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Symmetry reduction due to gallium substitution in the garnet $Li_{6.43(2)}Ga_{0.52(3)}La_{2.67(4)}Zr_2O_{12}$

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Single-crystal structure refinements on lithium lanthanum zirconate (LLZO; $Li_7La_3Zr_2O_{12}$) substituted with gallium were successfully carried out in the cubic symmetry space group $I\bar{4}3d$. Gallium was found on two lithium sites as well as on the lanthanum position. Due to the structural distortion of the resulting $Li_{6.43(2)}Ga_{0.52(3)}La_{2.67(4)}Zr_2O_{12}$ (Ga–LLZO) single crystals, a reduction of the LLZO cubic garnet symmetry from $Ia\bar{3}d$ to $I\bar{4}3d$ was necessary, which could hardly be analysed from X-ray powder diffraction data.

1. Chemical context

Garnets can be described with the ideal formula $A_3B_2(XO_4)_3$ in space group $Ia\bar{3}d$, with different coordination polyhedra of the respective elements with oxygen, resulting in a distorted cube for A (e.g. Ca), an octahedron for B (e.g. Al) and a tetrahedron for X (e.g. Si). The variability of the elements on the crystallographic sites (thereby keeping the high symmetry) gives rise to interesting material properties like ferrimagnetism (Geller, 1967). In recent years, garnet-type compounds containing Li have gained considerable interest as promising electrolyte materials for all-solid-state Li-ion batteries. The so-called 'Li-stuffed' garnets, which contain more Li than available on tetrahedral sites (X), meaning that excess Li occupies other sites as well, show an increase in Li-ion mobility. An exhaustive overview of these compounds was recently given by Thangadurai et al. (2014). The garnet-type fast lithium ion conductor $Li_7La_3Zr_2O_{12}$, abbreviated as LLZO, is such an 'Li-stuffed' garnet. Awaka et al. (2009) described the crystal structure of pure LLZO at ambient conditions in space group $I4_1/acd$. Even a small amount of Al in the structure (Al-LLZO) stabilizes the cubic garnet symmetry described in space group $Ia\bar{3}d$ by Geiger et al. (2011). These authors reported that Al could be found on two different tetrahedral sites using ^{27}Al MAS NMR spectroscopy but a final analysis was not possible due to the minor Al content. Rettenwander et al. (2014) reported on ^{71}Ga MAS NMR spectroscopy measurements on gallium substituted $Li_{7-3x}Ga_xLa_3Zr_2O_{12}$ (Ga–LLZO) indicating a fourfold coordination of the gallium atoms. The authors excluded the presence of Ga at the 24d position ($Ia\bar{3}d$) and assumed that the local symmetry could be lower than indicated by diffraction methods. In principle, the following exchanges are possible: (i) $3 Li^+ \leftrightarrow Ga^{3+} + 2$ voids, which is the most probable one and yields a good explanation for the higher conductivity due to the higher lithium atom jump probability to empty positions as
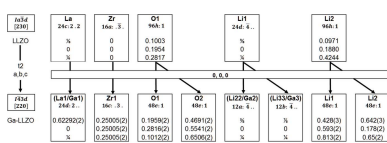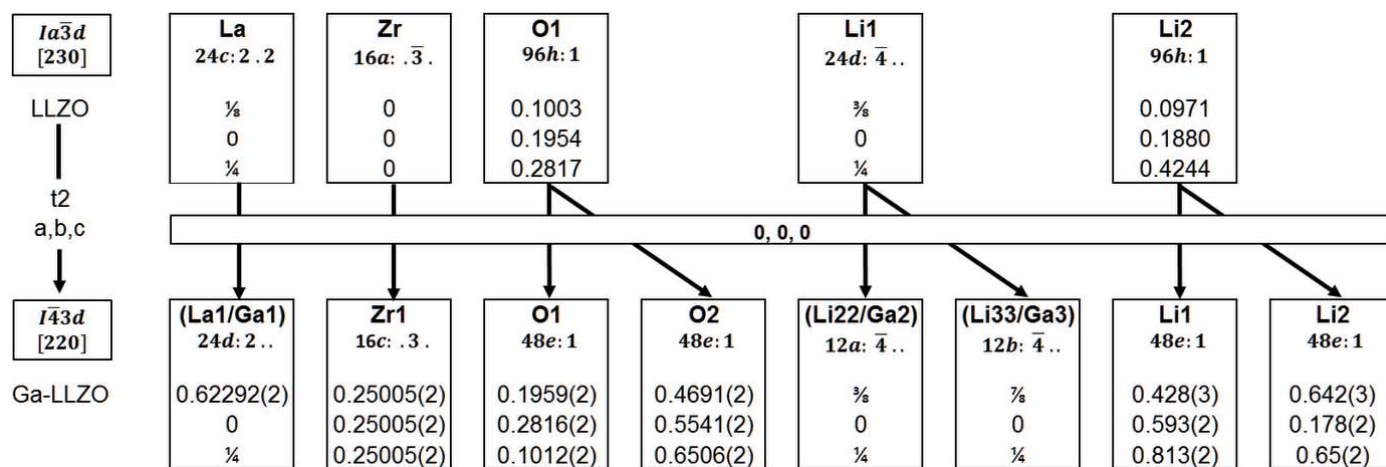
Figure 1
Bärnighausen tree (Bärnighausen, 1980) of the group–subgroup relation between cubic LLZO and the symmetry-reduced cubic Ga–LLZO.

discussed (Rettenwander *et al.*, 2014); (*ii*) $La^{3+} \leftrightarrow Ga^{3+}$, a valence-neutral exchange which should lead to a dynamical

Figure 2
Crystal structure of $Li_{6.43(2)}Ga_{0.52(3)}La_{2.67(4)}Zr_2O_{12}$ (Ga–LLZO) with all possible atom positions between the ZrO_6 octahedra (bottom) and the atom position specific coordination polyhedra (top). Displacement ellipsoids (top) are given at the 50% probability level.

disorder of the gallium atoms in order to lower the coordination number and shorten the Ga—O bond lengths for bond-valence balance, taking the different radii into account. The valence-neutral exchange should finally lead to higher displacement parameters of the atoms on the lanthanum position compared to that of the lighter zirconium atoms. (*iii*) $Zr^{4+} \leftrightarrow Ga^{3+} + Li^+$, which needs slightly more lithium for charge balance and could therefore be of minor probability.
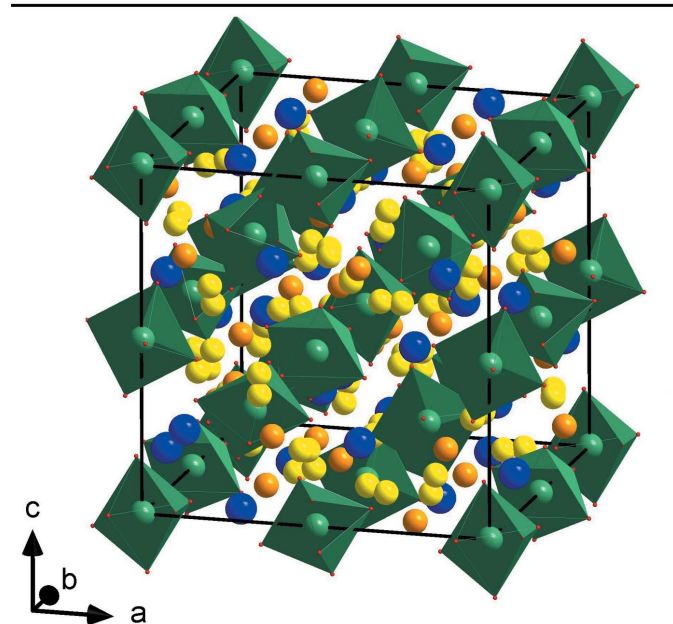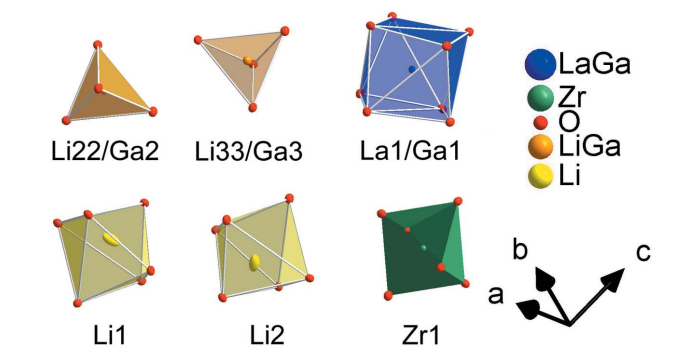
2. Structural commentary

The unit cell of the obtained single crystals could be well indexed using a body-centered cubic lattice with lattice parameter $a = 12.9681$ (15) Å. The space group determination with *XPREP* (Bruker, 2014) leads at once to the highest possible space group $Ia\bar{3}d$. However, a satisfactory structure solution or refinement with published structural data (Geiger *et al.*, 2011) in this space group type was not possible. Consequently, structure solutions by charge flipping (Bruker, 2009) were tried in all possible subgroups of $Ia\bar{3}d$ and the lowest R-values were obtained for the charge-flipping run in space group $I\bar{4}3d$. Subsequent refinements lead to the present structure model and clearly indicate the substitution of Ga^{3+} on the former $24c$ La^{3+} site as well as $24d$ Li^+ site in the aristotype in space group $Ia\bar{3}d$. The latter site splits into two sites due to the symmetry reduction as indicated by the Bärnighausen tree (Bärnighausen, 1980) given in Fig. 1. The deviation from six symmetry-equivalent Zr—O distances in LLZO ($Ia\bar{3}d$) results in a distortion of the ZrO_6 octahedron with Zr—O distances of 3×2.095 (2) and 3×2.113 (2) Å in Ga–LLZO. Another significant reduction of the highest possible symmetry for LLZO is the distortion of the eightfold coordinate La position (Fig. 2), for which distances between 2.496 (2) and 2.595 (2) Å are found in Ga–LLZO. This distortion results from the splitting of the $96h$ position of the oxygen atom in $Ia\bar{3}d$ into two $48e$ positions in $I\bar{4}3d$ (Fig. 1). Because the two lithium positions (Li22 and Li32) occupied by gallium are in principle identical to those positions of the higher symmetry structure (but with slightly shorter bond length due to the gallium

Table 1
Experimental details.

Crystal data	
Chemical formula	$Li_{6.43}Ga_{0.52}La_{2.67}Zr_2O_{12}$
M_r	826.20
Crystal system, space group	Cubic, $I\bar{4}3d$
Temperature (K)	301
a (Å)	12.9681 (15)
V (Å^3)	2180.9 (8)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	13.41
Crystal size (mm)	$0.25 \times 0.15 \times 0.13$
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.495, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	472450, 3678, 3508
R_{int}	0.046
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	1.340
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.026, 0.056, 1.46
No. of reflections	3678
No. of parameters	50
No. of restraints	3
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.08, −1.91
Absolute structure	Flack x determined using 1493 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.045 (9)

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *TOPAS* (Bruker, 2009), *SHELXL2014* (Sheldrick, 2015), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

substitution, *viz.* 4×1.916 (1) Å in LLZO and 4×1.908 (2) Å in Ga–LLZO), and the Li1 and Li2 positions are not occupied by gallium, the symmetry reduction is a confirmation of gallium atoms to be found also on the lanthanum position. This is also supported by the higher displacement parameter of the La site compared to the Zr site, as explained previously.

3. Synthesis and crystallization

The synthesis was configured to yield a compound with nominal composition $Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$. 2 g of a stoichiometric mixture of the pre-dried (30 h at 373 K in vacuum) educts Li_2O (with an excess of 10%$_{wt}$ to compensate the lithium loss due to thermal treatment), La_2O_3, ZrO_2 and Ga_2O_3 was weighted into a WC milling beaker (45 ml, 100 WC milling balls of 5 mm diameter, Fritsch, Germany) under inert conditions (glovebox) and high-energy ball-milled in a planetary ball mill (Pulverisette 7 *premium line*, Fritsch, Germany) under argon atmosphere for 8 h at a rotational speed of 10 s^{-1} as reported previously (Düvel *et al.*, 2012) for Al-substituted LLZO. The obtained powder was pressed to a pellet using a uniaxial pressure of 0.8 GPa. A stack of three pellets was placed on a platinum ring seated on a corundum plate, covered with a corundum crucible and heated for 12 h at 1323 K in a muffle furnace before cooling to room-temperature. The middle pellet from the stack had smooth green color

and showed visible grains. The surface of the pellet was grey and brittle and consisted mainly of lanthanum zirconates due to Li loss. From this pellet single crystals were extracted using a polarization microscope. Rietveld refinement of X-ray powder diffraction data of the green product shows a mixture of 96.8 (9)%$_{wt}$ cubic garnet-type Ga–LLZO and 3.2 (9)%$_{wt}$ Li_2ZrO_3 with a lattice parameter of $a = 12.9738$ (19) Å for its garnet-type structure. Energy dispersive X-ray analysis of the single crystal gave a tentative formula of $Li_{6.5\,(1)}Ga_{0.5\,(1)}La_{2.8\,(1)}Zr_{2.0\,(1)}O_{12}$, in good agreement with the refined formula $Li_{6.43\,(2)}Ga_{0.52\,(3)}La_{2.67\,(4)}Zr_2O_{12}$ determined from single crystal X-ray diffraction data.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Structure refinement was carried out as a two-component (merohedral) twin. Sites showing a statistical occupancy were constrained with respect to positions and anisotropic displacement parameters. An independent refinement of the anisotropic displacement parameters of Ga and Li on the Ga2/Li22 and Ga3/Li33 sites was not possible, although the reflection-to-parameter ratio is rather high. To ensure charge neutrality during the refinement of the Ga and Li occupancies on the Ga2/Li22 and Ga3/Li33 sites, the occupancies were restrained to exchange three Li atoms against one Ga atom.

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supporting information

Symmetry reduction due to gallium substitution in the garnet Li$_{6.43(2)}$Ga$_{0.52(3)}$La$_{2.67(4)}$Zr$_2$O$_{12}$
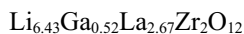
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Computing details

Data collection: *APEX2* (Bruker, 2014); cell refinement: *SAINT* (Bruker, 2014); data reduction: *SAINT* (Bruker, 2014); program(s) used to solve structure: *TOPAS* (Bruker, 2009); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Lithium gallium lanthanum zirconate

Crystal data

Li$_{6.43}$Ga$_{0.52}$La$_{2.67}$Zr$_2$O$_{12}$
M_r = 826.20
Cubic, $I\bar{4}3d$
a = 12.9681 (15) Å
V = 2180.9 (8) Å^3
Z = 8
$F(000)$ = 340
D_x = 5.033 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9913 reflections
θ = 3.1–72.3°
μ = 13.41 mm^{-1}
T = 301 K
Irregular, green
0.25 × 0.15 × 0.13 mm

Data collection

Bruker APEXII CCD
    diffractometer
φ and ω scans
Absorption correction: multi-scan
    (*SADABS*; Bruker, 2014)
T_{min} = 0.495, T_{max} = 0.754
472450 measured reflections

3678 independent reflections
3508 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 72.3°, θ_{min} = 2.2°
h = −34→34
k = −34→34
l = −34→34

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.056
S = 1.46
3678 reflections
50 parameters
3 restraints
$w = 1/[\sigma^2(F_o^2) + (0.011P)^2 + 8.6617P]$
    where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.049
$\Delta\rho_{max}$ = 2.08 e Å^{-3}
$\Delta\rho_{min}$ = −1.91 e Å^{-3}
Extinction correction: *SHELXL2014* (Sheldrick, 2015), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Absolute structure: Flack x determined using 1493 quotients [(I^+)-(I^-)]/[(I^+)+(I^-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.045 (9)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
La1	0.62292 (2)	0.0000	0.2500	0.00746 (2)	0.889 (4)
Ga1	0.62292 (2)	0.0000	0.2500	0.00746 (2)	0.111 (4)
Zr1	0.25005 (2)	0.25005 (2)	0.25005 (2)	0.00552 (4)	
O1	0.19586 (18)	0.28163 (18)	0.10116 (16)	0.0118 (3)	
O2	0.46910 (17)	0.55410 (17)	0.65064 (16)	0.0114 (2)	
Li1	0.428 (3)	0.593 (2)	0.813 (2)	0.029 (5)	0.33333 (14)
Li2	0.642 (3)	0.178 (2)	0.065 (2)	0.029 (5)	0.33333 (14)
Ga2	0.3750	0.5000	0.7500	0.0061 (4)	0.0857 (12)
Li22	0.3750	0.5000	0.7500	0.0061 (4)	0.743 (4)
Ga3	0.2500	0.3750	0.0000	0.0110 (9)	0.0403 (12)
Li32	0.2500	0.3750	0.0000	0.0110 (9)	0.879 (4)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.00912 (4)	0.00656 (5)	0.00668 (5)	0.000	0.000	−0.00141 (3)
Ga1	0.00912 (4)	0.00656 (5)	0.00668 (5)	0.000	0.000	−0.00141 (3)
Zr1	0.00552 (4)	0.00552 (4)	0.00552 (4)	0.00021 (3)	0.00021 (3)	0.00021 (3)
O1	0.0129 (6)	0.0138 (6)	0.0087 (5)	0.0014 (5)	−0.0007 (5)	0.0006 (5)
O2	0.0131 (6)	0.0116 (6)	0.0096 (5)	0.0010 (5)	0.0000 (5)	−0.0013 (4)
Li1	0.051 (15)	0.015 (6)	0.022 (6)	−0.013 (9)	−0.013 (8)	0.006 (6)
Li2	0.051 (15)	0.015 (6)	0.022 (6)	−0.013 (9)	−0.013 (8)	0.006 (6)
Ga2	0.0078 (10)	0.0052 (6)	0.0052 (6)	0.000	0.000	0.000
Li22	0.0078 (10)	0.0052 (6)	0.0052 (6)	0.000	0.000	0.000
Ga3	0.0100 (14)	0.013 (2)	0.0100 (14)	0.000	0.000	0.000
Li32	0.0100 (14)	0.013 (2)	0.0100 (14)	0.000	0.000	0.000

Geometric parameters (Å, º)

La1—O1[i]	2.496 (2)	O2—Li2[xxiii]	2.09 (3)
La1—O1[ii]	2.496 (2)	O2—Zr1[xxiv]	2.113 (2)
La1—O2[iii]	2.520 (2)	O2—Li1	2.23 (4)
La1—O2[iv]	2.520 (2)	O2—La1[xxv]	2.520 (2)
La1—O2[v]	2.590 (2)	O2—Li2[xxvi]	2.54 (3)
La1—O2[vi]	2.590 (2)	O2—La1[xxiii]	2.590 (2)
La1—O1[vii]	2.595 (2)	O2—Li2[xxvii]	2.61 (4)
La1—O1[viii]	2.595 (2)	Li1—O2[xxviii]	1.91 (4)
Zr1—O1[ix]	2.095 (2)	Li1—O2[xxii]	2.04 (3)

Zr1—O1[x]	2.095 (2)	Li1—O1[xxix]	2.16 (3)
Zr1—O1	2.095 (2)	Li1—O1[xxx]	2.65 (3)
Zr1—O2[xi]	2.113 (2)	Li2—O1[viii]	1.90 (3)
Zr1—O2[xii]	2.113 (2)	Li2—O2[vi]	2.09 (3)
Zr1—O2[xiii]	2.113 (2)	Li2—O1[xvi]	2.22 (4)
O1—Li2[xiv]	1.90 (3)	Li2—O1[xxxi]	2.32 (3)
O1—Ga3	1.918 (2)	Li2—O2[xxxii]	2.54 (3)
O1—Li1[xv]	2.16 (3)	Li2—O2[xxxiii]	2.61 (4)
O1—Li2[xvi]	2.22 (4)	Li2—Li2[xxxiv]	2.68 (6)
O1—Li2[xvii]	2.32 (3)	Ga2—O2[xxi]	1.908 (2)
O1—La1[xviii]	2.496 (2)	Ga2—O2[xxii]	1.908 (2)
O1—La1[xix]	2.595 (2)	Ga2—O2[xxviii]	1.908 (2)
O1—Li1[xx]	2.65 (3)	Ga3—O1[xxxv]	1.918 (2)
O2—Ga2	1.908 (2)	Ga3—O1[xxxvi]	1.918 (2)
O2—Li1[xxi]	1.91 (4)	Ga3—O1[xxxvii]	1.918 (2)
O2—Li1[xxii]	2.04 (3)		
O1[i]—La1—O1[ii]	73.18 (10)	La1[xviii]—O1—Li1[xx]	79.5 (6)
O1[i]—La1—O2[iii]	160.55 (5)	La1[xix]—O1—Li1[xx]	68.9 (8)
O1[ii]—La1—O2[iii]	111.27 (5)	Ga2—O2—Li1[xxi]	49.8 (10)
O1[i]—La1—O2[iv]	111.27 (5)	Ga2—O2—Li1[xxii]	48.0 (8)
O1[ii]—La1—O2[iv]	160.55 (5)	Li1[xxi]—O2—Li1[xxii]	77.4 (11)
O2[iii]—La1—O2[iv]	71.21 (10)	Ga2—O2—Li2[xxiii]	66.9 (11)
O1[i]—La1—O2[v]	73.18 (7)	Li1[xxi]—O2—Li2[xxiii]	18.2 (10)
O1[ii]—La1—O2[v]	95.73 (8)	Li1[xxii]—O2—Li2[xxiii]	85.1 (16)
O2[iii]—La1—O2[v]	123.67 (5)	Ga2—O2—Zr1[xxiv]	128.57 (12)
O2[iv]—La1—O2[v]	68.75 (9)	Li1[xxi]—O2—Zr1[xxiv]	104.4 (9)
O1[i]—La1—O2[vi]	95.73 (8)	Li1[xxii]—O2—Zr1[xxiv]	87.4 (8)
O1[ii]—La1—O2[vi]	73.18 (7)	Li2[xxiii]—O2—Zr1[xxiv]	88.5 (10)
O2[iii]—La1—O2[vi]	68.75 (9)	Ga2—O2—Li1	44.9 (8)
O2[iv]—La1—O2[vi]	123.67 (5)	Li1[xxi]—O2—Li1	72.9 (12)
O2[v]—La1—O2[vi]	166.44 (9)	Li1[xxii]—O2—Li1	85.9 (12)
O1[i]—La1—O1[vii]	125.03 (5)	Li2[xxiii]—O2—Li1	89.7 (13)
O1[ii]—La1—O1[vii]	68.53 (9)	Zr1[xxiv]—O2—Li1	173.2 (7)
O2[iii]—La1—O1[vii]	72.72 (6)	Ga2—O2—La1[xxv]	94.15 (8)
O2[iv]—La1—O1[vii]	94.96 (7)	Li1[xxi]—O2—La1[xxv]	143.6 (9)
O2[v]—La1—O1[vii]	73.07 (5)	Li1[xxii]—O2—La1[xxv]	80.5 (11)
O2[vi]—La1—O1[vii]	108.77 (5)	Li2[xxiii]—O2—La1[xxv]	161.0 (11)
O1[i]—La1—O1[viii]	68.53 (9)	Zr1[xxiv]—O2—La1[xxv]	103.05 (9)
O1[ii]—La1—O1[viii]	125.03 (5)	Li1—O2—La1[xxv]	77.0 (9)
O2[iii]—La1—O1[viii]	94.96 (7)	Ga2—O2—Li2[xxvi]	57.6 (8)
O2[iv]—La1—O1[viii]	72.72 (6)	Li1[xxi]—O2—Li2[xxvi]	76.3 (11)
O2[v]—La1—O1[viii]	108.77 (5)	Li1[xxii]—O2—Li2[xxvi]	99.9 (14)
O2[vi]—La1—O1[viii]	73.07 (5)	Li2[xxiii]—O2—Li2[xxvi]	91.0 (11)
O1[vii]—La1—O1[viii]	165.12 (9)	Zr1[xxiv]—O2—Li2[xxvi]	172.6 (9)
O1[ix]—Zr1—O1[x]	86.37 (10)	Li1—O2—Li2[xxvi]	14.0 (8)
O1[ix]—Zr1—O1	86.37 (10)	La1[xxv]—O2—Li2[xxvi]	79.4 (7)
O1[x]—Zr1—O1	86.37 (10)	Ga2—O2—La1[xxiii]	122.63 (10)

O1^ix—Zr1—O2^xi	93.51 (9)	Li1^xxi—O2—La1^xxiii	95.8 (10)
O1^x—Zr1—O2^xi	179.59 (11)	Li1^xxii—O2—La1^xxiii	170.6 (8)
O1—Zr1—O2^xi	94.02 (9)	Li2^xxiii—O2—La1^xxiii	90.4 (8)
O1^ix—Zr1—O2^xii	94.02 (9)	Zr1^xxiv—O2—La1^xxiii	100.77 (8)
O1^x—Zr1—O2^xii	93.51 (9)	Li1—O2—La1^xxiii	85.8 (7)
O1—Zr1—O2^xii	179.59 (11)	La1^xxv—O2—La1^xxiii	101.98 (8)
O2^xi—Zr1—O2^xii	86.10 (9)	Li2^xxvi—O2—La1^xxiii	71.8 (9)
O1^ix—Zr1—O2^xiii	179.59 (11)	Ga2—O2—Li2^xxvii	56.1 (7)
O1^x—Zr1—O2^xiii	94.02 (9)	Li1^xxi—O2—Li2^xxvii	83.4 (14)
O1—Zr1—O2^xiii	93.51 (9)	Li1^xxii—O2—Li2^xxvii	8.2 (9)
O2^xi—Zr1—O2^xiii	86.10 (9)	Li2^xxiii—O2—Li2^xxvii	89.2 (9)
O2^xii—Zr1—O2^xiii	86.10 (9)	Zr1^xxiv—O2—Li2^xxvii	80.4 (7)
Li2^xiv—O1—Ga3	55.1 (12)	Li1—O2—Li2^xxvii	93.0 (11)
Li2^xiv—O1—Zr1	100.2 (12)	La1^xxv—O2—Li2^xxvii	78.2 (6)
Ga3—O1—Zr1	129.12 (12)	Li2^xxvi—O2—Li2^xxvii	107.0 (12)
Li2^xiv—O1—Li1^xv	17.3 (11)	La1^xxiii—O2—Li2^xxvii	178.8 (7)
Ga3—O1—Li1^xv	71.3 (8)	O2^xxviii—Li1—O2^xxii	108.5 (14)
Zr1—O1—Li1^xv	84.8 (8)	O2^xxviii—Li1—O1^xxix	98.6 (18)
Li2^xiv—O1—Li2^xvi	80.8 (13)	O2^xxii—Li1—O1^xxix	93.9 (12)
Ga3—O1—Li2^xvi	50.0 (9)	O2^xxviii—Li1—O2	101.2 (12)
Zr1—O1—Li2^xvi	85.8 (9)	O2^xxii—Li1—O2	86.8 (14)
Li1^xv—O1—Li2^xvi	87.3 (14)	O1^xxix—Li1—O2	158.9 (18)
Li2^xiv—O1—Li2^xvii	78.1 (15)	O2^xxviii—Li1—O1^xxx	144.7 (15)
Ga3—O1—Li2^xvii	48.2 (10)	O2^xxii—Li1—O1^xxx	106.5 (15)
Zr1—O1—Li2^xvii	177.3 (10)	O1^xxix—Li1—O1^xxx	83.1 (9)
Li1^xv—O1—Li2^xvii	93.8 (10)	O2—Li1—O1^xxx	76.4 (12)
Li2^xvi—O1—Li2^xvii	91.8 (16)	O1^viii—Li2—O2^vi	101.0 (12)
Li2^xiv—O1—La1^xviii	147.5 (13)	O1^viii—Li2—O1^xvi	102.1 (17)
Ga3—O1—La1^xviii	92.55 (8)	O2^vi—Li2—O1^xvi	91.1 (12)
Zr1—O1—La1^xviii	103.48 (9)	O1^viii—Li2—O1^xxxi	98.5 (14)
Li1^xv—O1—La1^xviii	163.4 (9)	O2^vi—Li2—O1^xxxi	160.3 (14)
Li2^xvi—O1—La1^xviii	79.1 (7)	O1^xvi—Li2—O1^xxxi	82.0 (13)
Li2^xvii—O1—La1^xviii	77.3 (7)	O1^viii—Li2—O2^xxxii	151.8 (19)
Li2^xiv—O1—La1^xix	94.7 (9)	O2^vi—Li2—O2^xxxii	86.9 (13)
Ga3—O1—La1^xix	123.13 (10)	O1^xvi—Li2—O2^xxxii	104.8 (10)
Zr1—O1—La1^xix	100.26 (9)	O1^viii—Li2—O2^xxxiii	84.1 (12)
Li1^xv—O1—La1^xix	89.9 (10)	O2^vi—Li2—O2^xxxiii	85.2 (14)
Li2^xvi—O1—La1^xix	173.1 (9)	O1^xvi—Li2—O2^xxxiii	173.3 (16)
Li2^xvii—O1—La1^xix	82.1 (10)	O1^xxxi—Li2—O2^xxxiii	99.7 (11)
La1^xviii—O1—La1^xix	102.50 (8)	O2^xxxii—Li2—O2^xxxiii	69.5 (10)
Li2^xiv—O1—Li1^xx	81.4 (12)	O2^xxi—Ga2—O2^xxii	114.14 (7)
Ga3—O1—Li1^xx	60.5 (8)	O2^xxi—Ga2—O2^xxviii	100.49 (13)
Zr1—O1—Li1^xx	169.2 (8)	O2^xxii—Ga2—O2^xxviii	114.14 (7)
Li1^xv—O1—Li1^xx	95.1 (9)	O1—Ga3—O1^xxxv	113.48 (7)

Li2[xvi]—O1—Li1[xx]	105.0 (14)	O1—Ga3—O1[xxxvi]	101.73 (14)
Li2[xvii]—O1—Li1[xx]	13.3 (11)	O1[xxxv]—Ga3—O1[xxxvi]	113.48 (7)

Symmetry codes: (i) −y+3/4, x−1/4, −z+1/4; (ii) −y+3/4, −x+1/4, z+1/4; (iii) −x+5/4, −z+3/4, y−1/4; (iv) −x+5/4, z−3/4, −y+3/4; (v) −z+5/4, y−3/4, −x+3/4; (vi) −z+5/4, −y+3/4, x−1/4; (vii) −z+3/4, −y+1/4, x+1/4; (viii) −z+3/4, y−1/4, −x+1/4; (ix) y, z, x; (x) z, x, y; (xi) z−1/4, y−1/4, x−1/4; (xii) y−1/4, x−1/4, z−1/4; (xiii) x−1/4, z−1/4, y−1/4; (xiv) −z+1/4, y+1/4, −x+3/4; (xv) x−1/4, −z+5/4, −y+3/4; (xvi) −x+1, −y+1/2, z; (xvii) x−1/2, −y+1/2, −z; (xviii) −y+1/4, −x+3/4, z−1/4; (xix) z−1/4, −y+1/4, −x+3/4; (xx) y−1/2, z−1/2, x−1/2; (xxi) −x+3/4, z−1/4, −y+5/4; (xxii) x, −y+1, −z+3/2; (xxiii) z+1/4, −y+3/4, −x+5/4; (xxiv) y+1/4, x+1/4, z+1/4; (xxv) −x+5/4, z+1/4, −y+3/4; (xxvi) −z+1/2, x, −y+1; (xxvii) −z+1/2, −x+1, y+1/2; (xxviii) −x+3/4, −z+5/4, y+1/4; (xxix) x+1/4, −z+3/4, −y+5/4; (xxx) z+1/2, x+1/2, y+1/2; (xxxi) x+1/2, −y+1/2, −z; (xxxii) y, −z+1, −x+1/2; (xxxiii) −y+1, z−1/2, −x+1/2; (xxxiv) z+3/4, −y+1/4, −x+3/4; (xxxv) z+1/4, −y+3/4, −x+1/4; (xxxvi) −x+1/2, y, −z; (xxxvii) −z+1/4, −y+3/4, x−1/4.