Aragonite-type lanthanum orthoborate, LaBO$_3$

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(O–B) = 0.004 Å
R factor = 0.017
wR factor = 0.029
Data-to-parameter ratio = 12.7

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

The crystal structure of the low-temperature (LT) modification of LaBO$_3$ has been redetermined from single-crystal X-ray data; the resulting structure confirms the previous study [Abdullaev, Dzhafarov & Mamedov (1976). *Azerbaidzhanskii Khim. Zh.* pp. 117–120], but with improved precision. LT-LaBO$_3$ crystallizes in space group *Pnma* and adopts the aragonite-type structure. Except for one O atom, which is situated on a general position, all other atoms (one La, one B and a second O atom) lie on mirror planes. The structure is composed of LaO$_9$ polyhedra with an average La—O distance of 2.593 Å and trigonal BO$_3$ groups with an average B—O distance of 1.373 Å. Slight anisotropies of the thermal vibrations of La and B atoms suggest that the electrostatic La···La and La···B interactions across the shared edges are weak.

Comment

The crystal structure of the aragonite-type low-temperature (LT) form of LaBO$_3$ was first determined by Abdullaev *et al.* (1976) in space group *Pnma*. In this structure determination, the structure was refined with isotropic displacement parameters and the reliability index converged to $R(F)$ = 0.11. Recently, the deviation from the normal aragonite-type structure (space group *Pnma*) was reported for LT-LaBO$_3$, but no information on its structural parameters was provided (Giesber *et al.*, 2003). Thus, this structure has not been refined satisfactorily to date. An accurate structure model for this compound is indispensable because of its importance as the parent structure of Sr-doped LaBO$_3$ which is a promising high-temperature proton conductor (Shimura *et al.*, 2001; Amezawa
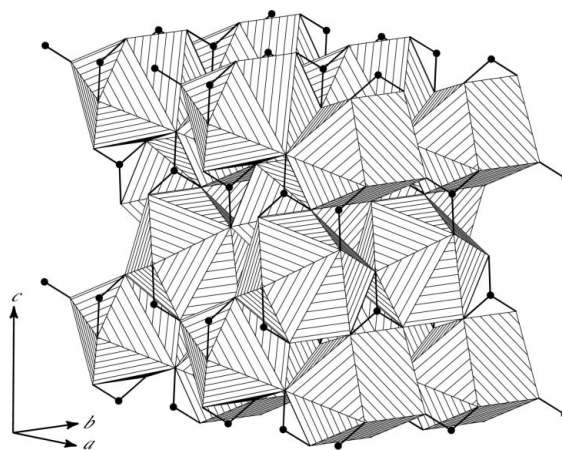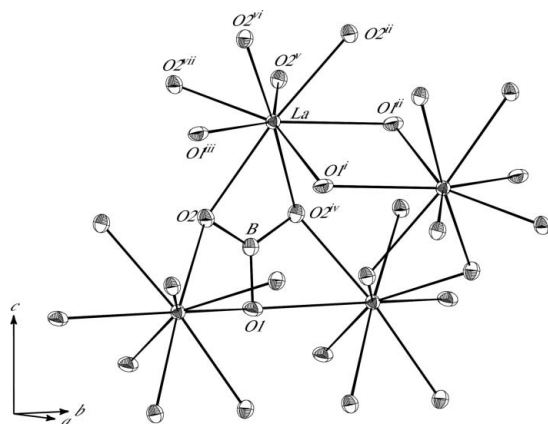

Figure 1
Representation of the aragonite-type LT-LaBO$_3$ structure. LaO$_9$ groups are shown as hatched polyhedra and B atoms as black spheres. B—O bonds are indicated as solid black lines.

Figure 2
Part of the aragonite-type LT-LaBO$_3$ structure with displacement ellipsoids drawn at the 65% probability level. [Symmetry codes: (i) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (ii) $-\frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$; (iii) $-\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$; (iv) $x, -\frac{3}{2} - y, z$; (v) $-2 - x, \frac{1}{2} + y, 1 - z$; (vi) $-\frac{3}{2} - x, -2 - y, \frac{1}{2} + z$; (vii) $-2 - x, -2 - y, 1 - z$.]

et al., 2004). We report here a full structure refinement of the aragonite-type LT-LaBO$_3$, including an anisotropic model of the thermal vibration.

Giesber *et al.* (2003) reported that the aragonite-type LaBO$_3$ belongs to the non-centrosymmetric space group $Cmc2_1$. However, from systematic absences and intensity statistics based on Wilson analysis, we conclude that the most probable space group of this compound is the centrosymmetric space group *Pnma,* as reported by Abdullaev *et al.* (1976). In the present study, the crystal structure was satisfactorily refined in the normal aragonite-type structure, and bond valence sums (Brown & Altermatt, 1985) resulted in reasonable values [2.98 valence units (v.u.) for La, 2.98 v.u. for B, 1.91 v.u. for O1 and 2.02 v.u. for O2].

As shown in Fig. 1 and Table 1, the La atom is coordinated by nine O atoms with a mean bond length of 2.593 Å, and the B atom is planar–triangularly coordinated by three O atoms with a mean bond length of 1.373 Å. Each LaO$_9$ polyhedron shares edges with six other LaO$_9$ polyhedra and three BO$_3$ triangles, whereas each BO$_3$ triangle shares edges with three LaO$_9$ polyhedra.

In compounds with shared edges between coordination polyhedra, thermal vibrations of cations can be restricted in the cation–cation directions across the shared edges because of electrostatic repulsions between these cations, as has been observed in garnet compounds (Nakatsuka *et al.*, 1995, 1999, 2003, 2004*a*,*b*; Yoshiasa *et al.*, 1997). However, the displacement ellipsoids of the La and B atoms in the present crystal structure indicate only a slight anisotropy (Fig. 2), suggesting that the electrostatic La$\cdots$La and La$\cdots$B interactions across the shared edges are weak.

Experimental

In a recent study we reported on the crystal structure of cubic perovskite-type single crystals of LaAlO$_3$, synthesized at 4.5 GPa and 1273 K (Nakatsuka *et al.*, 2005). During this high-pressure synthesis, single crystals of the aragonite-type LT-LaBO$_3$ were obtained as a

minor by-product due to contamination by boron from the boron nitride capsule used in the high-pressure cell assembly. The single crystal of LT-LaBO$_3$ used in the present study was selected from these products. The detailed procedure of the high-pressure synthesis is described elsewhere (Nakatsuka *et al.*, 2005).

Crystal data

LaBO$_3$	Mo $K\alpha$ radiation
$M_r = 197.71$	Cell parameters from 50
Orthorhombic, *Pnma*	reflections
$a = 5.8744$ (3) Å	$\theta = 22.5–25.0°$
$b = 5.1087$ (3) Å	$\mu = 16.88$ mm^{-1}
$c = 8.2581$ (5) Å	$T = 296$ K
$V = 247.83$ (2) Å^3	Irregular fragment, colorless
$Z = 4$	$0.06 \times 0.05 \times 0.04$ mm
$D_x = 5.299$ Mg m^{-3}	

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.030$
ω–2θ scans	$\theta_{max} = 30.0°$
Absorption correction: part of the	$h = -8 \rightarrow 8$
refinement model (ΔF)	$k = 0 \rightarrow 7$
(Walker & Stuart, 1983)	$l = -11 \rightarrow 11$
$T_{min} = 0.418$, $T_{max} = 0.509$	3 standard reflections
1591 measured reflections	every 150 reflections
396 independent reflections	intensity decay: 0.6%
369 reflections with $F^2 > 2\sigma(F^2)$	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.017$	$\Delta\rho_{max} = 1.24$ e Å^{-3}
$wR(F^2) = 0.029$	$\Delta\rho_{min} = -0.98$ e Å^{-3}
$S = 1.98$	Extinction correction: Zachariasen
369 reflections	(1967) type 2 Gaussian isotropic
29 parameters	Extinction coefficient: 0.056 (3)
$w = 1/[\sigma^2(F_o) + 0.00014|F_o|^2]$	

Table 1
Selected geometric parameters (Å, °).

La—O1^{viii}	2.451 (3)	La—O2^{xiii}	2.629 (2)
La—O1^{ix}	2.723 (1)	La—O2^{xiv}	2.601 (2)
La—O1^{x}	2.723 (1)	La—O2^{xv}	2.601 (2)
La—O2^{ix}	2.491 (2)	B—O1^{i}	1.374 (5)
La—O2^{xi}	2.491 (2)	B—O2	1.373 (3)
La—O2^{xii}	2.629 (2)	B—O2^{xvi}	1.373 (3)
O1^{viii}—B—O2	120.3 (2)	O2—B—O2^{xvi}	119.1 (3)
O1^{viii}—B—O2^{xvi}	120.3 (2)		

Symmetry codes: (i) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (viii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (ix) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (x) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (xi) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (xii) $x - \frac{1}{2}, -y + \frac{1}{2}, -z + \frac{1}{2}$; (xiii) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (xiv) $-x + 1, y + \frac{1}{2}, -z + 1$; (xv) $-x + 1, -y, -z + 1$; (xvi) $x, -y + \frac{1}{2}, z$.

The present study confirms the basic structural features determined from the previous investigation (Abdullaev *et al.*, 1976) with a much higher precision by about a factor of 10 (note that in the previous study the space-group setting *Pmcn* was chosen). The highest peak and the deepest hole in the final difference Fourier map are located 0.77 and 1.17 Å, respectively, from atom O1.

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* (Dowty, 2000); software used to prepare material for publication: *TEXSAN*.

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