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A New Family of Lithium Rare-Earth Oxyborates, Li$Ln_6O_5(BO_3)_3$ (Ln = Pr–Tm): Crystal Structure of the Gadolinium Phase $LiGd_6O_5(BO_3)_3$

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A new family of lithium rare earth oxyborates of formula Li$Ln_6O_5(BO_3)_3$ (Ln = Pr–Tm) has been discovered in the ternary-phase diagrams Li_2O–Ln_2O_3–B_2O_3. Single crystals of $LiGd_6O_5(BO_3)_3$ were grown by the flux method. The structure of the oxyborate was solved using a data collection with a four-circle automatic diffractometer (CAD-4) and with Mo$K\alpha$ radiation. The cell is monoclinic (space group $P2_1/c$, $Z = 4$) with $a = 8.489(4)$ Å, $b = 15.706(3)$ Å, $c = 12.117(6)$ Å, $\beta = 132.27(2)°$, and $V = 1195(1)$ Å^3. Refinement of 198 parameters using 4402 independent reflections having intensity $I > 3\sigma(I)$ led to $R = 0.037$ ($wR = 0.087$). The structure of $LiGd_6O_5(BO_3)_3$ can be described as a three-dimensional framework, $(Gd_6O_{14})^{10-}$, of Gd polyhedra connected by common edges and corners, forming cavities where Li and B atoms are inserted. Some oxygen atoms share only Gd polyhedra, justifying the oxyborate label. © 1999 Academic Press

Key Words: **crystal structure; oxyborate of lithium and gadolinium; rare earth compounds.**

INTRODUCTION

Borate compounds are currently very attractive to the scientific community owing to their wide range of applications (1–3). They exhibit high transparency far in the UV, good chemical stability, and, for some of them, crystals with high optical quality. Our interest in the search for new phosphors and scintillators led us to investigate borate systems. Two families of borates, $Li_6Ln(BO_3)_3$ with Ln = Nd–Yb (4–10) and $Li_3Ln_2(BO_3)_3$ with Ln = La–Yb (11–13), were previously studied. Recently some of us have demonstrated an interest in $Li_6M_{1-x}Ce_x(BO_3)_3$ (M = Y, Gd) as neutron detectors (14). An investigation of the Gd_2O_3-rich part of the Li_2O–Gd_2O_3–B_2O_3 ternary-phase diagram led us to discover the new composition $LiGd_6B_3O_{14}$. Single crystals have been grown using a Li_2O–B_2O_3-rich melt.

In this paper we describe the crystal structure determination of this new compound. A family of isostructural phases Li$Ln_6O_5(BO_3)_3$ has been obtained for Ln = Pr–Tm.

PREPARATION PROCESS

Powder Preparation

Polycrystalline samples were prepared using reagent-grade chemicals following the reaction

$$3Ln_2O_3 + 2H_3BO_3 + LiBO_2 \rightarrow LiLn_6B_3O_{14} + 3H_2O.$$

The preparation process consists of preheating at 700°C for 3 h and intermediate grinding and sintering at 900°C for 22 h under controlled atmosphere (O_2, Ar or H_2 depending on the rare earth).

The preparation temperature can be lowered using an initial step in aqueous solution: solubilization of starting materials in dilute nitric acid, then coprecipitation and drying at about 100°C. The resulting powder was progressively heated to 800°C and maintained for 24 h at this temperature.

The final products were controlled by X-ray powder diffraction analysis using Cu$K\alpha$ radiation.

Crystal Growth

Single crystals were grown by the flux method in the Li–Gd–B–O system using Li_2O–B_2O_3-rich melt. The mixture was heated at 950°C for 6 h, then slowly cooled at 2°C/h to 800°C and finally at 50°C/h to room temperature. The crystals were recovered by leaching the flux with dilute hydrochlorhydric acid. Crystals grew as transparent colorless wedge-shaped plates.

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TABLE 1
Crystal Data and Structure Refinement for $LiGd_6O_5(BO_3)_3$

Crystal Data	
Empirical formula	$LiGd_6O_5(BO_3)_3$
Formula weight	1206.9 g
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 8.489(4)$ Å $b = 15.706(3)$ Å $c = 12.117(6)$ Å $\beta = 132.27(2)^\circ$
Volume	1195.5(8) A^3
Z	4
$F(000)$	2036
Temperature	293(2) K
ρ_{cal}	6.706 Mg/m^3
Absorption coefficient	33.07 mm^{-1}
Crystal shape	Wedge-shaped plate
Crystal color	White
Crystal size	$0.250 \times 0.200 \times 0.040$ mm
Data Collection	
Diffractometer	Enraf–Nonius CAD4
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$ Å)
Monochromator	Graphite
θ range	2.5–35°
Index ranges	$-13 \leq h \leq 13$ $0 \leq k \leq 25$ $-19 \leq l \leq 19$
Scan type	$\omega/2\theta$
Scan width	$1.40 + 0.35 \tan \theta^\circ$
Reflections collected [$I > 3\sigma(I)$]	8435
Independent reflections [$I > 3\sigma(I)$]	4402 ($R_{int} = 0.058$)
Refinement	
Absorption correction	Psi scan
Maximum and minimum transmission	0.270 and 0.054
Refinement method	Full-matrix L.S. on F^2
Data/parameters refined	4402/198
Weighting scheme	$\omega = 1/[\sigma^2(F_o^2) + (0.0262P)^2 + 20.10P]$, where $P = (F_o^2 + 2F_c^2)/3$
Extinction coefficient	0.00403(14)
Goodness-of-fit on F^2	1.145
Final R indices [$I > 3\sigma(I)$]	$R_1 = 0.037$, $wR_2 = 0.087$
Maximum shift/esd	< 0.001
Largest diffraction peak and hole	4.64 and -2.89 $e\,A^{-3}$

STRUCTURE DETERMINATION OF $LiGd_6O_5(BO_3)_3$

Symmetry and Unit Cell Parameters

Single crystals of $LiGd_6O_5(BO_3)_3$ were selected by optical examination. Preliminary investigations with Weissenberg and Buerger photographs indicated that this compound crystallizes with monoclinic symmetry. Data collection with an Enraf Nonius CAD4 diffractometer using Mo$K\alpha$ radiation covered half the reciprocal space [8435 reflections with $I > 3\sigma(I)$]. The unit-cell parameters were refined from 25 reflections in the range $7.0^\circ < \theta < 26.35^\circ$. Table 1 lists the crystal data and the experimental conditions for data collection and structure refinement.

Structure Determination

The conditions of systematic reflection [$(h0l)$, $l = 2n$; $(0k0)$, $k = 2n$) lead to the centric space group $P2_1/c$ (No. 14). The data were corrected for Lorentz polarization effects, and empirical absorption corrections were carried out using psi scans on 10 reflections in the range $10.1^\circ < \theta < 26.9^\circ$. A R_{int} index of 0.058 resulted from the averaging of reflections; a total of 4402 unique reflections [$F_o^2 > 3\sigma(F_o^2)$] were used for the refinements.

The structure was solved by Patterson function deconvolution and heavy-atom methods. The first time, six $4e$ sites of gadolinium atoms were located [SHELXS86 (15)]. The positions of all other atoms (O, B, Li) were given by successive refinements and Fourier difference syntheses [SHELX93 (16)]. Finally, the refinements with anisotropic or isotropic (lithium and boron atoms) atomic displacement parameters and secondary extinction factor converged to $R_1 = 0.037$ ($wR_2 = 0.087$).

TABLE 2
Atomic Coordinates and Equivalent Isotropic (Isotropic for B and Li) Displacement Parameters (Å^2) for $LiGd_6O_5(BO_3)_3$

Atom	Site	x	y	z	$U_{eq}{}^{a}/U_{iso}$
Li	$4e$	0.880(3)	0.1036(12)	0.560(2)	0.023(3)
Gd(1)	$4e$	0.23742(5)	0.00436(2)	0.93759(4)	0.00510(7)
Gd(2)	$4e$	0.66450(5)	0.01372(2)	0.71676(4)	0.00554(7)
Gd(3)	$4e$	0.15169(5)	0.14376(2)	0.42384(4)	0.00637(8)
Gd(4)	$4e$	0.41069(5)	0.16556(2)	0.83286(4)	0.00662(8)
Gd(5)	$4e$	0.01204(6)	0.17531(2)	0.05306(4)	0.00811(8)
Gd(6)	$4e$	0.55262(5)	0.17795(2)	0.19408(4)	0.00495(7)
B(1)	$4e$	0.7920(12)	0.0005(5)	0.3552(9)	0.007(1)
B(2)	$4e$	0.5449(13)	0.1735(5)	0.4733(9)	0.009(1)
B(3)	$4e$	0.9585(13)	0.1926(5)	0.7792(9)	0.007(1)
O(1)	$4e$	0.8527(9)	0.0846(3)	0.3824(6)	0.0075(8)
O(2)	$4e$	0.3039(10)	0.0323(4)	0.5954(7)	0.0158(11)
O(3)	$4e$	0.1764(9)	0.0504(3)	0.7192(6)	0.0105(9)
O(4)	$4e$	0.4476(10)	0.2311(3)	0.4962(6)	0.0108(9)
O(5)	$4e$	0.5249(14)	0.0890(4)	0.4901(8)	0.0244(16)
O(6)	$4e$	0.6412(9)	0.2039(4)	0.4254(6)	0.0126(10)
O(7)	$4e$	0.9480(11)	0.1081(4)	0.7992(9)	0.0190(13)
O(8)	$4e$	0.0544(11)	0.2250(4)	0.7297(8)	0.0156(11)
O(9)	$4e$	0.8821(9)	0.2494(3)	0.3214(6)	0.0091(9)
O(10)	$4e$	0.5274(9)	0.0896(3)	0.0356(6)	0.0064(8)
O(11)	$4e$	0.0656(9)	0.0791(3)	0.2207(6)	0.0087(9)
O(12)	$4e$	0.7020(9)	0.0982(3)	0.8941(6)	0.0087(9)
O(13)	$4e$	0.2868(10)	0.0855(3)	0.1241(6)	0.0102(9)
O(14)	$4e$	0.2771(8)	0.2315(3)	0.6223(6)	0.0070(8)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Residual $\Delta\rho$ maxima are found with distances ranging from 0.70 to 1.00 Å from the gadolinium atoms, near the

TABLE 3
Anisotropic Displacement Parameters (Å^2) for $LiGd_6O_5(BO_3)_3$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Gd(1)	0.0041(1)	0.0054(1)	0.0054(1)	−0.0005(1)	0.0030(1)	−0.0006(1)
Gd(2)	0.0049(1)	0.0063(1)	0.0048(1)	−0.0002(1)	0.0029(1)	0.0000(1)
Gd(3)	0.0054(1)	0.0081(1)	0.0047(1)	−0.0014(1)	0.0030(1)	−0.0009(1)
Gd(4)	0.0055(1)	0.0082(1)	0.0057(1)	0.0025(1)	0.0036(1)	0.0015(1)
Gd(5)	0.0064(1)	0.0093(1)	0.0052(1)	0.0000(1)	0.0025(1)	−0.0033(1)
Gd(6)	0.0041(1)	0.0057(1)	0.0039(1)	−0.0006(1)	0.0022(1)	−0.0004(1)
O(1)	0.006(2)	0.007(2)	0.006(2)	−0.001(2)	0.003(2)	−0.001(2)
O(2)	0.008(2)	0.021(3)	0.016(3)	0.012(2)	0.007(2)	0.005(2)
O(3)	0.010(2)	0.011(2)	0.005(2)	0.000(2)	0.003(2)	0.001(2)
O(4)	0.014(2)	0.012(2)	0.011(2)	0.000(2)	0.010(2)	−0.002(2)
O(5)	0.041(4)	0.011(2)	0.013(3)	−0.001(2)	0.014(3)	0.000(2)
O(6)	0.010(2)	0.020(3)	0.011(2)	0.003(2)	0.008(2)	0.005(2)
O(7)	0.016(3)	0.006(2)	0.040(4)	0.001(2)	0.021(3)	0.000(2)
O(8)	0.016(3)	0.019(3)	0.020(3)	0.006(2)	0.016(3)	0.006(2)
O(9)	0.007(2)	0.010(2)	0.009(2)	0.001(2)	0.005(2)	−0.002(2)
O(10)	0.007(2)	0.006(2)	0.005(2)	−0.001(2)	0.003(2)	−0.001(2)
O(11)	0.007(2)	0.010(2)	0.007(2)	0.000(2)	0.004(2)	−0.001(2)
O(12)	0.008(2)	0.009(2)	0.009(2)	−0.001(2)	0.006(2)	0.000(2)
O(13)	0.016(3)	0.007(2)	0.013(2)	−0.001(2)	0.012(2)	0.000(2)
O(14)	0.005(2)	0.008(2)	0.007(2)	−0.001(2)	0.004(2)	−0.001(2)

[a] The anisotropic displacement factor exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2hka^*b^*U_{12} + \cdots)$.

middle of all the Gd–O bonds. This can be explained by systematic errors such as the use of an empirical absorption correction, but also the fact that scattering factors based on spherical atoms ignore bonding effects. Residual electron density peaks near the lithium site are small (1.47 e Å^{-3} compared with 6.54 e Å^{-3} for the Li site when the calculation is performed without Li) and cannot be caused by some disorder in Li positions because the distance to O(3) atoms, 1.70 Å, would be too short. Absence of disorder in Li positions is also attested by the satisfying mean value of the isotropic displacement parameter (Table 2).

The atomic coordinates and isotropic displacement parameters are reported in Table 2, the anisotropic displacement parameters are given in Table 3, and selected bond lengths and angles are listed in Table 4.

Valence bonds sums (Table 5) based on strength analysis (17) are in good agreement with the formal oxidation states of Li^+, Gd^{3+}, B^{3+}, and O^{2-} ions.

STRUCTURE DESCRIPTION

All atoms are located on the 4e site (x, y, z) of the $P2_1/c$ space group. The structure can be regarded as composed of six successive layers of Gd polyhedra parallel to the ac plane (Fig. 1):

Layers 1, 2, 4, and 5 are constituted each by Gd(3), Gd(4), Gd(5), and Gd(6) polyhedra.

Layers 3 and 6 are built from Gd(1) and Gd(2) polyhedra.

Layers 1, 2, 3 and layers 4, 5, 6 are related by the inversion center of the space group. These layers are connected in the b direction constituting a three-dimensional network whose cavities are occupied by Li and B atoms (Figs. 1 and 2).

Gd Atoms

The gadolinium atoms occupy different coordination polyhedra: Gd(1), Gd(2), Gd(4), and Gd(6) are in truncated cubes with one corner missing, and Gd(3) and Gd(5) are in 8-coordination (highly distorted cube) (Fig. 3).

The sevenfold-coordinated Gd atoms present regular Gd–O bond distances between 2.231 and 2.549 Å (mean, 2.372 Å) (Table 4). Comparable values are encountered in

TABLE 4
Selected Bond Lengths (Å) and Angles (°) for $LiGd_6O_5(BO_3)_3$[a]

B(1)–O(3)^c	1.360(9)	B(2)–O(6)	1.367(10)
B(1)–O(1)	1.375(9)	B(2)–O(5)	1.370(10)
B(1)–O(2)^c	1.393(10)	B(2)–O(4)	1.374(10)
⟨B(1)–O⟩	*1.376*	*⟨B(2)–O⟩*	*1.370*
O(1)–B(1)–O(2)^c	119.0(6)	O(4)–B(2)–O(5)	117.1(7)
O(1)–B(1)–O(3)^c	120.9(7)	O(4)–B(2)–O(6)	117.9(6)
O(2)^3–B(1)–O(3)	120.0(7)	O(5)–B(2)–O(6)	124.8(7)

B(3)–O(7)	1.363(9)	Li–O(1)	2.03(2)	Li–B(2)	2.52(2)
B(3)–O(8)^j	1.393(10)	Li–O(3)^j	2.06(2)	Li–B(1)	2.62(2)
B(3)–O(9)^g	1.399(9)	Li–O(6)	2.19(2)	Li–B(3)	2.66(2)
⟨B(3)–O⟩	*1.385*	Li–O(8)^j	2.44(2)	Li–B(1)^k	2.76(2)
		Li–O(5)	2.53(2)		
O(7)–B(3)–O(8)^j	124.0(7)	Li–O(7)	2.55(2)		
O(7)–B(3)–O(9)^g	117.9(7)	Li–O(2)^c	2.57(2)		
O(8)^j–B(3)–O(9)^g	117.9(6)				

Gd(1)–O(10)^a	2.309(5)	Gd(2)–O(13)^c	2.290(5)	Gd(3)–O(11)	2.281(6)
Gd(1)–O(11)^b	2.318(6)	Gd(2)–O(12)	2.358(5)	Gd(3)–O(14)	2.317(5)
Gd(1)–O(10)^c	2.323(5)	Gd(2)–O(2)	2.359(6)	Gd(3)–O(2)	2.333(6)
Gd(1)–O(12)^d	2.369(5)	Gd(2)–O(11)^c	2.369(6)	Gd(3)–O(9)^e	2.389(6)
Gd(1)–O(13)^a	2.373(5)	Gd(2)–O(7)	2.398(6)	Gd(3)–O(1)^e	2.417(6)
Gd(1)–O(3)	2.439(6)	Gd(2)–O(5)	2.443(7)	Gd(3)–O(4)	2.450(6)
Gd(1)–O(7)^e	2.441(6)	Gd(2)–O(5)^c	2.460(7)	Gd(3)–O(8)^f	2.802(7)
⟨Gd(1)–O⟩	*2.367*	*⟨Gd(2)–O⟩*	*2.382*	Gd(3)–O(5)	2.828(9)
				⟨Gd(3)–O⟩	*2.477*

Gd(4)–O(14)	2.231(5)	Gd(5)–O(12)^h	2.299(6)	Gd(6)–O(10)	2.259(5)
Gd(4)–O(10)^a	2.273(5)	Gd(5)–O(14)^f	2.318(5)	Gd(6)–O(13)	2.313(6)
Gd(4)–O(12)	2.306(6)	Gd(5)–O(11)	2.318(5)	Gd(6)–O(14)^f	2.348(5)
Gd(4)–O(3)	2.332(6)	Gd(5)–O(13)	2.339(6)	Gd(6)–O(9)	2.379(6)
Gd(4)–O(4)^g	2.411(6)	Gd(5)–O(8)^f	2.475(6)	Gd(6)–O(4)^f	2.390(6)
Gd(4)–O(6)^g	2.517(6)	Gd(5)–O(9)^i	2.516(6)	Gd(6)–O(6)	2.399(6)
Gd(4)–O(8)	2.549(6)	Gd(5)–O(7)^h	2.937(8)	Gd(6)–O(1)	2.455(5)
⟨Gd(4)–O⟩	*2.374*	Gd(5)–O(6)^i	3.058(6)	*⟨Gd(6)–O⟩*	*2.363*
		⟨Gd(5)–O⟩	*2.533*		

[a] Symmetry transformations used to generate equivalent atoms: $^a x, y, z+1$; $^b -x, -y, -z+1$; $^c -x+1, -y, -z+1$; $^d -x+1, -y, -z+2$; $^e x-1, y, z$; $^f x, -y+\frac{1}{2}, z-\frac{1}{2}$; $^g x, -y+\frac{1}{2}, z+\frac{1}{2}$; $^h x-1, y, z-1$; $^i x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; $^j x+1, y, z$; $^k -x+2, -y, -z+1$.

TABLE 5
Valence Bond Analysis of $LiGd_6O_5(BO_3)_3$[a]

	Li	B(1)	B(2)	B(3)	Gd(1)	Gd(2)	Gd(3)	Gd(4)	Gd(5)	Gd(6)	$\sum s$	Expected
O(1)	0.218	0.989					0.386			0.349	1.94	2
O(2)	0.051	0.942				0.452	0.485				1.93	2
O(3)	0.201	1.030			0.364			0.486			2.08	2
O(4)			0.992				0.353	0.393		0.415	2.15	2
O(5)	0.056		1.003			0.360	0.127				1.89	2
O(5)						0.344					—	—
O(6)	0.141		1.011					0.295	0.068	0.405	1.92	2
O(7)	0.053			1.022	0.362	0.407			0.095		1.94	2
O(8)	0.072			0.942			0.136	0.270	0.330		1.75	2
O(9)				0.927			0.417		0.296	0.428	2.07	2
O(10)					0.517			0.570		0.592	2.18	2
O(10)					0.498						—	—
O(11)					0.505	0.440	0.558		0.505		2.01	2
O(12)					0.440	0.453		0.521	0.531		1.95	2
O(13)					0.435	0.544			0.477	0.512	1.97	2
O(14)							0.506	0.638	0.505	0.465	2.11	2
$\sum s$	0.79	2.96	3.01	2.89	3.12	3.00	2.97	3.17	2.81	3.17		
Expected	1	3	3	3	3	3	3	3	3	3		

[a] Li–O, $s = \exp[(1.466 - d_i)/0.37]$; B–O, $s = \exp[(1.371 - d_i)/0.37]$; Gd–O, $s = \exp[(2.065 - d_i)/0.37]$.

other Gd oxide structures. As an example, Gd–O distances for the 7-coordinated Gd of Gd_2GeO_5 (18) range from 2.28 to 2.58 Å.

The two other Gd atoms [Gd(3) and Gd(5)] are in a distorted (6 + 2) oxygen environment with the first six Gd–O distances between 2.281 and 2.516 Å and the last two ranging from 2.802 to 3.058 Å.

Each Gd polyhedron is connected to six or seven neighboring Gd polyhedra by means of common edges or corners (Figs. 1 and 2). Distances between Gd atoms range from 3.62 to 3.99 Å.

The arrangement of Gd coordination polyhedra is related to that of the fluorite. In CaF_2 anions form cubes whose every second is occupied by calcium ions. In $LiGd_6O_5(BO_3)_3$, the coordination polyhedra of Gd form a similar three-dimensional array, but to accommodate lithium and borate groups, some of the cationic sites are not occupied by Gd. The relationship to the CaF_2-type unit cell is indicated

TABLE 6
Lattice Parameters and Densities Calculated from Powder Data as a Function of Rare-Earth Cationic Radii

	Pr	Nd	Sm	Eu	Gd[a]	Tb	Dy	(Y)	Ho	Er	Tm
r (Å)[b]	1.126	1.109	1.079	1.066	1.053	1.04	1.027	1.019	1.015	1.004	0.994
a (Å)	8.683(1)	8.654(1)	8.571(1)	8.511(1)	8.489(4)	8.429(1)	8.396(1)	8.334(1)	8.355(1)	8.305(1)	8.297(2)
b (Å)	15.996(2)	15.953(1)	15.808(1)	15.726(1)	15.706(3)	15.606(1)	15.552(1)	15.472(1)	15.491(1)	15.414(1)	15.359(4)
c (Å)	12.339(1)	12.311(1)	12.193(1)	12.12(1)	12.117(6)	12.03(1)	11.984(1)	11.924(1)	11.945(1)	11.889(1)	11.859(3)
β (°)	131.986(4)	132.042(3)	132.228(2)	132.262(1)	132.27(2)	132.399(1)	132.441(1)	132.469(1)	132.472(2)	132.507(1)	133.26(1)
V (Å^3)	1274(4)	1262(3)	1223(4)	1200(4)	1195(8)	1169(4)	1155(3)	1135(2)	1140(2)	1122(2)	1100.6(7)
Calculated density, ρ	5.783(2)	5.942(2)	6.330(2)	6.500(2)	6.705(5)	6.920(2)	7.120(2)	4.660(2)	7.300(2)	7.500(2)	7.700(2)
Experimental density, ρ					6.75			4.70			
$\Delta\rho$					± 0.01			± 0.01			

[a] Unit cell dimensions determined from crystal data.
[b] Atoms in VIII coordination (22).

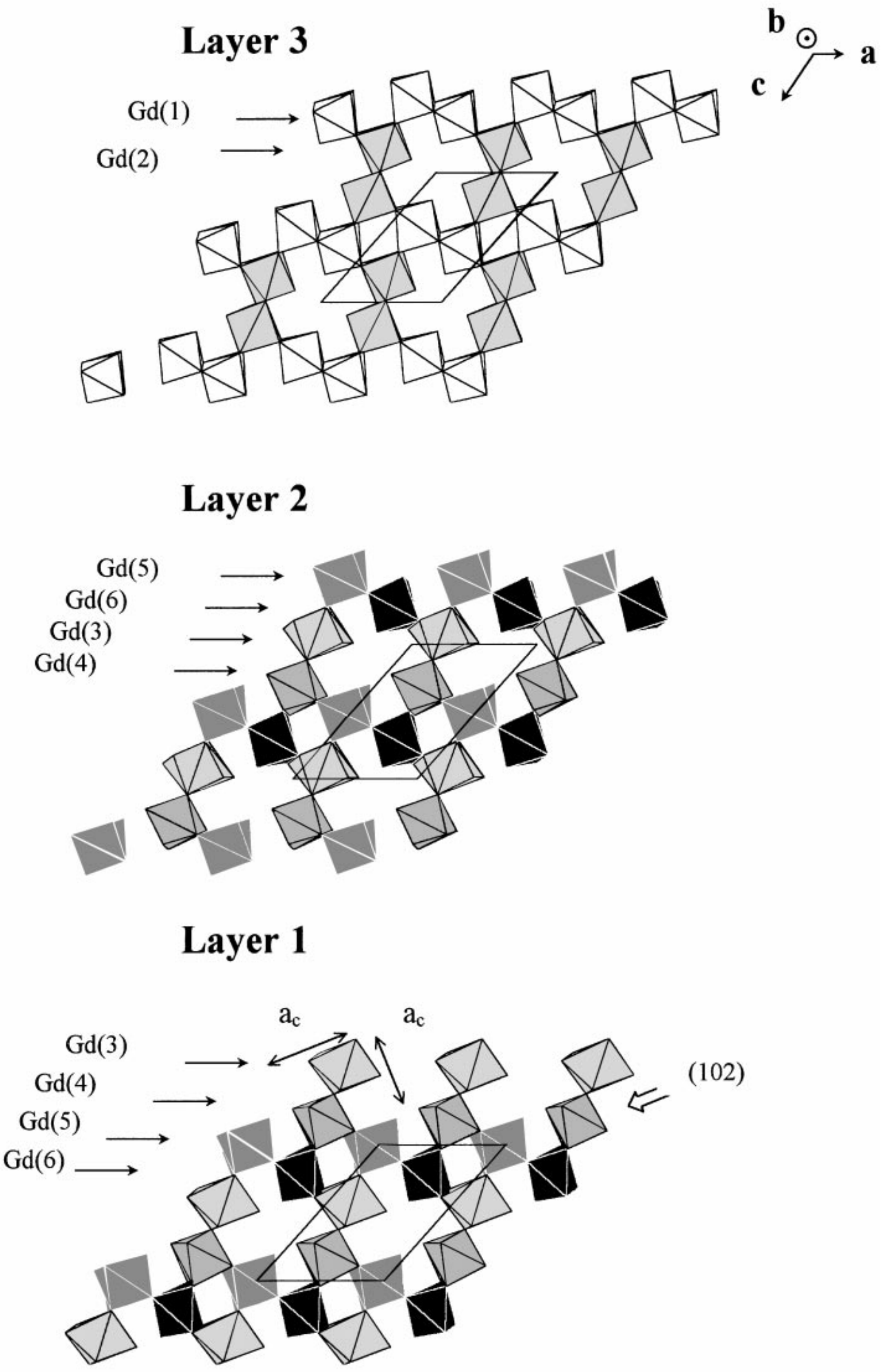

FIG. 1. Successive layers of Gd polyhedra along the b direction (a_c represents the dimension of a fluorite-type unit cell).

in Figs. 1 and 2. In each layer parallel to the *ac* plane, Gd atoms occupy four-fifths of the cationic sites of the fluorite-type array. A pair of lithium ions connected by borate groups (Fig. 4) as described below occupies a cavity formed by the vacant sites of three successive layers (Fig. 2).

B Atoms

The unit cell contains three types of crystallographically independent isolated $(BO_3)^{3-}$ groups. All borate groups consist of a boron triangularly coordinated to oxygen

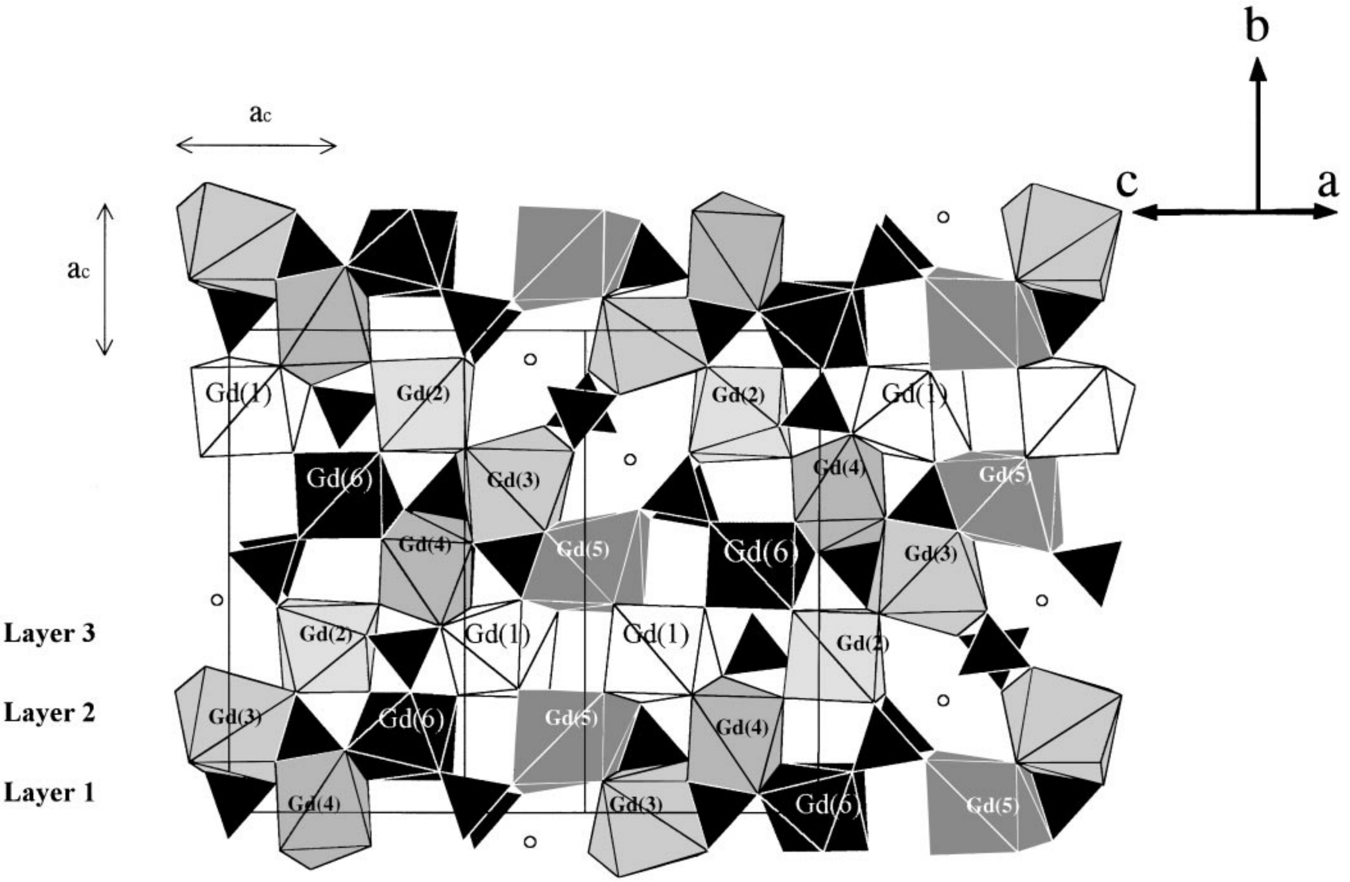

FIG. 2. Connection of the Gd layers on the (102) plane (a_c represents the dimension of a fluorite-type unit cell).

atoms. The B–O bond distances vary from 1.360 to 1.399 Å. All angles are close to 120°. B–O distances in structures containing isolated B triangles range in the same order: 1.34 to 1.42 Å in $La_{26}(BO_3)_8O_{27}$ (19), 1.357 to 1.396 Å in $Na_3Nd(BO_3)_2$ (20), 1.350 to 1.413 Å in $Li_3Pr_2(BO_3)_3$ (12), 1.36 to 1.40 Å in $Li_6Ho(BO_3)_3$ (5), 1.353 to 1.411 Å in $Li_6Y(BO_3)_3$ (21).

B triangles are connected by common edges and corners to Li and Gd polyhedra (Figs. 2 and 4). B(1) exchanges its three oxygen corners with two lithium atoms by a common edge and a corner, while B(2) and B(3) share only one edge of their coordination triangle with a neighboring lithium atom (Fig. 4).

Note the orientation of the B triangles which are all nearly parallel to the (102) plane.

Li Atoms

There is only one lithium atom type in the unit cell located on position 4*e*. The Li atom is surrounded by seven oxygen atoms with bond distances ranging from 2.03 to 2.57 Å. The polyhedron is greatly distorted with two short distances, 2.03 and 2.06 Å, one intermediate distance, 2.19 Å, and four very long distances, 2.44, 2.53, 2.55, and 2.57 Å. Because of the weak strength of Li–O bonds, the shape of this site depends strongly on the three-dimensional network of Gd polyhedra and boron triangles. Lithium polyhedra are connected two by two by way of B(1) triangles, giving rise with B(2) and B(3) triangles to a $(Li_2B_6O_{18})^{16-}$ anionic group (Fig. 4).

O Atoms

Oxygen atoms can be divided into three groups depending on their cationic bonding. Oxygen atoms O(1), O(2), O(3), O(5), O(6), O(7) and O(8) share Li, B, and Gd atoms while O(4) and O(9) are linked only to B and Gd atoms. Oxygen atoms O(10), O(11), O(12), O(13), and O(14) are only bound to Gd atoms and consequently the structure can be labeled oxyborate of lithium and gadolinium, $LiGd_6O_5(BO_3)_3$. It can be noted that all these last Gd–O distances correspond to the shortest bonds (2.231–2.348 Å). Because

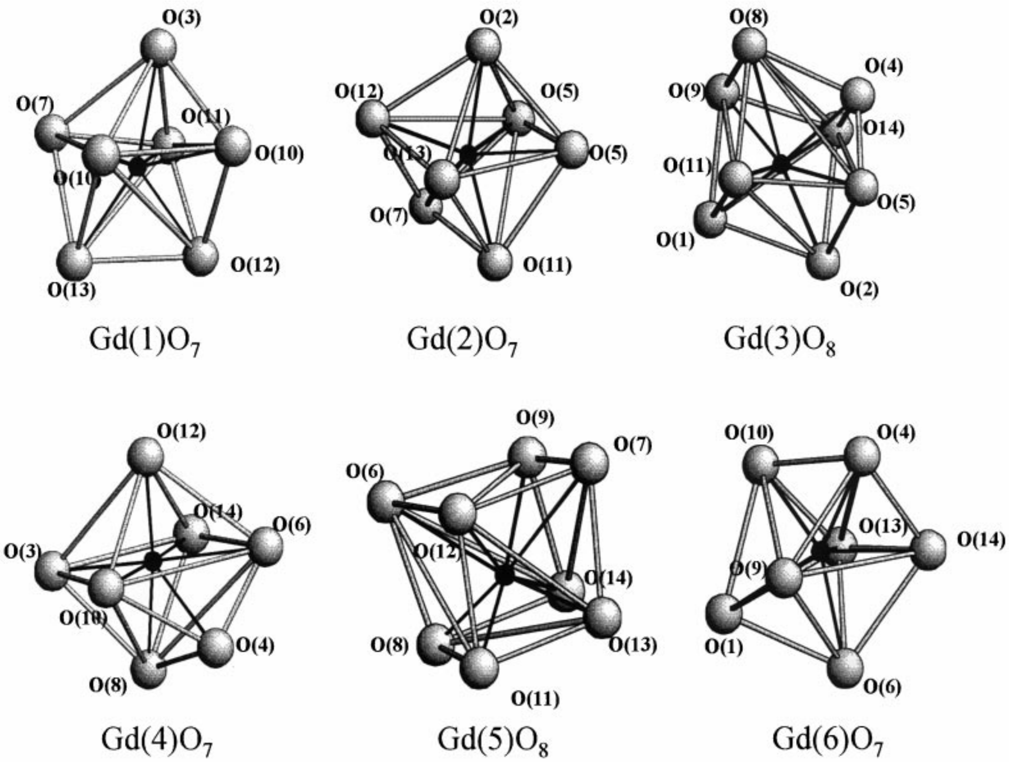

FIG. 3. Coordination polyhedra of gadolinium atoms.

of the highly covalent character of B–O bonds, the Gd–O bonds formed with oxygen of borate groups are weakened (Table 4).

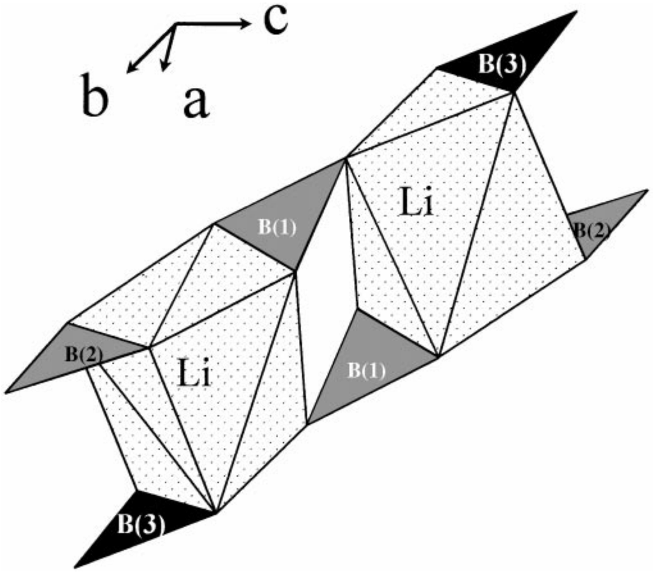

FIG. 4. $(Li_2B_6O_{18})^{16-}$ anionic group formed by two Li coordination polyhedra and six BO_3 triangles.

ISOSTRUCTURAL BORATES

$LiGd_6O_5(BO_3)_3$ is one member of a new family of oxyborates. Homologous phases were prepared as described above for *Ln* = Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, and Y. Each compound was characterized by X-ray powder diffraction. Diffraction data were recorded at room temperature on a Philips PW3040 (θ–θ) diffractometer in Bragg–Brentano geometry with Cu$K\alpha$ radiation. The unit cell parameters were refined with the complete powder diffraction data set (whole-pattern fitting). In Table 6 are given the lattice parameters with the experimental (Gd and Y) and calculated densities. As usual, density increases markedly with filling of the 4*f* shell of lanthanides.

CONCLUDING REMARKS

A novel family of oxyborates of formula $LiLn_6O_5(BO_3)_3$ have been discovered. Eleven phases have been isolated and characterized by X-ray powder diffraction for *Ln* = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Y. The structure of the Gd phase was solved by a single-crystal X-ray diffraction study. The three-dimensional framework of Gd polyhedra, $(Gd_6O_{14})^{10-}$, connected by common edges and corners presents a distorted fluorite-type array. One-fifth of the Gd cationic sites are vacant, forming cavities occupied by lithium and borate groups, $(Li_2B_6O_{18})^{16-}$. Some oxygen atoms share only Gd polyhedra, justifying the oxyborate label. It can be noted that similarly to this Gd_2O_3-rich phase, the cubic form (C) of Ln_2O_3 oxides is also structurally related to CaF_2. While in the oxyborate Gd is 7- or 8-coordinated, in the C form of rare-earth oxides, *Ln* is coordinated to six oxygen atoms with two vacant sites at the corners of the cube (23). Also, the structure of the oxyborate $La_{26}(BO_3)O_{27}$ is related to the fluorite (19).

Luminescence properties of Ce^{3+}, Eu^{3+}, and Tm^{3+} in $LiGd_6O_5(BO_3)_3$ and $LiY_6O_5(BO_3)_3$ matrices are under study and will be the subject of future papers.

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