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Lanthanum indium oxide from X-ray powder diffraction

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$LaInO_3$, a promising ion conductor for a holistic solid oxide fuel cell, was synthesized by a solid-state reaction method. The structure was refined by the Rietveld method using X-ray powder diffraction data. The structure of $LaInO_3$ is distorted by the in-phase and antiphase tilting of oxygen octahedra in the $a^+b^-b^-$ system of the InO_6 polyhedra. In the *Pmna* space group, the In atom lies on an inversion centre and the La atom and one of the O atoms lie on a mirror plane.

Comment

Oxides with a perovskite structure have a variety of electrical, optical and electrochemical applications, *e.g.* ferroelectric memories, luminescence and solid oxide fuel cells. $LaInO_3$ is an example of one of these oxides. The chemical formula $LaInO_3$ simply indicates that the oxide is a member of the perovskite family, but its crystallographic structure has not previously been assessed in detail. The room-temperature structure of $LaXO_3$ (X = B, Al, Ga, In and Tl) exhibits different space groups (*viz*. *Pmcn*, $R\bar{3}m$, *Pnma*, *Pnma* and $P6_3$, respectively; Galasso, 1990; Lerch *et al.*, 2001) depending on the ionic radius of X. Padurow & Schlusterius (1955) reported only the cell parameters (a = 11.402 Å, b = 8.198 Å and c = 11.796 Å in the orthorhombic system) of $LaInO_3$, without determining the space group. Keith & Roy (1954) reported that $LaInO_3$ had a $YCrO_3$-type structure, while presenting only the X-ray powder pattern without the space group. Roth (1957) reported that $LaInO_3$ is orthorhombic (with cell parameters a = 5.723 Å, b = 8.207 Å and c = 5.914 Å) but could not determine the structure. Therefore, we report here a detailed analysis of the crystal structure of $LaInO_3$, obtained by the X-ray Rietveld method.

Fig. 1 shows the observed X-ray diffraction pattern, the calculated pattern and the difference profile for $LaInO_3$. The structure, illustrated in Fig. 2, is composed of distorted InO_6 octahedra, with La atoms lying intermediate between neighboring octahedra. Each In atom is located at the center of an oxygen octahedron. The InO_6 octahedron at the center of the unit cell has $b = \frac{1}{2}$, and the La atoms are at $b = \frac{1}{4}$ and $\frac{3}{4}$. There are three types of In—O bond, with bond lengths of 2.11 (2), 2.164 (9) and 2.22 (2) Å (Table 1).

Although $LaInO_3$ has an orthorhombic cell, it can be transformed to a cubic cell for comparison with a simple perovskite cell. Most of the diffraction peaks shown in Fig. 1 could be indexed on the basis of the cubic cell (a_o = 4.12 Å), except for some extra peaks, which are indicated by asterisks (see inset). Two such peaks, labeled as $1/2(111)_c$ and $1/2(311)_c$, have been attributed to the antiphase tilting of oxygen octahedra (Glazer, 1972, 1975); the $1/2(310)_c$ peak can be explained by the in-phase tilting of oxygen octahedra, and the last extra peak, $1/2(210)_c$, indicates the antiparallel shift of the *A*-site cations in $LaInO_3$. On the basis of these results, we are able to conclude that orthorhombic $LaInO_3$ is distorted by the in-phase and antiphase tilting of oxygen octahedra, with the $a^+b^-b^-$ tilt system proposed by Glazer (Glazer, 1972, 1975). The ionic radius difference, which can be represented by the tolerance factor, plays an important role in determining the crystal structure in these $LaXO_3$ compounds. The tolerance factor (t) is given by

$$t = [r(\mathrm{La}) + r(\mathrm{O})]/1.414[r(X) + r(\mathrm{O})],$$

where r(La), r(O) and $r(X)$ are the radii of the La^{3+}, O^{2-} and X^{3+} ions, respectively.

The ionic radii used here were those according to Shannon (1976) [$r(La^{3+})$ = 1.36 Å, $r(O^{2-})$ = 1.40 Å, $r(Ga^{3+})$ = 0.62 Å, $r(In^{3+})$ = 0.80 Å and $r(Tl^{3+})$ = 0.89 Å] and the tolerance factors of $LaGaO_3$, $LaInO_3$ and $LaTlO_3$ are 0.966, 0.887 and 0.852, respectively. From the changes in the tolerance factors, these compounds could be expected to have the same structure. Recently, Lerch *et al.* (2001) reported that the crystal structure of pure $LaGaO_3$ at ambient temperature was that of a distorted perovskite similar to $LaInO_3$, with the space group *Pnma*. By contrast, it is reported that $LaTlO_3$ has the space

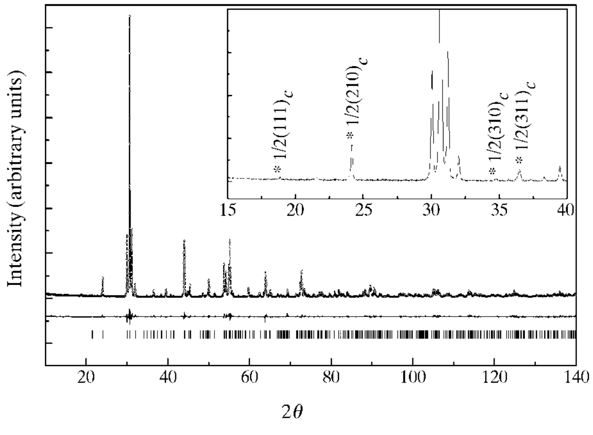

Figure 1
Observed, calculated and difference profiles for $LaInO_3$. The inset shows the peaks (marked with asterisks) that could not be indexed in the cubic perovskite cell (a_o = 4.12 Å).

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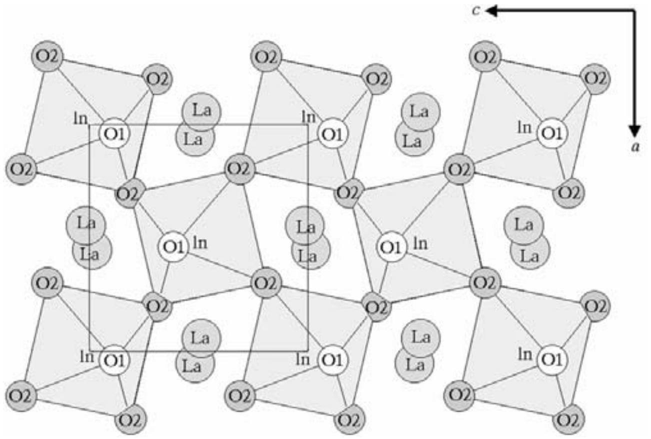

Figure 2
A schematic view of the crystal structure of $LaInO_3$, viewed along the *b* axis.

group $P6_3$ (Inorganic Crystal Structure Database No. 200088; URL: http://icsd.ill.fr/icsd/). From the present results, it appears that $LaInO_3$ is in satisfactory agreement with the relationship between crystal symmetry and tilting, which is influenced by the tolerance factor.

Experimental

Samples of $LaInO_3$ were synthesized by a conventional solid-state reaction method (He *et al.*, 2000) from individual oxide and carbonate powders, La_2O_3 (99.9%, Aldrich) and In_2O_3 (99.9%, Trinitech International Inc., Twinsburg, OH). The materials were weighed in the appropriate molar ratio and mixed with ZrO_2 balls in ethanol for 24 h. The powders were dried, calcined at 1573 K for 4 h in air, pressed into discs and then sintered at 1723 K for 4 h in air. The crystal structures of sintered specimens were investigated by conventional X-ray powder diffractometry.

Crystal data

$LaInO_3$
$M_r = 301.73$
Orthorhombic, *Pnma*
$a = 5.9404$ (1) Å
$b = 8.2158$ (1) Å
$c = 5.7229$ (1) Å
$V = 279.307$ (8) $Å^3$
$Z = 4$
$D_x = 7.173$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 180.73$ mm^{-1}
$T = 295$ K
Irregular, yellow
Specimen shape: flat sheet
20 × 25 × 1 mm

Data collection

Rigaku D/max-B diffractometer
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode
$2\theta_{min} = 10$, $2\theta_{max} = 140°$
Increment in $2\theta = 0.02°$

Table 1
Selected geometric parameters (Å, °).

$In—O2^{i}$	2.11 (2)	$La—O1^{iii}$	2.59 (3)
$In—O1$	2.164 (9)	$La—O2^{iii}$	2.67 (2)
$In—O2$	2.22 (2)	$La—O2^{iv}$	2.975 (17)
$La—O1^{ii}$	2.35 (3)		
$O2^{i}—In—O1$	90.4 (8)	$O2—La—O2^{iii}$	116.8 (4)
$O2^{i}—In—O2$	90.6 (3)	$O2^{iii}—La—O2^{iv}$	126.0 (3)
$O1—In—O2$	88.8 (8)	$O1^{ii}—La—O2^{v}$	70.9 (5)
$O1^{ii}—La—O2$	105.5 (7)	$O1^{iii}—La—O2^{v}$	65.7 (4)
$O1^{ii}—La—O1^{iii}$	85.2 (6)	$O2^{iii}—La—O2^{v}$	65.8 (2)
$O2—La—O1^{iii}$	137.9 (5)	$O2^{iv}—La—O2^{v}$	119.2 (7)
$O1^{ii}—La—O2^{iii}$	136.2 (6)		

Symmetry codes: (i) $\frac{1}{2}-x, -y, \frac{1}{2}+z$; (ii) $x, y, z-1$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}-z$; (iv) $-x, -y, -z$; (v) $-x, \frac{1}{2}+y, -z$.

Refinement

Refinement on I_{net}
$R_p = 0.0435$
$R_{wp} = 0.0602$
$R_{exp} = 0.0739$
$S = 0.81$
Wavelength of incident radiation: 1.5418 Å
Profile function: pseudo-Voigt
30 parameters
$(\Delta/\sigma)_{max} = 0.01$

Data collection: *D/max-B Software* (Rigaku Corporation, 1990); cell refinement: *FULLPROF*98 (Rodriguez-Carvajal, 2000); data reduction: *FULLPROF*98; program(s) used to solve structure: *FULLPROF*98; program(s) used to refine structure: *FULLPROF*98; molecular graphics: *ATOMS* (Dowty, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1033). Services for accessing these data are described at the back of the journal.

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