RbLi$_2$Ga$_2$(BO$_3$)$_3$

Judith L. Kissick and Douglas A. Keszler*

Department of Chemistry and Center for Advanced Materials Research, Oregon State University, 153 Gilbert Hall, Corvallis, OR 97331-4003, USA
Correspondence e-mail: douglas.keszler@orst.edu

The structure of rubidium dilithium digallium tris(borate), RbLi$_2$Ga$_2$(BO$_3$)$_3$, contains two-dimensional sheets of open-branched rings of GaO$_4$ tetrahedra and planar BO$_3$ triangles that are joined by LiO$_4$ tetrahedra to form a three-dimensional framework. Ten-coordinate Rb atoms lie on twofold axes and occupy channels within the framework that extend along the b axis.

Comment

Metal borates are widely utilized materials as phosphors and non-linear optical materials (Keszler, 1999). To date, only two single-crystal studies have been reported on alkali-metal borates containing Ga, namely K$_2$Ga$_2$(BO$_3$)$_2$O (Smith *et al.*, 1997) and Cs$_2$Ga$_2$(BO$_3$)$_2$O (Smith, 1995). In this contribution we describe the structure of the new formulation RbLi$_2$-Ga$_2$(BO$_3$)$_3$.

The structure of RbLi$_2$Ga$_2$(BO$_3$)$_3$ is characterized by a three-dimensional framework built from corner-sharing LiO$_4$ and GaO$_4$ distorted tetrahedra and BO$_3$ triangles. As can be seen in Fig. 1, the Rb atoms are isolated in channels that extend along [010]. The structure is, in fact, a derivative of KZn$_4$(BO$_3$)$_3$ (Smith, 1989), wherein the Li and Ga atoms are well ordered on the two crystallographically distinct Zn sites of KZn$_4$(BO$_3$)$_3$.

In a conventional description, the BO$_3$ groups may be considered to rest in planes extending parallel to ($\bar{1}$01). The tetrahedra are then positioned with one Li—O or Ga—O vector directed approximately orthogonal to this plane.

Topologically similar M_2B$_2$O$_4$ (M = Ga, Li) rings are present throughout the structure. The Ga$_2$B$_2$O$_4$ rings connect *via* shared BO$_3$ groups to give Ga–borate layers parallel to ($\bar{1}$02). The Li$_2$B$_2$O$_4$ rings are also connected into sheets, here parallel to (100), but in addition to linkages through BO$_3$ groups, the LiO$_4$ tetrahedra share a common vertex, O1, resulting in the formation of the group Li$_2$O$_7$. This linkage provides a clear chemical distinction between Ga- and Li-centered polyhedra, and it likely provides a significant energetic contribution favoring the ordered occupation of the two available distorted tetrahedral sites.

The Rb atom occupies a ten-coordinate site with C_2 symmetry and a view along the b axis reveals that it sits half-

way between Ga$_2$B$_2$O$_4$ rings in adjacent Ga borate sheets. On the basis of the metrical parameters, a valence of +1.00 (1) is calculated for this atom (Brese & O'Keeffe, 1991). Bond valences consistent with expected integral values are computed for each of the remaining atoms in the structure.
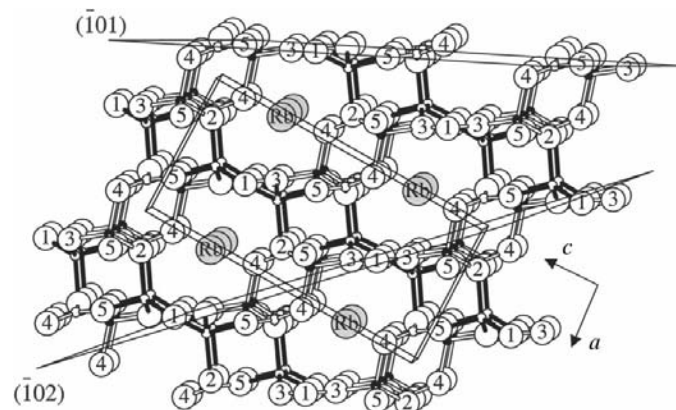

Figure 1
Schematic diagram showing the crystal structure of RbLi$_2$Ga$_2$(BO$_3$)$_3$ viewed along [010]. Large open spheres represent O atoms, large filled spheres represent Rb atoms, small filled spheres with open bonds represent Ga atoms, small open spheres with filled bonds represent Li atoms and small open spheres with open bonds represent B atoms (*ATOMS*; Shape Software, 1998).

Experimental

Single crystals of Li$_2$RbGa$_2$(BO$_3$)$_3$ were grown in a covered Pt crucible by melting a mixture of 26.6 wt% LiBO$_2$ (99.995%, Alfa), 34.5 wt% Rb$_2$CO$_3$ (99.8%, Alfa), 28.0 wt% Ga$_2$O$_3$ (99.99%, Alfa) and 10.9 wt% B$_2$O$_3$ (99.98%, Alfa). The melt was heated at 1073 K for 12 h to ensure homogeneity. It was then cooled to room temperature at a rate of 0.07 K min^{-1}. A clear colorless crystal was physically separated from the matrix for analysis.

Crystal data

RbLi$_2$Ga$_2$(BO$_3$)$_3$	D_x = 3.470 Mg m^{-3}
M_r = 415.22	Mo $K\alpha$ radiation
Monoclinic, $P2/c$	Cell parameters from 25
a = 6.297 (4) Å	reflections
b = 4.951 (3) Å	θ = 15–20°
c = 12.751 (6) Å	μ = 12.893 mm^{-1}
β = 91.65 (6)°	T = 296 (2) K
V = 397.4 (4) Å^3	Block, colorless
Z = 2	0.30 × 0.15 × 0.05 mm

Data collection

Rigaku AFC-6R diffractometer	θ_{max} = 35.07°
$\omega/2\theta$ scans	h = −10 → 10
Absorption correction: ψ scan	k = −8 → 8
(North *et al.*, 1968)	l = −20 → 20
T_{min} = 0.113, T_{max} = 0.565	3 standard reflections
3632 measured reflections	every 200 reflections
1753 independent reflections	intensity decay: 0.3%
R_{int} = 0.022	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.026	$+ 0.1503P]$
$wR(F^2)$ = 0.072	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.050	$(\Delta/\sigma)_{max}$ = 0.001
1753 reflections	$\Delta\rho_{max}$ = 1.72 e Å^{-3}
79 parameters	$\Delta\rho_{min}$ = −1.32 e Å^{-3}

inorganic compounds

Table 1
Selected geometric parameters (Å, °).

Rb—O1	3.284 (2)	B1—O2	1.382 (3)
Rb—O2^i	2.992 (2)	B1—O4^v	1.369 (3)
Rb—O3^{ii}	3.354 (2)	B1—O5^{vi}	1.377 (3)
Rb—O4^{iii}	3.059 (2)	B2—O1	1.335 (4)
Rb—O4^{iv}	3.120 (2)	B2—O3^{vii}	1.395 (2)
Ga—O2	1.8464 (16)	Li—O1^{viii}	1.845 (4)
Ga—O3	1.8245 (18)	Li—O2^i	1.997 (5)
Ga—O4	1.839 (2)	Li—O3^{ix}	1.918 (4)
Ga—O5	1.8317 (18)	Li—O5^{viii}	1.951 (5)
O3—Ga—O5	112.05 (7)	O1—B2—O3^{vii}	123.07 (13)
O3—Ga—O4	107.37 (9)	O1—B2—O3	123.07 (13)
O5—Ga—O4	109.16 (8)	O3^{vii}—B2—O3	113.9 (3)
O3—Ga—O2	109.52 (8)	O1^{viii}—Li—O3^{ix}	110.1 (2)
O5—Ga—O2	113.95 (8)	O1^{viii}—Li—O5^{viii}	104.7 (2)
O4—Ga—O2	104.31 (8)	O3^{ix}—Li—O5^{viii}	108.0 (2)
O4^v—B1—O5^{vi}	121.08 (19)	O1^{viii}—Li—O2^i	125.9 (2)
O4^v—B1—O2	120.66 (18)	O3^{ix}—Li—O2^i	102.73 (19)
O5^{vi}—B1—O2	118.25 (18)	O5^{viii}—Li—O2^i	104.4 (2)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-x, y-1, \frac{3}{2}-z$; (iii) $-x, y, \frac{3}{2}-z$; (iv) $x, y-1, z$; (v) $-x, 2-y, 1-z$; (vi) $x, 1+y, z$; (vii) $1-x, y, \frac{3}{2}-z$; (viii) $x-1, y, z$; (ix) $x-1, y-1, z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997).

References

Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Keszler, D. A. (1999). *Curr. Opin. Solid State Mater. Sci.* **4**, 155–162.
Molecular Structure Corporation (1997). *TEXSAN for Windows*. Version 1.0. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
Molecular Structure Corporation (1999). *MSC/AFC Diffractometer Control Software*. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Shape Software (1998). *ATOMS*. Shape Software, 521 Hidden Valley Rd, Kingsport, TN 37663, USA.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Smith, R. W. (1989). PhD dissertation, Oregon State University, USA.
Smith, R. W. (1995). *Acta Cryst.* C**51**, 547–549.
Smith, R. W., Kennard, M. A. & Dudick, M. J. (1997). *Mater. Res. Bull.* **32**, 649–656.