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Synchrotron study of the garnet-type oxide $\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$

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Key indicators: powder synchrotron study; $T = 298\text{ K}$; mean $\sigma(\text{Ta}-\text{O}) = 0.007\text{ \AA}$; disorder in main residue; R factor = 15.0; wR factor = 22.0; data-to-parameter ratio = 7.6.

Hexalithium calcium disamarium(III) ditantalum(V) dodecaoxide, $\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$, crystallizes in a cubic garnet-type structure. In the crystal structure, disordered Li atoms occupy two crystallographic sites. One Li has a tetrahedral coordination environment in the oxide lattice, whereas the other Li atom occupies a significantly distorted octahedral site, with site occupancies for the two Li atoms of 0.26 (7) and 0.44 (2), respectively. Ca and Sm atoms are statistically distributed over the same crystallographic position with a occupancy of 2/3 for Sm and of 1/3 for Ca, and are eightfold coordinated by O atoms. The TaO_6 octahedron is joined to six others *via* corner-sharing LiO_4 tetrahedra. One Li and the O atoms lie on general positions, while the other atoms are situated on special positions. The Sm/Ca position has $\bar{2}22$, Ta has $\bar{3}$, and the tetrahedrally coordinated Li atom has $\bar{4}$ site symmetry.

Related literature

For a general description of structures and physical properties of garnets, see: Geller (1967). Recently, high Li-ion conductivity was discovered in garnet-related compounds such as $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ ($M = \text{Nb}, \text{Ta}$), see: Thangadurai *et al.* (2003); Cussen (2006). For studies focused on the substitution of La^{3+} by divalent alkaline earth ions (Ca, Sr, Ba), see: Murugan *et al.* (2007); Thangadurai & Weppner (2005a,b); O'Callaghan & Cussen (2007); Percival & Slater (2007). For indexing the powder diffraction pattern, see: Boulitf & Louër (2004).

Experimental

Crystal data

$\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$
 $M_r = 936.45$
 Cubic, $Ia\bar{3}d$

$a = 12.55128(7)\text{ \AA}$
 $V = 1977.26(2)\text{ \AA}^3$
 $Z = 8$

Synchrotron radiation
 $\lambda = 1.54900\text{ \AA}$
 $T = 298\text{ K}$
 Specimen shape: flat sheet
 $20 \times 20 \times 0.5\text{ mm}$

Specimen prepared at 103 kPa
 Specimen prepared at 1223 K
 Particle morphology: particle,
 yellowish-white

Data collection

Pohang Light Source 8C2 HRPD
 Beamline diffractometer
 Specimen mounting: 'packed
 powder pellet'

Specimen mounted in reflection
 mode
 Scan method: step
 $2\theta_{\text{min}} = 10.0$, $2\theta_{\text{max}} = 131.0^\circ$
 Increment in $2\theta = 0.01^\circ$

Refinement

$R_p = 15.0$
 $R_{wp} = 22.0$
 $R_{exp} = 13.1$
 $R_B = 6.62$
 $S = 1.67$
 Excluded region(s): None

Profile function: pseudo Voigt
 151 reflections
 20 parameters
 Preferred orientation correction:
 none

Table 1

Selected bond lengths (\AA).

(Sm,Ca)—O1	2.561 (17)	Li2—O1 ⁱⁱⁱ	2.12 (6)
Ta1—O1	2.014 (6)	Li2—O1 ^{iv}	2.20 (6)
Li1—O1	1.843 (7)	Li2—O1 ^v	2.55 (6)
Li2—O1 ⁱ	1.63 (6)	Li2—O1 ^{vi}	2.69 (6)
Li2—O1 ⁱⁱ	2.14 (6)		

Symmetry codes: (i) $-z + \frac{3}{4}, -y + \frac{1}{4}, x + \frac{1}{4}$; (ii) $z - \frac{1}{2}, x, -y + \frac{1}{2}$; (iii) $-y, z - \frac{1}{2}, -x + \frac{1}{2}$; (iv) $y, -z + 1, -x + \frac{1}{2}$; (v) $y + \frac{1}{4}, -x + \frac{1}{4}, z - \frac{1}{4}$; (vi) $-y + \frac{1}{4}, -x + \frac{1}{4}, -z + \frac{5}{4}$.

Data collection: local software at 8C2 HRPD beamline; cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2001); data reduction: *FULLPROF*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *FULLPROF*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *FULLPROF*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2261).

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supporting information

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Synchrotron study of the garnet-type oxide $\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$

Chung-Yul Yoo, Sung-Chul Kim, Seung-Soo Lee and Seung-Joo Kim

S1. Comment

Conventional garnet-type oxides with general formula $A_3B_3C_2O_{12}$ contain tetrahedral, cubic and octahedral coordination environments filled with *A*, *B*, and *C* atoms, respectively. The garnet structure has attracted renewed interest since a Li^+ ionic conductivity was observed in the compound $\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$, which contains an excess of Li beyond the usual garnet composition. The ionic conductivity was enhanced through the increase of the Li content *via* partial substitution of trivalent La^{3+} by divalent alkaline earth ions (Murugan *et al.*, 2007). The structure of the title compound is closely related to that of $\text{Li}_6\text{SrLa}_2\text{Ta}_2\text{O}_{12}$ (Percival & Slater, 2007). Li1 atoms are located at site 24*d* (tetrahedral), Li2 atoms at site 96*h* (distorted octahedral), Sm/Ca atoms are at site 24*c* (cubic), Ta atoms at site 16*a* (octahedral), and O atoms at general site 96*h* (Fig. 1). As shown in Fig. 2, the partially occupied Li2 site exhibits a significantly distorted [4 + 2] coordination polyhedron with Li—O bond lengths between 1.63 (6) - 2.69 (6) Å. The Li1 atoms at the tetrahedral sites and adjacent Li2 atoms at the octahedral sites are connected by common oxygen atoms *via* face-sharing. Considering the site occupation factors (SOF) for Li1 and Li2 sites, $\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$ can be described as $\text{Li}_{2(3+x)}[\text{Li}_{1(3-x)}(\text{Ca}_{1/3}\text{Sm}_{2/3})_3\text{Ta}_2\text{O}_{12}]$ with $x = 2.23$.

For a general description of structures and physical properties of garnets, see: Geller (1967). High Li-ion conductivity was discovered in garnet-related compounds such as $\text{Li}_5\text{La}_3M_2\text{O}_{12}$, where $M = \text{Nb}, \text{Ta}$ (Thangadurai *et al.*, 2003; Cussen, 2006). For studies focused on the substitution of La^{3+} by divalent alkaline earth ions (Ca, Sr, Ba), see: Thangadurai & Weppner (2005a,b), O'Callaghan & Cussen (2007).

S2. Experimental

The polycrystalline sample of $\text{Li}_6\text{Sm}_2\text{CaTa}_2\text{O}_{12}$ was prepared by solid-state reaction of stoichiometric amounts of Sm_2O_3 , Ta_2O_5 , CaCO_3 and 10% excess of Li_2CO_3 . Sm_2O_3 was preheated at 1173 K for 24 h to remove absorbed water before using. The finely ground samples were heated at 1123 and 1173 K for 12 h and then 1223 K for 24 h, with intermediate regrindings. Synchrotron X-ray diffraction (sXRD) measurement was performed on beamline 8 C2-HRPD at Pohang Accelerator Laboratory, Pohang, Korea. The incident X-rays were vertically collimated by a mirror, and monochromated to the wavelength of 1.5490 Å by double-crystal Si (111) monochromator. The datasets were collected in the range of $10^\circ \leq 2\theta \leq 130^\circ$ with a step size of 0.01° (2θ range).

S3. Refinement

All reflections could be indexed with a body centered cubic cell. Any additional peaks due to symmetry lowering or impurity phase were not detected. The unit-cell parameter was determined with the DICVOL program (Boultif & Louër, 2004). The figures of merit were $M(20) = 175.8$, $F(20) = 134.8(0.0013, 114)$. The reflection conditions for (*hkl*): $h + k + l = \text{even}$, (*0kl*): $k, l = \text{even}$, (*hhl*): $2h + l = 4n$ and $l = \text{even}$, (*00l*): $l = 4n$ suggested that the Li containing-garnet structure belonged to $Ia\bar{3}d$ space group. The atomic positions of Ta, Sm, Ca and O atoms were determined employing direct

methods using the synchrotron XRD data. The total amplitude factors (148, F_{obs}) were converted into structure factors and used as an input for the *SHELXS97* program (Sheldrick, 2008). The positions of Li1 and Li2 were then determined by difference Fourier analysis in *SHELXL97* program (Sheldrick, 2008). Structure refinements of atomic positions, occupancy and isotropic displacement parameters were carried out by the Rietveld method using the *FULLPROF* program with pseudo-Voigt peak shapes and manually selected backgrounds (Rodríguez-Carvajal, 2001). In the refinement, the SOFs of two Li sites were constrained in such a way that the total amount of Li atoms was constant to maintain the chemical composition. The isotropic displacement parameters for two Li atoms were set to the same refined value because there was a strong correlation between the isotropic displacement parameters and the SOFs for both Li1 and Li2 sites. The Rietveld refinement plot based on the synchrotron XRD data is shown in Fig. 3.

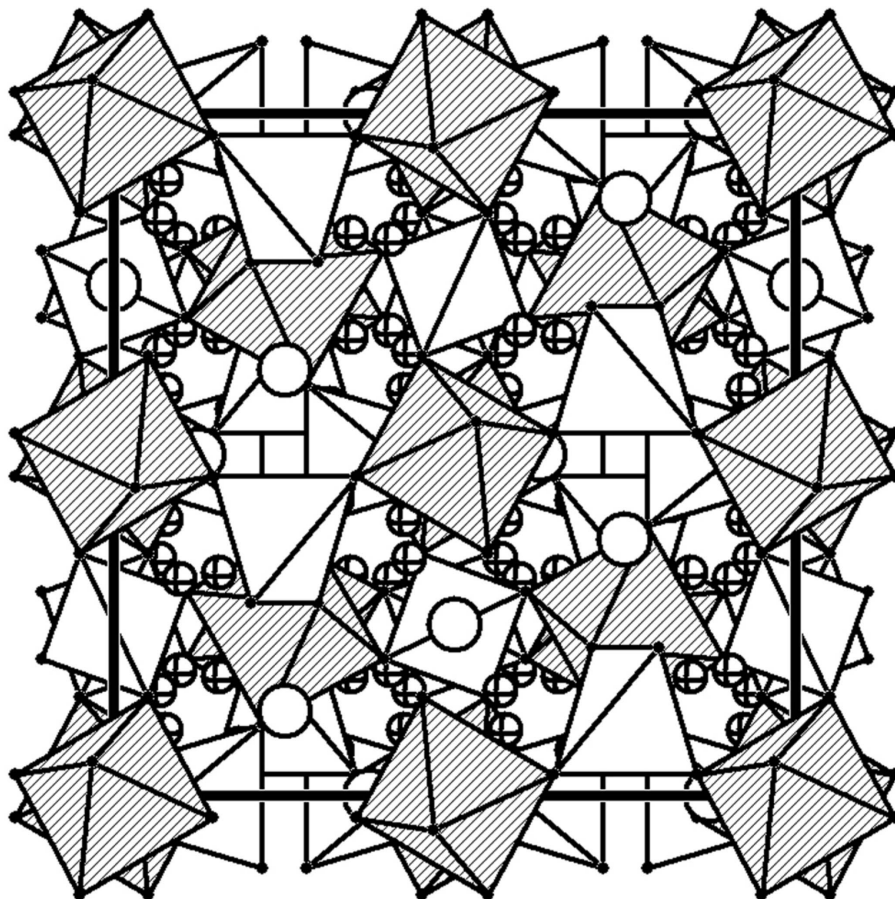


Figure 1

Schematic representation of the crystal structure of $\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$; the crossed spheres and the hollow spheres represent Li and Sm/Ca atoms, respectively.

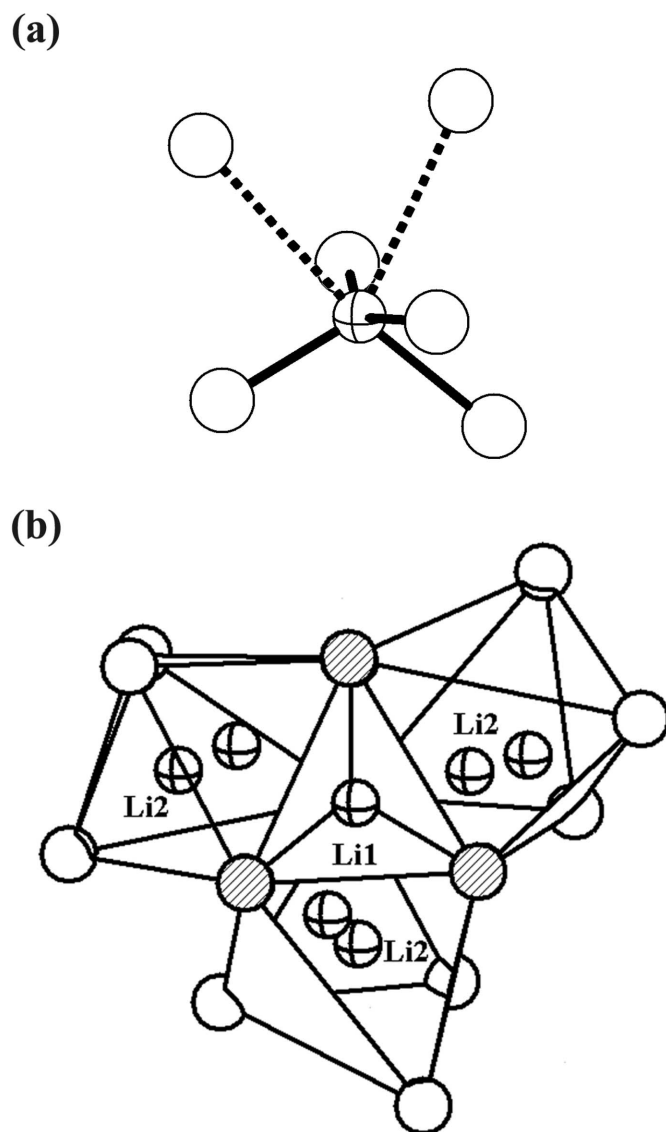


Figure 2

(a) Local environment of Li2 site: The crossed spheres and the hollow spheres represent lithium and oxygen atoms, respectively. The relatively long Li—O bonds are dotted. (b) The Li1O₄ tetrahedron shares each face with a Li₂O₆ octahedron.

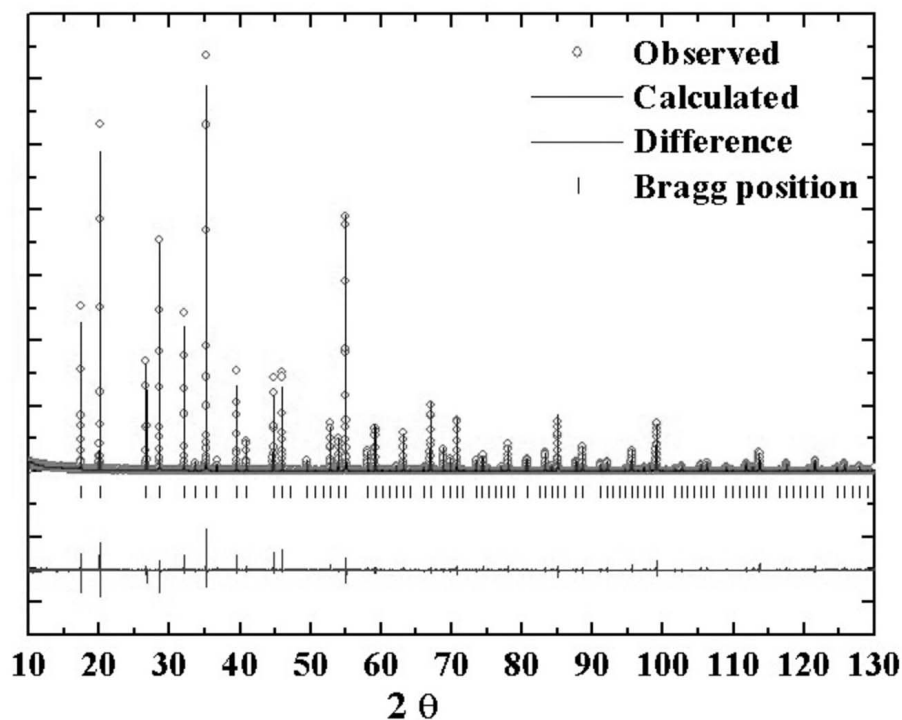


Figure 3

Rietveld refinement plot of $\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$ based on synchrotron X-ray powder diffraction data.

Hexalithium calcium disamarium(III) ditantalum(V) dodecaoxide

Crystal data

$\text{Li}_6\text{CaSm}_2\text{Ta}_2\text{O}_{12}$

$M_r = 936.45$

Cubic, $Ia\bar{3}d$

Hall symbol: $-I\ 4bd\ 2c\ 3$

$a = 12.55128\ (7)\ \text{\AA}$

$V = 1977.26\ (2)\ \text{\AA}^3$

$Z = 8$

$F(000) = 3200$

$D_x = 6.292\ \text{Mg m}^{-3}$

Synchrotron radiation, $\lambda = 1.5490\ \text{\AA}$

$T = 298\ \text{K}$

Particle morphology: particle

yellowish-white

flat sheet, $20 \times 20\ \text{mm}$

Specimen preparation: Prepared at 1223 K and
103 kPa, cooled at $5\ \text{K/min K min}^{-1}$

Data collection

Pohang Light Source 8C2 HRPD Beamline
diffractometer

Radiation source: Synchrotron

Si 111 monochromator

Specimen mounting: 'packed powder pellet'

Data collection mode: reflection

Scan method: step

$2\theta_{\min} = 10.000^\circ$, $2\theta_{\max} = 131.000^\circ$, $2\theta_{\text{step}} = 0.010^\circ$

Refinement

$R_p = 15.0$

$R_{\text{wp}} = 22.0$

$R_{\text{exp}} = 13.1$

$R_{\text{Bragg}} = 6.62$

12100 data points

Excluded region(s): None

Profile function: pseudo Voigt

20 parameters

0 restraints

$(\Delta/\sigma)_{\max} < 0.001$

Background function: manual background

Preferred orientation correction: 'None'

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Sm1	0.00000	0.25000	0.62500	0.0089 (2)*	0.6666
Ca1	0.00000	0.25000	0.62500	0.0089 (2)*	0.3333
Ta1	0.00000	0.00000	0.50000	0.0071 (2)*	
Li1	0.12500	0.00000	0.75000	0.0278 (11)*	0.26 (7)
Li2	0.101 (5)	0.192 (5)	0.412 (5)	0.0278 (11)*	0.44 (2)
O1	0.0323 (5)	0.0521 (5)	0.6488 (6)	0.0079 (13)*	

Geometric parameters (\AA , $^\circ$)

(Sm,Ca)—O1 ⁱ	2.441 (18)	Li1—O1 ^{xiv}	1.843 (7)
(Sm,Ca)—O1 ⁱⁱ	2.441 (18)	Li2—O1 ^{xv}	1.63 (6)
(Sm,Ca)—O1 ⁱⁱⁱ	2.441 (18)	Li2—O1 ^{xi}	2.14 (6)
(Sm,Ca)—O1 ^{iv}	2.441 (18)	Li2—O1 ⁱ	2.12 (6)
(Sm,Ca)—O1 ^v	2.561 (17)	Li2—O1 ⁱⁱⁱ	2.20 (6)
(Sm,Ca)—O1	2.561 (17)	Li2—O1 ^{xvi}	2.55 (6)
(Sm,Ca)—O1 ^{vi}	2.561 (17)	Li2—O1 ^{vii}	2.69 (6)
(Sm,Ca)—O1 ^{vii}	2.561 (17)	Li1—Li2 ^{viii}	1.53 (6)
Ta1—O1 ^{viii}	2.014 (6)	Li1—Li2 ^{xvii}	1.53 (6)
Ta1—O1	2.014 (6)	Li1—Li2 ^{xviii}	1.53 (6)
Ta1—O1 ^{ix}	2.014 (6)	Li1—Li2 ^{xix}	1.53 (6)
Ta1—O1 ^x	2.014 (6)	Li1—Li2 ^{xx}	2.33 (6)
Ta1—O1 ^{xi}	2.014 (6)	Li1—Li2 ^{ix}	2.33 (6)
Ta1—O1 ⁱ	2.014 (6)	Li1—Li2 ^{vii}	2.33 (6)
Li1—O1 ^{xii}	1.843 (7)	Li1—Li2 ^{xxi}	2.33 (6)
Li1—O1	1.843 (7)	Li2—Li2 ^{xxii}	2.27 (9)
Li1—O1 ^{xiii}	1.843 (7)	Li2—Li2 ^{xxiii}	2.27 (9)
O1 ⁱ —(Sm,Ca)—O1 ⁱⁱ	158.8 (8)	O1—Ta1—O1 ^x	180.000 (1)
O1 ⁱ —(Sm,Ca)—O1 ⁱⁱⁱ	72.8 (2)	O1 ^{ix} —Ta1—O1 ^x	87.2 (3)
O1 ⁱⁱ —(Sm,Ca)—O1 ⁱⁱⁱ	111.2 (2)	O1 ^{viii} —Ta1—O1 ^{xi}	180.0 (4)
O1 ⁱ —(Sm,Ca)—O1 ^{iv}	111.2 (2)	O1—Ta1—O1 ^{xi}	92.8 (3)
O1 ⁱⁱ —(Sm,Ca)—O1 ^{iv}	72.8 (2)	O1 ^{ix} —Ta1—O1 ^{xi}	87.2 (3)
O1 ⁱⁱⁱ —(Sm,Ca)—O1 ^{iv}	158.8 (8)	O1 ^x —Ta1—O1 ^{xi}	87.2 (3)
O1 ⁱ —(Sm,Ca)—O1 ^v	74.0 (2)	O1 ^{viii} —Ta1—O1 ⁱ	87.2 (3)
O1 ⁱⁱ —(Sm,Ca)—O1 ^v	124.5 (4)	O1—Ta1—O1 ⁱ	87.2 (3)
O1 ⁱⁱⁱ —(Sm,Ca)—O1 ^v	95.4 (2)	O1 ^{ix} —Ta1—O1 ⁱ	180.000 (2)
O1 ^{iv} —(Sm,Ca)—O1 ^v	67.2 (2)	O1 ^x —Ta1—O1 ⁱ	92.8 (3)
O1 ⁱ —(Sm,Ca)—O1	67.9 (8)	O1 ^{xi} —Ta1—O1 ⁱ	92.8 (3)
O1 ⁱⁱ —(Sm,Ca)—O1	95.4 (2)	O1 ^{xii} —Li1—O1	113.7 (6)
O1 ⁱⁱⁱ —(Sm,Ca)—O1	124.5 (4)	O1 ^{xii} —Li1—O1 ^{xiii}	101.7 (3)
O1 ^{iv} —(Sm,Ca)—O1	74.0 (2)	O1—Li1—O1 ^{xiii}	113.7 (6)
O1 ^v —(Sm,Ca)—O1	108.13 (16)	O1 ^{xii} —Li1—O1 ^{xiv}	113.7 (6)
O1 ⁱ —(Sm,Ca)—O1 ^{vi}	124.5 (4)	O1—Li1—O1 ^{xiv}	101.7 (3)
O1 ⁱⁱ —(Sm,Ca)—O1 ^{vi}	74.0 (2)	O1 ^{xiii} —Li1—O1 ^{xiv}	113.7 (6)
O1 ⁱⁱⁱ —(Sm,Ca)—O1 ^{vi}	67.2 (2)	O1 ^{xv} —Li2—O1 ⁱ	110 (3)

O1 ^{iv} —(Sm,Ca)—O1 ^{vi}	95.4 (2)	O1 ^{xi} —Li2—O1 ⁱ	87 (2)
O1 ^v —(Sm,Ca)—O1 ^{vi}	73.41 (16)	O1 ^{xv} —Li2—O1 ⁱⁱⁱ	106 (3)
O1—(Sm,Ca)—O1 ^{vi}	167.0 (2)	O1 ^{xi} —Li2—O1 ⁱⁱⁱ	150 (10)
O1 ⁱ —(Sm,Ca)—O1 ^{vii}	95.4 (2)	O1 ⁱ —Li2—O1 ⁱⁱⁱ	83 (2)
O1 ⁱⁱ —(Sm,Ca)—O1 ^{vii}	67.2 (2)	O1 ^{xv} —Li2—O1 ^{xvi}	87 (10)
O1 ⁱⁱⁱ —(Sm,Ca)—O1 ^{vii}	74.0 (2)	O1 ^{xi} —Li2—O1 ^{xvi}	82 (2)
O1 ^{iv} —(Sm,Ca)—O1 ^{vii}	124.5 (4)	O1 ⁱ —Li2—O1 ^{xvi}	165 (10)
O1 ^v —(Sm,Ca)—O1 ^{vii}	167.0 (2)	O1 ⁱⁱⁱ —Li2—O1 ^{xvi}	101 (2)
O1—(Sm,Ca)—O1 ^{vii}	73.41 (16)	O1 ^{xv} —Li2—O1 ^{vii}	148 (10)
O1 ^{vi} —(Sm,Ca)—O1 ^{vii}	108.13 (16)	O1 ^{xi} —Li2—O1 ^{vii}	78.4 (19)
O1 ^{viii} —Ta1—O1	87.2 (3)	O1 ⁱ —Li2—O1 ^{vii}	98 (10)
O1 ^{viii} —Ta1—O1 ^{ix}	92.8 (3)	O1 ⁱⁱⁱ —Li2—O1 ^{vii}	74.8 (18)
O1—Ta1—O1 ^{ix}	92.8 (3)	O1 ^{xvi} —Li2—O1 ^{vii}	67 (6)
O1 ^{viii} —Ta1—O1 ^x	92.8 (3)		

Symmetry codes: (i) $-y, z-1/2, -x+1/2$; (ii) $-z+3/4, y+1/4, x+3/4$; (iii) $y, -z+1, -x+1/2$; (iv) $z-3/4, -y+1/4, x+3/4$; (v) $y-1/4, x+1/4, -z+5/4$; (vi) $-x, -y+1/2, z$; (vii) $-y+1/4, -x+1/4, -z+5/4$; (viii) $-z+1/2, -x, y+1/2$; (ix) $y, -z+1/2, x+1/2$; (x) $-x, -y, -z+1$; (xi) $z-1/2, x, -y+1/2$; (xii) $-x+1/4, -z+3/4, y+3/4$; (xiii) $-x+1/4, z-3/4, -y+3/4$; (xiv) $x, -y, -z+3/2$; (xv) $-z+3/4, -y+1/4, x+1/4$; (xvi) $y+1/4, -x+1/4, z-1/4$; (xvii) $z-1/4, y-1/4, x+3/4$; (xviii) $z-1/4, -y+1/4, -x+3/4$; (xix) $-z+1/2, x, -y+1$; (xx) $-y+1/4, x-1/4, z+1/4$; (xxi) $y, z-1/2, -x+1$; (xxii) $y-1/4, -x+1/4, -z+3/4$; (xxiii) $-y+1/4, x+1/4, -z+3/4$.