 (5) × 2	$La_{(1)}$–$O_{(4)}$	2.559 (7) × 2
$Bi_{(2)}$–$O_{(5)}$	2.158 (8) × 2	$La_{(1)}$–$O_{(5)}$	2.469 (9) × 1
$Bi_{(2)}$–$O_{(6)}$	2.73 (3) × 2	$La_{(1)}$–$O_{(5)}$	2.495 (5) × 2
$La_{(2)}$–$O_{(1)}$	2.537 (9) × 4	$La_{(1)}$–$O_{(6)}$	2.91 (3) × 1
$La_{(2)}$–$O_{(4)}$	2.672 (9) × 4		

The coordination of bismuth is more complex since $Bi_{(1)}$ and $Bi_{(2)}$ have four and two $O_{(6)}$ as neighboring sites, respectively. The distance between two adjacent $O_{(6)}$ sites along **b** is very short (1.81 Å) and prevents the occupation of both sites by oxygen atoms simultaneously. Consequently only two out of the four $O_{(6)}$ neighboring sites of $Bi_{(1)}$ can be occupied, leading to a

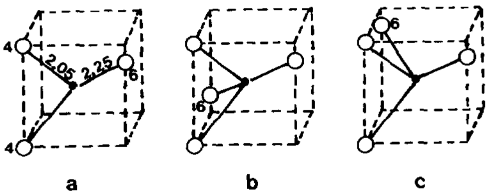

FIG. 4. Possible oxygen environments for $Bi_{(1)}$ sites according to the different possibilities for the occupation of the $O_{(6)}$ neighboring sites: (a) one oxygen atom, (b) and (c) two oxygen atoms.

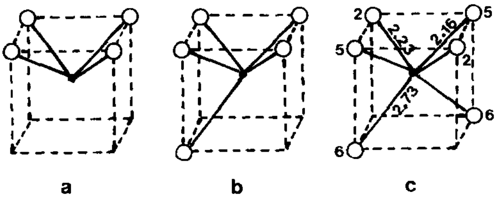

FIG. 5. Possible oxygen environments for $Bi_{(2)}$ sites according to the number n of oxygen atoms in the $O_{(6)}$ neighboring sites: (a) $n = 0$, (b) $n = 1$, (c) $n = 2$.

threefold or a fourfold coordination (Fig. 4). One of the fourfold coodinations of $Bi_{(1)}$ (Fig. 4b) has already been observed for $Bi_{0.7}La_{0.3}O_{1.5}$ (16): it is characterized by short Bi–O distances (2.05 and 2.25 Å) and a $O_{(6)}$–$Bi_{(1)}$–$O_{(6)}$ angle (167°) close to 180°. $Bi_{(2)}$ sites have four neighboring oxygen atoms at distances ranging from 2.16 Å ($O_{(5)}$) to 2.23 Å ($O_{(2)}$) and two possible oxygens ($O_{(6)}$) at 2.73 Å. If the two neighboring sites are unoccupied (Fig. 5a), the resulting coordination is four, like in the Aurivillius phases. It can be five (Fig. 6b) or six (Fig. 6c) according to one or two occupied $O_{(6)}$ sites. In the latter case the environment of bismuth is like the one postulated by P. D. Battle *et al.* (10) in the study of the cubic oxygen deficient fluorite $Bi_{1-x}Y_xO_{1.5}$(x = 0.27, 0.34, 0.40) considering the accomodation of the lone pair of Bi^{3+} ion with regard to the oxygen vacancies.

The distribution of three oxygen atoms over eight sites ($O_{(6)}$) and the abnormally high B values observed for these oxygens suggest that they are mobile and that this oxide should exhibit high ionic conductivity.

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