Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Perovskite-related $LaTiO_{3.41}$

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Received 26 November 2002
Accepted 23 December 2002
Online 25 January 2003

Crystals of pentalanthanum pentatitanium heptadecaoxide ($La_5Ti_5O_{17}$ with 0.3% oxygen excess, or $LaTiO_{3.41}$) have been synthesized by floating-zone melting, and the structure has been solved using single-crystal X-ray diffraction intensities. The monoclinic ($P2_1/c$) structure consists of perovskite-like slabs of vertex-sharing TiO_6 octahedra, which are separated by additional oxygen layers. The slabs are five octahedra wide. Due to the adjustment of the TiO_6 octahedra to meet the coordination requirements of the La^{3+} cations, a superstructure develops along the *a* axis.

Comment

A group of compounds with the chemical formula $A_nB_nO_{3n+2}$ (A is Sr, La or Ca, and B is Nb or Ti) have been studied recently because of their interesting electronic properties (Lichtenberg *et al.*, 2001; Kuntscher *et al.*, 2002, 2003). The crystal structures of the members of this family consist of (110) slabs of the perovskite structure separated by layers of additional O atoms. The width of the slabs in terms of the number of octahedra corresponds to the value of n in the chemical formula. The ideal formula of the $n = 5$ member in the $LaTiO_x$ system is $La_5Ti_5O_{17}$, or $LaTiO_{3.40}$, but this compound exists in the homogeneity range $3.40 < x < 3.42$, as revealed by powder X-ray diffraction, high-resolution electron microscopy and thermogravimetry (Lichtenberg *et al.*, 1991). The composition of the title compound, $LaTiO_{3.41}$ (0.3% oxygen excess), has been determined by thermogravimetric oxidation (Lichtenberg *et al.*, 2001). It is not clear if this non-stoichiometry corresponds to cation deficiency or oxygen excess, but there are indications for the latter in related niobates with $n = 4$ (Lichtenberg *et al.*, 2001).

The single crystal used for the present X-ray diffraction data collection was broken off a larger piece of material synthesized by floating-zone melting, with a composition of $LaTiO_{3.41}$ (Lichtenberg *et al.*, 2001). Due to its layered structure, the material shows a perfect (001) cleavage, leading to the production of extremely thin plates when preparing single crystals. This property makes the correction for absorption effects indispensable and leads to an increased mosaic spread of crystals. In conjunction with the large cell dimension in the *c* direction, the mosaic spread limits the number of scans useful for obtaining integrated intensities. Depending on the scan direction in reciprocal space, some scans contained intensity from more than one reflection. These scans were recognized and discarded.

The chemical composition of the compound is slightly non-stoichiometric, but the presence of cation vacancies, or alternatively of excess oxygen, could not be analyzed with the data presented here. The anisotropic displacement parameters describe very oblate ellipsoids, which is due either to the absence of some reflections or to insufficient absorption correction. Hence, the physical meaning of the displacement parameters cannot be discussed. Their strong correlation with occupancy parameters also prohibits the refinement of the latter.

The refinement of the crystal structure shows that it consists of perovskite-type slabs with a width of five octahedra (Fig. 1). The topology proposed by Williams *et al.* (1991), based on electron-microscopy observations, is confirmed, and the position estimates of Williams *et al.* (1991) are replaced by more precise values referring to the correct unit cell and symmetry. The unit-cell volume of $LaTiO_{3.41}$ is approximately twice as

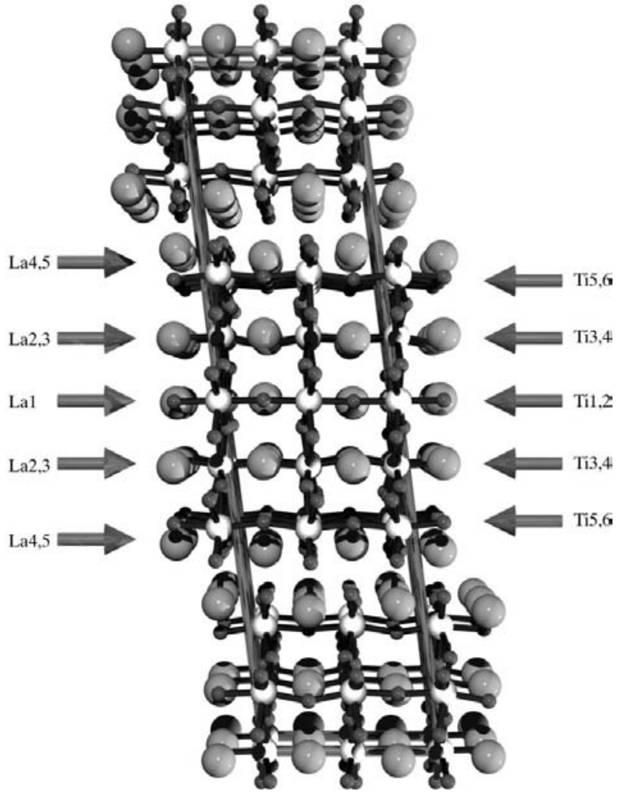

Figure 1
The crystal structure of $LaTiO_{3.41}$, viewed along **b**. Large grey spheres represent La, smaller light-grey spheres Ti, and the smallest and darkest grey spheres represent O atoms. The unit cell is outlined.

DOI: 10.1107/S0108270102023612

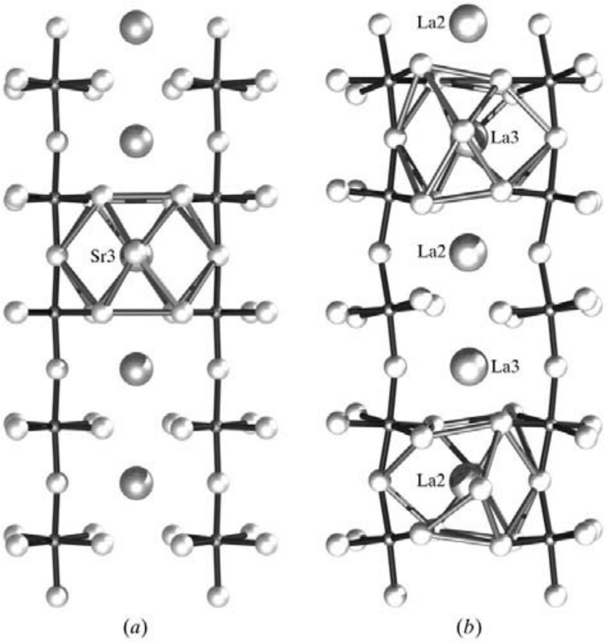

Figure 2
The coordination of (*a*) Sr3 in $SrNbO_{3.41}$ viewed along **a***, and (*b*) La2 and La3 in $LaTiO_{3.41}$ viewed along **c***. The view directions relative to the topology are the same in both cases; only the unit-cell settings are different.

large as that of $SrNbO_{3.41}$ (Abrahams *et al.*, 1998), while the symmetry is monoclinic for the former as opposed to orthorhombic for the latter. The differences between these two isotypic structures can be understood from the different chemical compositions. Divalent Sr is replaced by trivalent La, and nearly tetravalent Ti replaces approximately pentavalent Nb, thus transferring bond strength from the octahedral sites to the *A* sites. This substitution, in conjunction with differences in radii, distorts the oxygen environment of the metal atoms, causing local strain. This strain, in turn, is relieved by a commensurate modulation of the structure, leading to a twofold superstructure in the [100] direction of $LaTiO_{3.41}$ compared with $SrNbO_{3.41}$. Indeed, the reflections with odd *h* indices have only 20% of the intensities of the reflections with even *h* indices. This is reflected by the atomic coordinates, whereby a counterpart near $(x + \frac{1}{2}, y, z)$ can be found for every atom site at (x, y, z).

The difference between orthorhombic $SrNbO_{3.41}$ and monoclinic $LaTiO_{3.41}$ can best be seen in the coordination of the *A* sites. Surprisingly, the major differences are not found for atoms near the additional oxygen layer, but for those in positions intermediate between the oxygen layer and the centre of the octahedral slab, *i.e.* atoms La2 and La3 (Fig. 1). While in $SrNbO_{3.41}$ the Sr atoms in this position are all symmetry equivalent and occupy the centre of the coordinating cuboctahedron (Fig. 2*a*), atoms La2 and La3 in $LaTiO_{3.41}$ are shifted away from the centres of their coordination polyhedra (Fig. 2*b*). The shifts of the La2 and La3 positions are accompanied by rotations of the octahedra, in agreement with the lower symmetry of the La compound.

The distortions of the coordination polyhedra can be analyzed in terms of mean metal–oxygen bond lengths and angles and their standard uncertainties (Table 1). The TiO_6 octahedra at the centre of the perovskite slabs are virtually undistorted with respect to bond lengths and angles. The distortion grows as the octahedra approach the rim of the slab, as shown by the increasing standard uncertainties of the mean Ti—O bond lengths (Table 1). No such significant difference can be found with respect to the average O—Ti—O angles. This agrees well with the situation found in $SrNbO_{3.41}$ (Abrahams *et al.*, 1998), where the bond-length distortions of the corresponding NbO_6 octahedra are almost identical and the angular distortion grows by only a small amount when approaching the rim of the perovskite slab. While the La sites within the octahedral slabs (La1, La2, and La3) allow the description of their coordination by a distorted cuboctahedron, such a description is useless for La4 and La5. The latter are at the rim of the slabs, and consequently, two of the 12 O atoms of the cuboctahedron are missing. The actual positions of La4 and La5 are shifted away from the would-be centre of the cuboctahedron into the direction of the opposite slab. The resulting irregular coordination is similar to that of Sr in $Sr_2Nb_2O_7$ (Daniels *et al.*, 2002) and is tenfold for La4 and [seven + three]-fold for La5.

Experimental

The title compound was prepared by sintering of oxides at 1473–1673 K and subsequent floating-zone melting in argon.

Crystal data

$La_5Ti_5O_{17}$
$M_r = 1205.90$
Monoclinic, $P2_1/c$
$a = 7.8580$ (11) Å
$b = 5.5281$ (9) Å
$c = 31.449$ (5) Å
$\beta = 97.166$ (16)°
$V = 1355.5$ (4) Å^3
$Z = 4$
$D_x = 5.906$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 18.0$–$22.7°$
$\mu = 18.25$ mm^{-1}
$T = 293$ (2) K
Irregular plate, dark blue–black
0.10 × 0.08 × 0.01 mm

Data collection

Enraf–Nonius MACH3 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Herrendorf, 1992)
$T_{\min} = 0.31$, $T_{\max} = 0.89$
21 243 measured reflections
6456 independent reflections
5164 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 36.9°$
$h = -12 \rightarrow 12$
$k = -7 \rightarrow 9$
$l = -53 \rightarrow 50$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.082$
$S = 1.13$
6456 reflections
248 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0238P)^2 + 11.7499P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 3.22$ e Å^{-3}
$\Delta\rho_{\min} = -3.16$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00024 (2)

Table 1
Mean Ti—O and La—O distances (Å) and O—Ti—O angles (°).

Mean La—O distances are given for coordination numbers of 12 (La1–La3), 10 (La4) and [7+3] (La5).

Ti1—O	1.983 (26)	La1—O	2.754 (247)
Ti2—O	1.979 (22)	La2—O	2.735 (287)
Ti3—O	1.989 (110)	La3—O	2.759 (277)
Ti4—O	1.985 (105)	La4—O	2.697 (244)
Ti5—O	1.977 (141)	La5—O	2.784 (520)
Ti6—O	1.986 (161)		
O—Ti1—O	90.00 (119)	O—Ti4—O	89.68 (666)
O—Ti2—O	90.00 (122)	O—Ti5—O	89.77 (647)
O—Ti3—O	89.66 (677)	O—Ti6—O	89.71 (673)

In the difference Fourier synthesis, the highest peak is 0.56 Å from La5 and the deepest hole 0.59 Å from La4.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *HELENA* (Spek, 1993); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

Financial support from the German research organization DFG (grant Sm 55/6) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC1002). Services for accessing these data are described at the back of the journal.

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