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Cubic phase of single-crystal $LaAlO_3$ perovskite synthesized at 4.5 GPa and 1273 K

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(Al–O) = 0.0001 Å
R factor = 0.008
wR factor = 0.010
Data-to-parameter ratio = 19.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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Single crystals of $LaAlO_3$ (lanthanum aluminium trioxide) have been synthesized at 4.5 GPa and 1273 K, in the presence of an NaCl + KCl flux. The compound crystallizes with the cubic perovskite structure (space group $Pm\overline{3}m$). The thermal vibration of the O atom is remarkably suppressed in the directions of the Al—O bonds, and this anisotropy ranks among the largest observed in stoichiometric cubic perovskites.

Comment

Lanthanum aluminate, $LaAlO_3$, has a rhombohedral perovskite structure (space group $R\overline{3}c$) at ambient conditions. This compound has been widely used as a substrate material and a buffer layer for high-temperature superconductor thin films (Lee *et al.*, 1990) and is also of interest as an analogue for non-cubic $MgSiO_3$ perovskite, a major constituent in the earth's lower mantle (Harrison & Redfern, 2002). Because of such importance for the fields of materials science and earth science, the stability of $LaAlO_3$ under high temperatures and high pressures has been investigated (Howard *et al.*, 2000; Bouvier & Kreisel, 2002; Zhao *et al.*, 2004).

It is well known that $LaAlO_3$ perovskite undergoes a rhombohedral–cubic phase transition at 820 K under 1 atm (*e.g.* Howard *et al.*, 2000; Lehnert *et al.*, 2000). Moreover, a recent study (Bouvier & Kreisel, 2002) reported that the pressure-induced phase transition from rhombohedral to cubic occurs at about 14 GPa at room temperature. As in these studies, the cubic phase, *viz*. the high-P–T form, has been reported only in *in situ* observations under high temperatures or high pressures using powder samples. In particular, the *in situ* high-pressure study (Bouvier & Kreisel, 2002) only reported the pressure dependence of lattice parameters of the cubic phase up to 40 GPa. Thus, the pressure effect on the thermal motions of atoms in the cubic phase is not yet known, although this effect is important for the understanding of its stability. To understand this effect, accurate displacement parameters need to be determined under high pressure; hence, it is meaningful to synthesize single crystals of the cubic phase. We report here the synthesis of cubic $LaAlO_3$ perovskite single crystals and the structure refinement at ambient conditions prior to *in situ* single-crystal X-ray diffraction under high pressure.

The present crystal structure was satisfactorily refined in the cubic perovskite structure (space group $Pm\overline{3}m$). This result indicates that the quenching point (1273 K and 4.5 GPa) in the present high-pressure synthesis lies in the cubic phase region. Recently, Howard *et al.* (2000) showed that the lattice parameters a of cubic $LaAlO_3$ perovskite under 1 atm, observed above the transition temperature (820 K), can be fitted to the

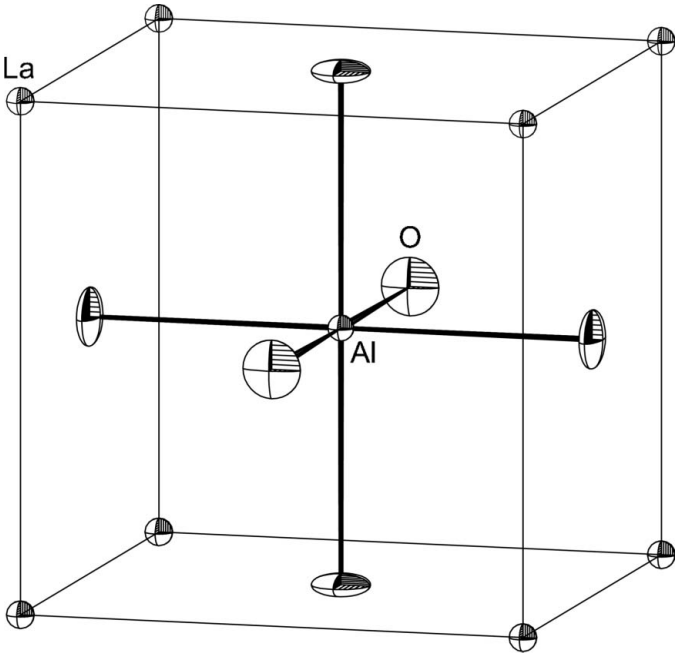

Figure 1
Displacement ellipsoids in cubic $LaAlO_3$ perovskite, drawn at the 50% probability level.

following equation: $a = 3.7849(1 + 2.6223 \times 10^{-6}T + 9.6488 \times 10^{-9}T^2 - 3.4083 \times 10^{-12}T^3)$ Å. The lattice parameter of the present crystal [a = 3.7913 (2) Å] is in good agreement with the extrapolated value (a = 3.7907 Å) at room temperature (296 K) from this equation.

The anisotropic displacement parameters reported in other cubic perovskites, such as $SrTiO_3$ (Abramov *et al.*, 1995), $(K_{0.87}Bi_{0.13})BiO_3$ (Khasanova *et al.*, 1999), $KTaO_3$ (Zhurova *et al.*, 2000), $SrFeO_3$ (Hodges *et al.*, 2000) and $BaZrO_3$ (Levin *et al.*, 2003), show that the smallest mean-square displacements of the O atoms, $\langle u_0^2 \rangle$, are in the directions of the M—O bonds (M = octahedral cations) and the largest, $\langle u^2 \rangle$, are in the directions perpendicular to the M—O directions. The same situation is also observed in the present crystal (Fig. 1). However, the $\langle u_0^2 \rangle / \langle u^2 \rangle$ ratio (= 0.14) of the present crystal ranks among the smallest observed in cubic perovskites with stoichiometric compositions [*cf.* $\langle u_0^2 \rangle / \langle u^2 \rangle$ = 0.43 for $SrTiO_3$ (Abramov *et al.*, 1995), 0.23 for $(K_{0.87}Bi_{0.13})BiO_3$ (Khasanova *et al.*, 1999), 0.38 for $KTaO_3$ (Zhurova *et al.*, 2000), 0.50 for $SrFeO_3$ (Hodges *et al.*, 2000) and 0.29 for $BaZrO_3$ (Levin *et al.*, 2003)].

Experimental

High-pressure synthesis of $LaAlO_3$ single crystals was carried out using a 700 ton cubic anvil-type high-pressure apparatus. A 12.5 mm cube of pyrophyllite was used as a pressure medium. Special grade reagents (99.99%) of La_2O_3 and Al_2O_3 were used as starting materials and were mixed thoroughly together with an NaCl + KCl flux in the molar ratio La_2O_3:Al_2O_3:NaCl:KCl = 2:2:5:5. The mixture was sealed in a platinum capsule and then put into a boron nitride capsule, after which it was inserted into a cylindrical graphite heater embedded in the pyrophyllite cube, where the boron nitride capsule was used as an insulator between the platinum capsule and the graphite heater. The sample temperature was monitored by a Pt–Pt13%Rh thermocouple. The junction of the thermocouple was put at the midpoint of the outer surface of the boron nitride capsule. No correction was made for the pressure effect on e.m.f. The pressure was increased slowly to 4.5 GPa, and then the temperature was elevated slowly to 1673 K. After being kept under these conditions for 15 min, the sample was cooled slowly to 1273 K at the rate of 0.8 K min^{-1} and then quenched by shutting off the electric power supply. The pressure was released slowly and the sample was recovered under ambient conditions. The recovered sample consisted of single crystals of the title compound and lanthanum orthoborate ($LaBO_3$), together with the NaCl + KCl flux. The production of $LaBO_3$ is probably due to contamination by boron from the boron nitride capsule. The flux was removed by washing with water, and a single crystal of $LaAlO_3$ was then selected for X-ray diffraction.

Crystal data

$LaAlO_3$	Cell parameters from 25 reflections
M_r = 213.89	θ = 20.5–22.0°
Cubic, $Pm\bar{3}m$	μ = 19.60 mm^{-1}
a = 3.7913 (2) Å	T = 296 K
V = 54.50 (1) $Å^3$	Irregular fragment, colorless
Z = 1	0.05 × 0.05 × 0.05 mm
D_x = 6.517 Mg m^{-3}	
Mo $K\alpha$ radiation	

Data collection

Rigaku AFC-7*R* diffractometer	R_{int} = 0.015
$\omega/2\theta$ scans	θ_{max} = 60.0°
Absorption correction: ψ scan (North *et al.*, 1968)	$h = 0 \rightarrow 9$
T_{min} = 0.395, T_{max} = 0.414	$k = 0 \rightarrow 9$
521 measured reflections	$l = 0 \rightarrow 9$
116 independent reflections	3 standard reflections
116 reflections with $F > 3\sigma(F)$	every 150 reflections
	intensity decay: 0.4%

Refinement

Refinement on F	$(\Delta/\sigma)_{max} < 0.0001$
$R[F > 3\sigma(F)]$ = 0.008	$\Delta\rho_{max}$ = 0.84 e $Å^{-3}$
$wR(F)$ = 0.010	$\Delta\rho_{min}$ = −0.64 e $Å^{-3}$
S = 1.07	Extinction correction: Zachariasen (1967), type 2 Gaussian isotropic
116 reflections	Extinction coefficient: 0.34 (2)
6 parameters	
$w = 1/[\sigma^2(F_o) + 0.00008\|F_o\|^2]$	

Table 1
Selected interatomic distances (Å).

La—O	2.6809 (1)	O···O^{i}	2.6809 (1)
Al—O	1.8957 (1)		

Symmetry code: (i) z, x, y.

Data collection: *WinAFC* (Rigaku Corporation, 1999); cell refinement: *WinAFC*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *TEXSAN*; program(s) used to refine structure: *TEXSAN*; molecular graphics: *ATOMS for Windows* (Dowty, 2000); software used to prepare material for publication: *TEXSAN*.

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