

Structure of LiGa_5O_8

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Lithiumpentagalliumoctaoxide, LiGa_5O_8 , crystallizes as an inverse spinel with gallium both in tetrahedral and octahedral sites, while lithium is in an octahedral environment. The oxygen tetrahedron surrounding gallium is nearly perfect with O–Ga–O bond angles of 109.4(1) and 109.6(1)°. Ideally, the spinel chains of edge-sharing octahedra have every fourth gallium octahedron occupied by lithium. The actual chains are disordered with 17.0(2)% of the gallium positions occupied by lithium and 53.9(1)% of the lithium positions occupied by gallium. Crystals were grown from a $\text{PbO-B}_2\text{O}_3$ flux with a cooling rate of 2.3 K h⁻¹ from 1573 to 773 K, yielding clear colourless octahedral crystals with edges of up to 5 mm. LiGa_5O_8 crystallizes in the cubic space group $P4_332$ (or $P4_132$) with $a=8.2023(6)$ Å and four formula units per cell. The least-squares refinement converged at $R_w=0.043$ for 544 reflections with $I>3\sigma(I)$.

The inverse spinel LiGa_5O_8 has been widely used as a carrier compound for optical studies of d elements in tetrahedral sites.^{1–5} Doped with small amounts of Co^{2+} it is a possible photo-echo material^{6,7} or host material for tunable lasers⁸ in the near-infrared region, 0.7–2 µm. Co^{2+} doped LiGa_5O_8 displays an unusually strong crystal field in which the ${}^4T_1(4p)$ level lies below the 2E level resulting in a series of spin allowed transitions which can compete successfully with the non-radiative relaxation process at this level.⁸ Co^{2+} in the tetrahedral site has a radiative lifetime of ca. 200 ns, at low temperature, of the luminescences at 685, 950 and 1025 nm. The structure of LiGa_5O_8 has previously been described by Joubert *et al.*⁹ The present single-crystal X-ray diffraction study was undertaken because a full understanding of the optical processes occurring in Co^{2+} -doped LiGa_5O_8 and the results of the circular dichroism studies¹⁰ require a more precise structure than that given in Ref. 9.

Experimental

The crystal used for the single-crystal study was grown from a $\text{PbO-B}_2\text{O}_3$ flux with a method similar to that given by Tate.¹¹ Equimolar amounts of Li_2CO_3 and Ga_2O_3 were mixed in a mortar with the double molar amounts of both PbO and B_2O_3 . Compared to the stoichiometry of the crystals, the flux contains a five-fold excess of lithium. After drying the mixture at 393 K for 3 h the temperature was increased slowly to 1573 K, at which temperature the resulting mixture of melted oxides was soaked during 10 h. The temperature was then

decreased by 2.3 K h⁻¹ to 773 K, at which point the furnace was turned off. The flux was removed by being dissolved in a 1:3 solution of nitric acid and water, yielding octahedral crystals with edges of up to 5 mm. One of the larger crystals was cut in half and analyzed using SEM/EDX for possible PbO contamination. Whereas no lead was found inside the crystal, small traces were detected on the crystal surface.

Parameters pertinent to the X-ray diffraction study are given in Table 1. The Ga positions in the structure were found using the direct methods program GENTAN (XTAL 3.2),¹² and the rest of the atoms were located in subsequent $\Delta\rho$ maps. The structure was refined by a full-matrix least-squares method (program UPALS).¹³ Anisotropic displacement parameters were used for all atoms. Atomic scattering and anomalous dispersion factors were taken from Ref. 14. Four reflections (044, 311, 400 and 022) were affected by extinction with correction factors ≥ 1.18 on F_0 in the final cycles of refinement.

The Ga/Li disorder was investigated by introducing gallium in the octahedral lithium site and vice versa. A least-squares refinement of the occupancies was carried out, restraining both types of atoms to the same positions and the sums of the occupation numbers to 1/2 and 1/6 for the Ga and Li sites, respectively. In the final cycles the occupation numbers were allowed to vary freely; the resulting shifts were less than 3σ .

Results and discussion

The final atomic coordinates and equivalent isotropic displacement parameters are given in Table 2.* A per-

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* Lists of structure factors and anisotropic displacement parameters are available from one of the authors (J. Å.).

Table 1. Crystal data and the determination and refinement of lithium gallium oxide, LiGa₅O₈.

Formula	Li _{0.97} Ga _{5.02} O ₈
<i>M_r</i>	483.54
Crystal system	Cubic
Space group	<i>P4₃32</i> (<i>P4₃32</i>) (No. 212)
<i>a</i> /Å	8.2023(6)
<i>V</i> /Å ³	551.8(1)
<i>Z</i>	4
<i>D_x</i> /g cm ⁻³	5.82
<i>F</i> (000)	888
<i>μ</i> /cm ⁻¹	240.5
Crystal size/mm ³	0.12 × 0.12 × 0.12
Crystal colour	Colourless
No. of faces	8 {111}
Grid for absorption correction (numerical integration)	10 × 10 × 10
Diffractometer	Enraf-Nonius CAD-4
Radiation/Å	Mo <i>Kα</i> (λ = 0.71069)
Scan type	ω/2θ
Scan width	Δω = 0.54° + 0.44° tanθ
θ-Range for data collection/°	2 < θ < 45
θ-Range for unit cell determination/°	36 < θ < 43 (23 reflections)
Transmission factor range	0.0996–0.1808
<i>hkl</i> range	<i>h</i> – 14 → 14 <i>k</i> – 14 → 14 <i>l</i> – 14 → 14
Measured reflections	12924
Independent reflections	650
Observed reflections, <i>I</i> > 3σ(<i>I</i>)	544
<i>R_{int}</i>	0.063
Least squares weight	<i>w</i> = [σ _c ² (<i>F_o</i>) + (0.01 <i>F_o</i>) ² + 1] ⁻¹
Extinction coefficient (Ref. 13) ^a	3.0(2) × 10 ³
<i>R</i> , <i>R_w</i>	0.036, 0.044
<i>S</i>	1.44
(Δ/σ) _{max}	0.054
Δρ _{max} , Δρ _{min} /e Å ⁻³	2.94, –1.90
Refined parameters	26

^a Isotropic.

Table 2. Atomic coordinates, equivalent displacement parameters and occupancies for LiGa₅O₈ (space group *P4₃32*) with e.s.d.s in parentheses.

Atom	Posn.	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> /Å ²	Occupancy
Ga1	12(d)	3/8	0.63018(4)	0.38018(4)	0.0034(1)	0.414(2)
Ga2	8(c)	0.25173(4)	0.25173(4)	0.25173(4)	0.0034(1)	1/3
Ga3	4(b)	1/8	7/8	3/8	0.0149(4)	0.090(1)
Li1	4(b)	1/8	7/8	3/8	0.0241(4)	0.077(1)
Li2	12(d)	3/8	0.6302(4)	0.3802(4)	0.0123(1)	0.085(2)
O1	8(c)	0.3844(3)	0.3844(3)	0.3844(3)	0.0048(3)	1/3
O2	24(e)	0.1339(3)	0.6283(3)	0.3679(2)	0.0050(4)	1

^a *U_{eq}* = 1/3(*U₁₁* + *U₂₂* + *U₃₃*).

spective view of the polyhedral arrangement in LiGa₅O₈ is shown in Fig. 1, and the coordination around the Ga1/Li2 and Ga2 sites in Figs. 2a and 2b, respectively.

A comparison of the occupation numbers of the Li1/Ga3 and Ga1/Li2 sites 4(*b*) and 12(*d*) indicates that, in the investigated crystal, about half of the octahedral lithium positions are in fact occupied by Ga³⁺ ions [53.9(1)%] and about one sixth of the octahedral Ga1 positions are occupied by Li⁺ ions [17.0(2)%], indicating a composition near Li_{0.97}Ga_{5.02}O₈. A complete disorder of Ga³⁺ and Li⁺ over the 4(*b*) + 12(*d*) sites would give

25% Li⁺ and 75% Ga³⁺ on each position. There is much less disorder in the isostructural compound LiAl₅O₈,¹⁵ where 95.7(3)% of the 4(*b*) positions are occupied by Li⁺ ions and 98.6(2)% of the 12(*d*) positions are occupied by Al³⁺ ions. No disorder has been reported for the likewise isostructural compound LiFe₅O₈.¹⁶ The transition to a random arrangement is at 1563 K for the aluminium¹⁷ and at 1008 K for the iron¹⁸ compound. A similar phase transition is indicated at about 1411 K for LiGa₅O₈.¹⁹

To verify that the large amount of disorder in the

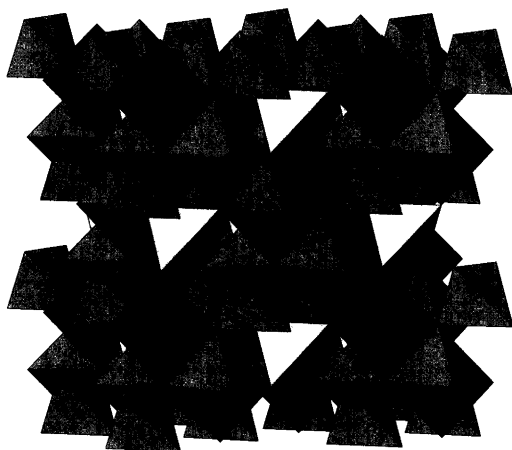


Fig. 1. A perspective view of the inverse spinel arrangement of oxygen polyhedra in LiGa_5O_8 . The darker octahedra are occupied by Li1/Ga3 and the lighter ones by Ga1/Li2 . All tetrahedra are occupied by Ga2 .

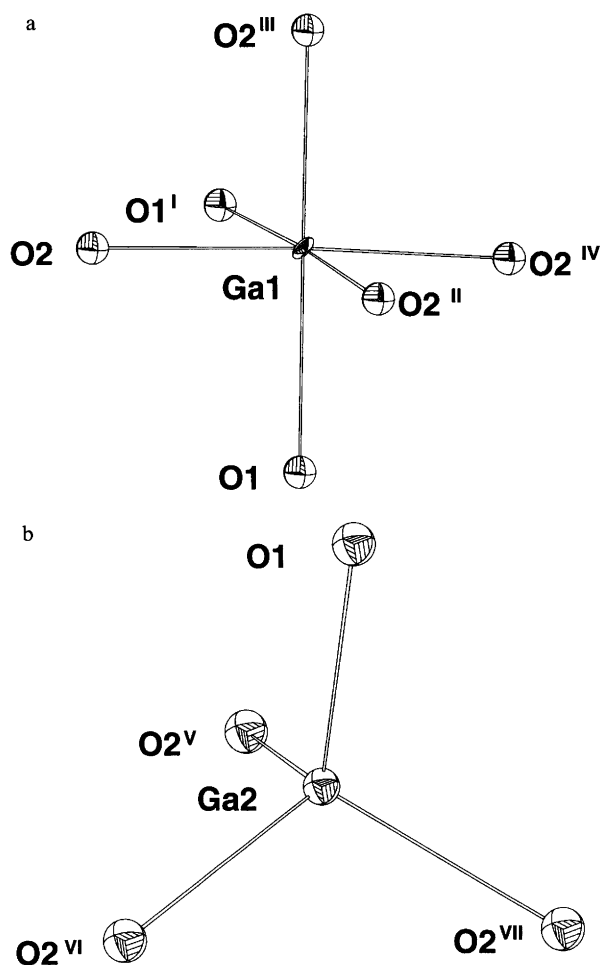


Fig. 2. The coordination around Ga1/Li3 (a) and Ga2 (b). Symmetry codes are given in Table 3. The atoms are displayed as displacement ellipsoids drawn at a probability level of 95%.

room temperature phase of LiGa_5O_8 was no artefact, another set of intensity data was collected and the structure re-refined using this set. The crystal used was from another preparation than the first; the main difference between the preparations was a doubled cooling rate, 5 K h^{-1} , from 1573 to 773 K for the second one. The new least-squares refinement converged at $R=0.040$, $R_w=0.042$ and $S=1.36$ for 528 independent observed reflections with $I > 3\sigma(I)$. The resulting population parameters were 60.0(7)% Ga^{3+} in the 4(b) positions and 17.9(4)% Li^+ in the 12(d) positions, i.e. the disorder is slightly larger in the second crystal than in the first.*

Why is LiGa_5O_8 disordered to a much higher extent than the corresponding aluminium and iron compounds? The ionic radii r_M for coordination number six are for Ga^{3+} 0.620, Li^+ 0.590, Fe^{3+} 0.55 (low-spin) and Al^{3+} 0.535 Å.²⁰ The disorder in the low-temperature form of LiGa_5O_8 may be related to the more similar size of Ga^{3+} and Li^+ than of Al^{3+} or Fe^{3+} and Li^+ . It may be easier for Ga^{3+} and Li^+ to substitute for each other in the oxide polyhedra than it is for Al^{3+} or Fe^{3+} and Li^+ .

The bond lengths and angles given in Table 3 show that both types of oxygen octahedra, surrounding either the 4(b) or the 12(d) positions, are distorted. The distance Li1-O [2.025(2) Å] is shorter than in LiAl_5O_8 ¹⁵ [2.044(2) Å], which may be a result of the large presence of Ga^{3+} on the Li1 site. On the other hand, the Ga1-O distances [1.953(2)–2.018(2) Å] are comparable to the octahedral Ga-O bond lengths in $\alpha\text{-Ga}_2\text{O}_3$ with corundum structure [1.921(8)–2.077(10) Å],²¹ but on this site the amount of gallium is quite high. The octahedral bond angles are about the same in LiGa_5O_8 and LiAl_5O_8 , i.e. the distortions of these polyhedra are of similar magnitudes in both compounds.

The bond lengths and angles given in Table 3 show that the GaO_4 tetrahedron is quite regular. The tetrahed-

Table 3. Bond distances (in Å) and angles (in °) with e.s.d.s in parentheses for Ga1, Ga2 and Li1.

Ga1-O1	2.018(2)	Ga2-O1	1.882(4)
Ga1-O2	1.980(2)	Ga2-O2 ^v	1.876(2)
Ga1-O2 ⁱⁱ	1.953(2)	Li1-O2	2.025(2)
O1-Ga1-O2	91.8(1)	O2-Ga1-O2 ^{iv}	175.2(1)
O1-Ga1-O2 ⁱⁱ	85.6(1)	O1-Ga2-O2 ^v	109.55(7)
O1-Ga1-O2 ^{iv}	84.9(1)	O2 ^v -Ga2-O2 ^{vi}	109.42(7)
O1-Ga1-O1 ⁱ	92.0(2)	O2-Li1-O2 ⁱⁱⁱ	86.21(8)
O2-Ga1-O2 ⁱⁱ	93.7(1)	O2-Li1-O2 ^{xi}	93.3(1)
O2-Ga1-O2 ⁱⁱⁱ	89.5(2)	O2 ⁱⁱⁱ -Li1-O2 ^x	94.1(1)
O2 ⁱⁱ -Ga1-O2 ⁱⁱⁱ	96.8(1)	O2-Li1-O2 ^{ix}	179.4(1)
O1-Ga1-O2 ⁱⁱⁱ	177.2(4)		

Symmetry codes for Table 3 and Fig. 2 are (i) $3/4 - y, 1/4 + x, -1/4 + z$; (ii) $-1/4 + y, 3/4 - x, 1/4 + z$; (iii) $1 - y, 1/2 + z, 1/2 - x$; (iv) $3/4 - x, 1/4 + z, -1/4 + y$; (v) $3/4 - y, 1/4 + x, -1/4 + z$; (vi) $-1/4 + x, 3/4 + y, 1/4 + x$; (vii) $1/4 + x, -1/4 + z, 3/4 - y$; (viii) $-3/4 + y, -1/4 + x, 3/4 - z$; (ix) $-1/4 + x, 7/4 - y, 1/4 + x$; (x) $1/2 - x, 1 - x, -1/2 + y$; (xi) $1/4 - x, 5/4 - z, 5/4 - y$.

* All relevant data and results are available from J. Å.

ral bond distances Ga2–O [average value 1.879(3) Å] are somewhat longer than in LiGaO₂ with wurtzite structure [average value 1.848(4) Å],²² and the tetrahedron is more regular.

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