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Crystal structure and magnetic properties of $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$

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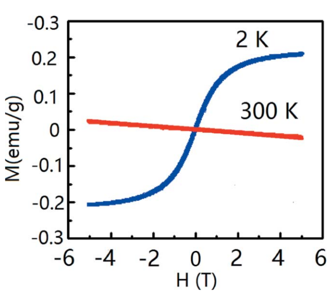
The synthesis, structure, and magnetic properties of lithium dibarium calcium oxide fluoride disulfide are reported. $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$ crystallizes in the tetragonal space group *P*4/*nmm*. The structure exhibits disorder of the Ca^{2+} and Bi^{3+} cations, and the O^{2-} and F^- anions. The structure is composed of a stacking of $[(O,F)_2La_2]$ layers and double $[(Bi,Ca)S_2]$ layers. Magnetic property measurements indicate a very small magnetization at 300 K and the existence of weak ferromagnetism at 2 K.



1. Chemical context

Layered crystal structures seem to be a common stage on which to explore superconductivity (Vershinin *et al.*, 2004; Kamihara *et al.*, 2008; Chen *et al.*, 2008; Fang *et al.*, 2010). The discovery of $[Fe_2An_2]$ (*An* = P, As, S, Se or Te) and $[CuO_2]$ superconducting layers has opened a new field in physics and chemistry for the exploration of low-dimensional superconductivity. Recently, superconductivity with transition temperatures of 4.5 K was reported in the BiS_2-based compound $Bi_4O_4S_3$ (Singh *et al.*, 2012). Soon after, $LnO_{1-x}F_xBiS_2$ (*Ln* = La, Ce, Pr and Nd), were reported to be superconducting with transition temperatures T_c of 3–10.6 K (Nagao *et al.*, 2013; Demura *et al.*, 2013). The mother BiS_2-based layered compound $AeFBiS_2$ (*Ae* = Ca, Sr or Ba; Lei *et al.*, 2013; Han *et al.*, 2008) is isostructural to $LnOBiS_2$, with the $[Ln_2O_2]^{2-}$ layer being replaced by an isocharged $[Sr_2F_2]^{2-}$ block. The parent phase of $SrFBiS_2$ shows semiconducting behavior, but electron-doped $Sr_{0.5}La_{0.5}FBiS_2$ has a superconducting transition of 2.8 K (Lin *et al.*, 2013). Herein the synthesis, structure and magnetic properties of $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$ are reported.

2. Structural commentary

We attempted to prepare the Ca and F double-doped compound $La_{1-x}Ca_xO_{1-2x}F_{2x}BiS_2$, but the results indicate the single-crystal composition is $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$. An SEM image shows thick plate-shaped crystals of $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$ (Fig. 1). $LaO_{1-x}F_x$-BiS_2 crystals usually show a thin-sheet shape (Fig. 2). From the EDXS analysis, we obtained the elemental components of La, Ca, Bi, S, F and O. The final composition was obtained by structure refinement (details can be seen in the *Refinement* section).

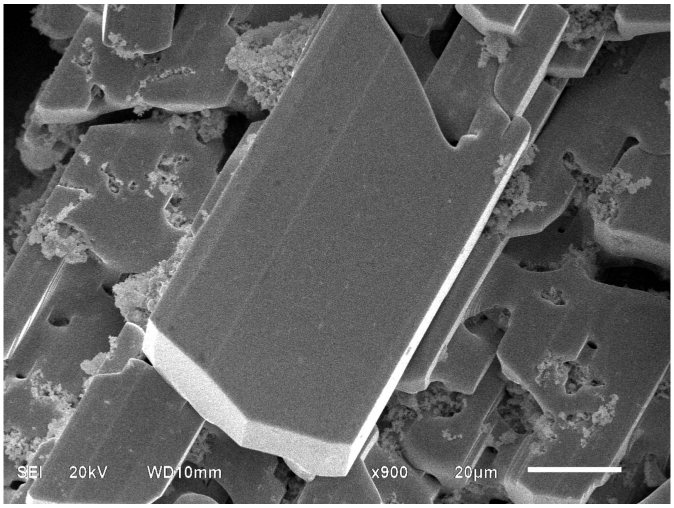


Figure 1
SEM image of $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$.

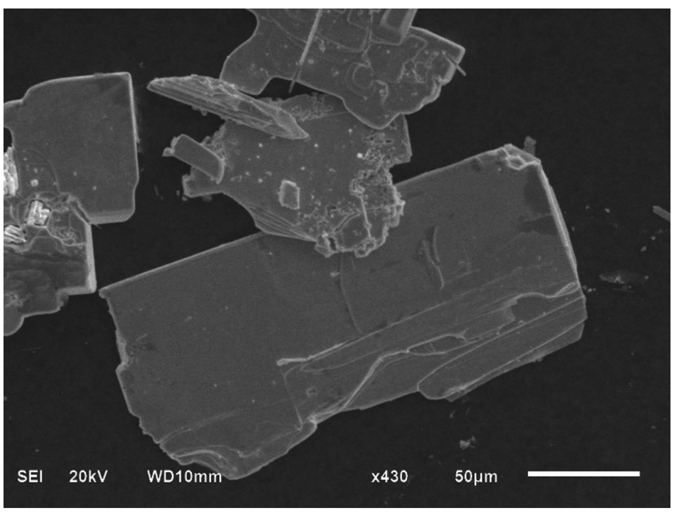


Figure 2
SEM image of $LaO_{0.6}F_{0.4}BiS_2$.

The structure of $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$, shown in Fig. 3, is composed of a stacking of $[(O,F)_2La_2]$ layers and double $[(Bi,Ca)S_2]$ layers as in $LaO_{1-x}F_xBiS_2$. The double $[(Bi,Ca)S_2]$ layers show Bi1/Ca1—S2 distances of 2.8672 (6) Å representing equatorial bonds and Bi1/Ca1—S1 distances of 2.530 (3) Å representing axial bonds; these are a little shorter than the Bi1—S1 distance of 2.87476 (15) and Bi1—S2 distance of 2.530 (6) Å in $LaO_{1-x}F_xBiS_2$. The $[(O,F)_2La_2]$ layers exhibit O1/F1—La1 bond lengths of 2.4414 (6) Å and La1—O1/F1—La1 bond angles of 108.08 (2) and 112.29 (4)°, which are close to the La—O/F bond length of 2.4402 (8) Å and La1—O1/F1—La1 bond angles of 107.82 (3) and 112.82 (6)° in $LaO_{1-x}F_xBiS_2$. The ionic radius of Ca^{2+} is 114 pm which is a little shorter than that of 117.2/117 pm for La^{3+}/Bi^{3+}. The distinct reduced Bi1/Ca1—S2 distances in the title compound reflect the fact that Ca substitutes Bi sites rather than La sites.

3. Magnetic property measurements

The magnetization *versus* temperature under a 1 T field for the title compound is given in Fig. 4. Magnetization *versus* magnetic field is given in Fig. 5 for fields ranging from −5 to 5 T at 2 K and 300 K. The magnetic properties indicate weak ferromagnetism at 2 K and a very low magnetization at 300 K. The superconducting transition is not observed in the measured temperature range. This might be related to the Ca substitution of the Bi site in the title compound. For superconducting $LaO_{1-x}F_xBiS_2$ crystals, the density of states at the Fermi level is mainly directed by the Bi *p* orbital. $[BiS_2]$ layers play a vital role in the transport and superconducting properties. The Ca substitution of the Bi site leads to a hole doping which changed the electronic band structure and density of state of $LaO_{1-x}F_xBiS_2$. Another reason might be the reduced F content in $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$ compared with $LaO_{1-x}F_xBiS_2$.

4. Database survey

$LnO_{1-x}F_xBiS_2$ (*Ln* = La, Ce, Pr and Nd) compounds were reported by Nagao *et al.* (2013) and Demura *et al.* (2013).

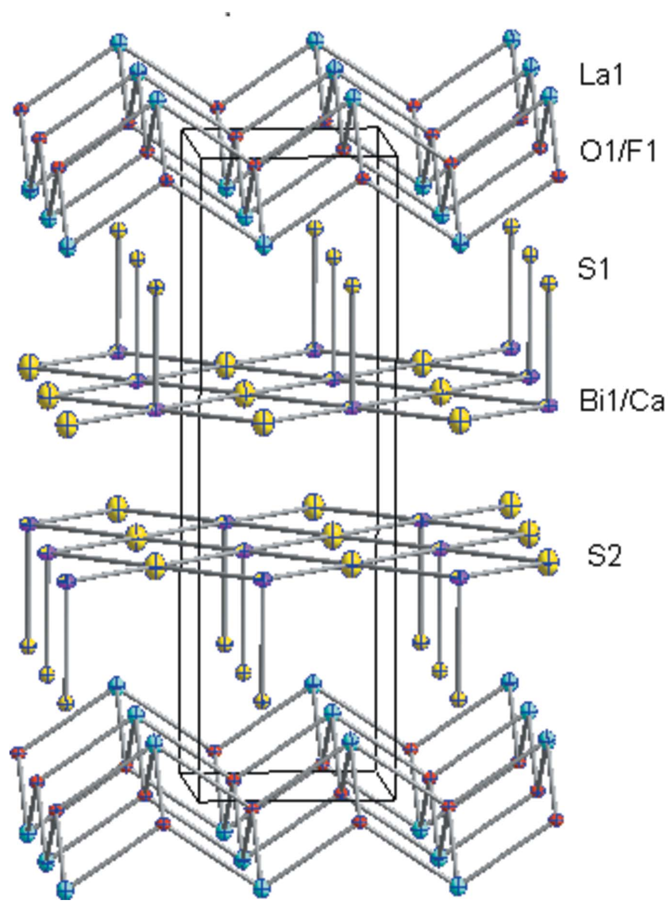


Figure 3
Crystal structure of $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$, showing $[(O,F)_2La_2]$ layers and double $[BiS_2]$ layers (O/F in red, La in blue, Bi/Ca in pink and S in yellow; 50% probability ellipsoids).

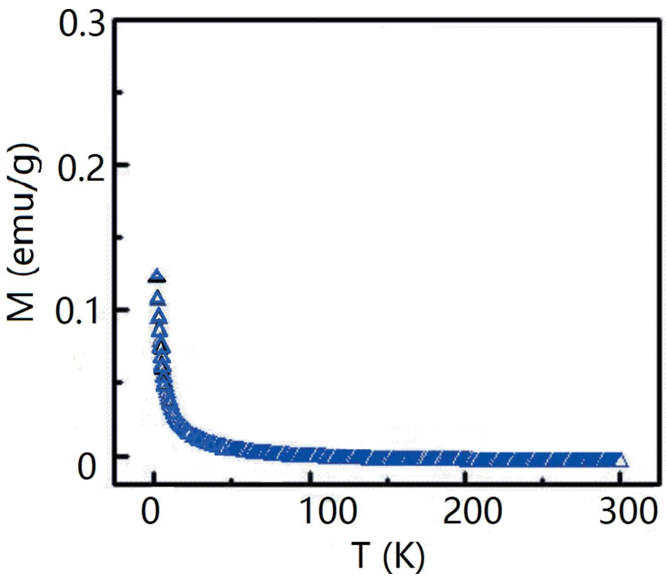


Figure 4
Magnetic moment *versus* temperature for $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}$-$Bi_{0.857\,(4)}S_2$ under a 1 T field.

AeFBiS$_2$ (Ae = Ca, Sr, Ba) (Lei *et al.*, 2013; Han *et al.*, 2008) are isostructural to LnOBiS$_2$. The doped $Sr_{0.5}La_{0.5}FBiS_2$ (Lin *et al.*, 2013) is isostructural to AeFBiS$_2$.

5. Synthesis and crystallization

$LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$ was prepared using of Bi_2O_3, CaF_2, La_2S_3, Bi_2S_3 and Bi raw materials. The mixtures with a nominal composition of $La_{0.85}Ca_{0.15}O_{0.70}F_{0.30}BiS_2$ were ground, pressed into pellets, sealed in an evacuated quartz tube, and heated at 1073 K for 3 d. High-quality single crystals were grown by using KI as the flux. Nominal $La_{0.85}Ca_{0.15}O_{0.70}F_{0.30}BiS_2$ and KI in the molar ratio of 1:3 were mixed and placed in a quartz tube, which was sealed and heated to 1273 K and kept at this temperature for 1 d, then cooled to room temperature in 10 d. The product was washed with distilled water and acetone, then dried at 353 K for 12 h; finally black plate-shaped crystals were obtained.

The morphology and element compositions were investigated by a scanning electronic microscope equipped with an energy dispersive X-ray spectroscopy (EDXS, Oxford Instruments). The EDXS shows the atom % ratio for S:Ca:La:Bi to be 48.23: 6.94: 24.36: 20.48. O and F could not be determined precisely. Magnetic properties were measured on a multifunctional physical properties measurement system (PPMS, Quantum Design).

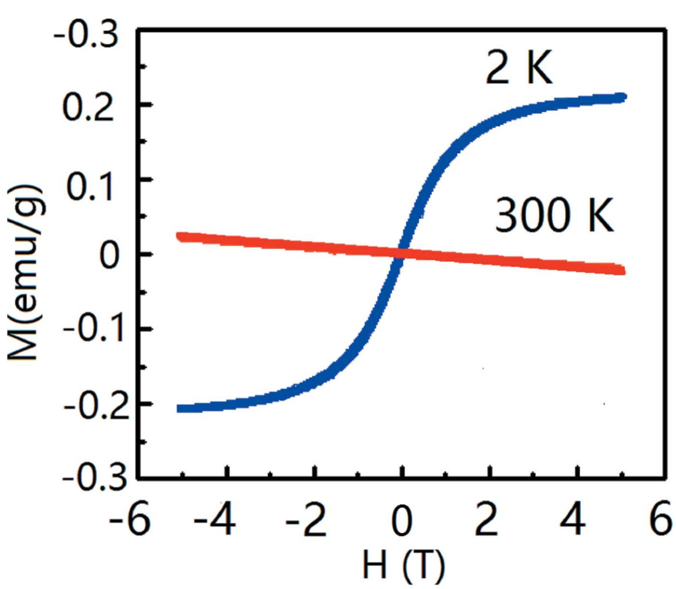


Figure 5
Magnetic moment *versus* field for $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$ from −5 T to 5 T at 2 K and 300 K.

Table 1
Experimental details.

Crystal data	
Chemical formula	$LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$
M_r	404.26
Crystal system, space group	Tetragonal, $P4/nmm$
Temperature (K)	300
a, c (Å)	4.0548 (9), 13.370 (3)
V (Å^3)	219.82 (11)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	44.78
Crystal size (mm)	0.05 × 0.05 × 0.02
Data collection	
Diffractometer	Bruker D8 Quest
Absorption correction	Multi-scan (*SADABS*; Bruker, 2001)
T_{min}, T_{max}	0.154, 0.511
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3493, 191, 190
R_{int}	0.046
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.648
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.052, 1.31
No. of reflections	191
No. of parameters	17
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.48, −1.53

Computer programs: *APEX2* and *SAINT* (Bruker, 2004), *SHELXS* (Sheldrick, 2008), *SHELXL2014* (Sheldrick 2015), *DIAMOND* (Brandenburg, 2004) and *publCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The La, Bi, S and O atoms were located in difference maps and their positions were freely refined. Ca was assumed at La sites at first, but the refinement show no reducing occupancy of La. The partial occupancy of Bi indicates a mixed occupancy with Ca. Ca and Bi were refined together later. EDXS measurements could not determine occupancies of O and F precisely. If the occupancies of F and O are refined together, the obtained composition is $La_2Bi_{1.859\,(4)}Ca_{0.141\,(4)}O_{0.48\,(14)}F_{0.52\,(14)}S_4$ with high standard errors for O and F. In order to keep charge neutrality, the occupancy of F was fixed to be the same as Ca so the final composition of $LaCa_{0.143\,(4)}O_{0.857\,(4)}F_{0.143\,(4)}Bi_{0.857\,(4)}S_2$ was obtained.

Acknowledgements

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Rongtie Huang, Hui Zhang, Dong Wang, Chuanbing Cai and Fuqiang Huang

Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT* (Bruker, 2004); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick 2015); molecular graphics: *DIAMOND* (Brandenburg, 2004); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Lanthanum calcium bismuth oxide fluoride disulfide

Crystal data

$Bi_{0.857}Ca_{0.143}F_{0.143}LaO_{0.857}S_2$
M_r = 404.26
Tetragonal, $P4/nmm$
a = 4.0548 (9) Å
c = 13.370 (3) Å
V = 219.82 (11) Å^3
Z = 2
F(000) = 342.3
D_x = 6.108 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 189 reflections
θ = 4.6–27.4°
μ = 44.78 mm^{-1}
T = 300 K
Block, blue
0.05 × 0.05 × 0.02 mm

Data collection

Bruker D8 Quest diffractometer
Radiation source: fine-focus sealed tube
Profile fitted $2\theta/\omega$ scans (Clegg, 1981)
Absorption correction: multi-scan (SADABS; Bruker, 2001)
T_{min} = 0.154, T_{max} = 0.511
3493 measured reflections
191 independent reflections
190 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 27.4°, θ_{min} = 4.6°
h = −5→5
k = −5→4
l = −17→17
3 standard reflections every 90 reflections
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.052
S = 1.31
191 reflections
17 parameters
0 restraints
Primary atom site location: difference Fourier map
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.5025P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 1.48 e Å^{-3}
$\Delta\rho_{min}$ = −1.53 e Å^{-3}
Extinction correction: SHELXL2014 (Sheldrick, 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.033 (3)

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
La1	0.7500	0.7500	0.89827 (6)	0.0127 (3)	
Ca1	0.2500	0.2500	0.62178 (4)	0.0126 (3)	0.143 (4)
Bi1	0.2500	0.2500	0.62178 (4)	0.0126 (3)	0.857 (4)
F1	0.7500	0.2500	1.0000	0.0079 (14)	0.143 (4)
O1	0.7500	0.2500	1.0000	0.0079 (14)	0.857 (4)
S1	0.2500	0.2500	0.8110 (2)	0.0104 (6)	
S2	0.7500	0.7500	0.6221 (3)	0.0236 (8)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
La1	0.0115 (4)	0.0115 (4)	0.0151 (5)	0.000	0.000	0.000
Ca1	0.0146 (3)	0.0146 (3)	0.0087 (3)	0.000	0.000	0.000
Bi1	0.0146 (3)	0.0146 (3)	0.0087 (3)	0.000	0.000	0.000
F1	0.0087 (18)	0.0087 (18)	0.006 (3)	0.000	0.000	0.000
O1	0.0087 (18)	0.0087 (18)	0.006 (3)	0.000	0.000	0.000
S1	0.0101 (7)	0.0101 (7)	0.0109 (12)	0.000	0.000	0.000
S2	0.0200 (10)	0.0200 (10)	0.0306 (18)	0.000	0.000	0.000

Geometric parameters (Å, º)

La1—O1^{i}	2.4414 (6)	Ca1—Ca1^{v}	4.0548 (9)
La1—O1^{ii}	2.4414 (6)	Ca1—Ca1^{viii}	4.0548 (9)
La1—F1^{i}	2.4414 (6)	Ca1—Bi1^{ii}	4.0548 (9)
La1—F1^{ii}	2.4414 (6)	Ca1—Bi1^{viii}	4.0548 (9)
La1—F1	2.4414 (6)	F1—La1^{i}	2.4414 (6)
La1—O1^{iii}	2.4414 (6)	F1—La1^{viii}	2.4414 (6)
La1—O1	2.4414 (6)	F1—La1^{iii}	2.4414 (6)
La1—F1^{iii}	2.4414 (6)	O1—La1^{i}	2.4414 (6)
La1—S1	3.0954 (13)	O1—La1^{viii}	2.4414 (6)
La1—S1^{iv}	3.0954 (13)	O1—La1^{iii}	2.4414 (6)
La1—S1^{ii}	3.0954 (13)	S1—La1^{vi}	3.0954 (13)
La1—S1^{v}	3.0954 (13)	S1—La1^{vii}	3.0954 (13)
Ca1—S1	2.530 (3)	S1—La1^{viii}	3.0954 (13)
Ca1—S2	2.8672 (6)	S2—Bi1^{iv}	2.8672 (6)
Ca1—S2^{vi}	2.8672 (6)	S2—Ca1^{iv}	2.8672 (6)
Ca1—S2^{vii}	2.8672 (6)	S2—Ca1^{v}	2.8672 (6)
Ca1—S2^{viii}	2.8672 (6)	S2—Ca1^{ii}	2.8672 (6)
Ca1—S2^{ix}	3.261 (4)	S2—Bi1^{ii}	2.8672 (6)

Ca1—Ca1^{ii}	4.0548 (9)	S2—Bi1^{v}	2.8672 (6)
Ca1—Ca1^{vii}	4.0548 (9)	S2—Ca1^{ix}	3.261 (4)
O1^{i}—La1—O1^{ii}	71.917 (18)	S2^{viii}—Ca1—Ca1^{vii}	135.0
O1^{i}—La1—F1^{i}	0.0	S2^{ix}—Ca1—Ca1^{vii}	90.0
O1^{ii}—La1—F1^{i}	71.917 (18)	Ca1^{ii}—Ca1—Ca1^{vii}	90.0
O1^{i}—La1—F1^{ii}	71.917 (18)	S1—Ca1—Ca1^{v}	90.0
O1^{ii}—La1—F1^{ii}	0.0	S2—Ca1—Ca1^{v}	45.0
F1^{i}—La1—F1^{ii}	71.917 (18)	S2^{vi}—Ca1—Ca1^{v}	135.0
O1^{i}—La1—F1	71.917 (18)	S2^{vii}—Ca1—Ca1^{v}	135.0
O1^{ii}—La1—F1	112.29 (4)	S2^{viii}—Ca1—Ca1^{v}	45.0
F1^{i}—La1—F1	71.917 (18)	S2^{ix}—Ca1—Ca1^{v}	90.0
F1^{ii}—La1—F1	112.29 (4)	Ca1^{ii}—Ca1—Ca1^{v}	90.0
O1^{i}—La1—O1^{iii}	112.29 (4)	Ca1^{vii}—Ca1—Ca1^{v}	180.0
O1^{ii}—La1—O1^{iii}	71.917 (18)	S1—Ca1—Ca1^{viii}	90.0
F1^{i}—La1—O1^{iii}	112.29 (4)	S2—Ca1—Ca1^{viii}	135.0
F1^{ii}—La1—O1^{iii}	71.917 (18)	S2^{vi}—Ca1—Ca1^{viii}	45.0
F1—La1—O1^{iii}	71.917 (18)	S2^{vii}—Ca1—Ca1^{viii}	135.0
O1^{i}—La1—O1	71.917 (18)	S2^{viii}—Ca1—Ca1^{viii}	45.0
O1^{ii}—La1—O1	112.29 (4)	S2^{ix}—Ca1—Ca1^{viii}	90.0
F1^{i}—La1—O1	71.917 (18)	Ca1^{ii}—Ca1—Ca1^{viii}	180.0
F1^{ii}—La1—O1	112.29 (4)	Ca1^{vii}—Ca1—Ca1^{viii}	90.0
F1—La1—O1	0.0	Ca1^{v}—Ca1—Ca1^{viii}	90.0
O1^{iii}—La1—O1	71.917 (18)	S1—Ca1—Bi1^{ii}	90.0
O1^{i}—La1—F1^{iii}	112.29 (4)	S2—Ca1—Bi1^{ii}	45.0
O1^{ii}—La1—F1^{iii}	71.917 (18)	S2^{vi}—Ca1—Bi1^{ii}	135.0
F1^{i}—La1—F1^{iii}	112.29 (4)	S2^{vii}—Ca1—Bi1^{ii}	45.0
F1^{ii}—La1—F1^{iii}	71.917 (18)	S2^{viii}—Ca1—Bi1^{ii}	135.0
F1—La1—F1^{iii}	71.917 (18)	S2^{ix}—Ca1—Bi1^{ii}	90.0
O1^{iii}—La1—F1^{iii}	0.0	Ca1^{ii}—Ca1—Bi1^{ii}	0.000 (15)
O1—La1—F1^{iii}	71.917 (18)	Ca1^{vii}—Ca1—Bi1^{ii}	90.0
O1^{i}—La1—S1	138.93 (2)	Ca1^{v}—Ca1—Bi1^{ii}	90.0
O1^{ii}—La1—S1	138.93 (3)	Ca1^{viii}—Ca1—Bi1^{ii}	180.0
F1^{i}—La1—S1	138.93 (2)	S1—Ca1—Bi1^{viii}	90.0
F1^{ii}—La1—S1	138.93 (3)	S2—Ca1—Bi1^{viii}	135.0
F1—La1—S1	70.49 (4)	S2^{vi}—Ca1—Bi1^{viii}	45.0
O1^{iii}—La1—S1	70.49 (4)	S2^{vii}—Ca1—Bi1^{viii}	135.0
O1—La1—S1	70.49 (4)	S2^{viii}—Ca1—Bi1^{viii}	45.0
F1^{iii}—La1—S1	70.49 (4)	S2^{ix}—Ca1—Bi1^{viii}	90.0
O1^{i}—La1—S1^{iv}	70.49 (4)	Ca1^{ii}—Ca1—Bi1^{viii}	180.0
O1^{ii}—La1—S1^{iv}	70.49 (4)	Ca1^{vii}—Ca1—Bi1^{viii}	90.0
F1^{i}—La1—S1^{iv}	70.49 (4)	Ca1^{v}—Ca1—Bi1^{viii}	90.0
F1^{ii}—La1—S1^{iv}	70.49 (4)	Ca1^{viii}—Ca1—Bi1^{viii}	0.000 (15)
F1—La1—S1^{iv}	138.93 (3)	Bi1^{ii}—Ca1—Bi1^{viii}	180.0
O1^{iii}—La1—S1^{iv}	138.93 (2)	La1^{i}—F1—La1^{viii}	108.082 (18)
O1—La1—S1^{iv}	138.93 (3)	La1^{i}—F1—La1^{iii}	112.29 (4)
F1^{iii}—La1—S1^{iv}	138.93 (2)	La1^{viii}—F1—La1^{iii}	108.082 (18)
S1—La1—S1^{iv}	135.72 (11)	La1^{i}—F1—La1	108.082 (18)

O1^{i}—La1—S1^{ii}	138.93 (3)	La1^{viii}—F1—La1	112.29 (4)
O1^{ii}—La1—S1^{ii}	70.49 (4)	La1^{iii}—F1—La1	108.082 (18)
F1^{i}—La1—S1^{ii}	138.93 (3)	La1^{i}—O1—La1^{viii}	108.082 (18)
F1^{ii}—La1—S1^{ii}	70.49 (4)	La1^{i}—O1—La1^{iii}	112.29 (4)
F1—La1—S1^{ii}	138.93 (3)	La1^{viii}—O1—La1^{iii}	108.082 (18)
O1^{iii}—La1—S1^{ii}	70.49 (4)	La1^{i}—O1—La1	108.082 (18)
O1—La1—S1^{ii}	138.93 (3)	La1^{viii}—O1—La1	112.29 (4)
F1^{iii}—La1—S1^{ii}	70.49 (4)	La1^{iii}—O1—La1	108.082 (18)
S1—La1—S1^{ii}	81.84 (4)	Ca1—S1—La1	112.14 (5)
S1^{iv}—La1—S1^{ii}	81.84 (4)	Ca1—S1—La1^{vi}	112.14 (5)
O1^{i}—La1—S1^{v}	70.49 (4)	La1—S1—La1^{vi}	135.72 (11)
O1^{ii}—La1—S1^{v}	138.93 (3)	Ca1—S1—La1^{vii}	112.14 (5)
F1^{i}—La1—S1^{v}	70.49 (4)	La1—S1—La1^{vii}	81.84 (4)
F1^{ii}—La1—S1^{v}	138.93 (3)	La1^{vi}—S1—La1^{vii}	81.84 (4)
F1—La1—S1^{v}	70.49 (4)	Ca1—S1—La1^{viii}	112.14 (5)
O1^{iii}—La1—S1^{v}	138.93 (3)	La1—S1—La1^{viii}	81.84 (4)
O1—La1—S1^{v}	70.49 (4)	La1^{vi}—S1—La1^{viii}	81.84 (4)
F1^{iii}—La1—S1^{v}	138.93 (3)	La1^{vii}—S1—La1^{viii}	135.72 (11)
S1—La1—S1^{v}	81.84 (4)	Ca1—S2—Bi1^{iv}	179.8
S1^{iv}—La1—S1^{v}	81.84 (4)	Ca1—S2—Ca1^{iv}	179.82 (17)
S1^{ii}—La1—S1^{v}	135.72 (11)	Bi1^{iv}—S2—Ca1^{iv}	0.0
S1—Ca1—S2	89.91 (9)	Ca1—S2—Ca1^{v}	90.0
S1—Ca1—S2^{vi}	89.91 (9)	Bi1^{iv}—S2—Ca1^{v}	90.0
S2—Ca1—S2^{vi}	179.82 (17)	Ca1^{iv}—S2—Ca1^{v}	90.0
S1—Ca1—S2^{vii}	89.91 (9)	Ca1—S2—Ca1^{ii}	90.0
S2—Ca1—S2^{vii}	90.000 (1)	Bi1^{iv}—S2—Ca1^{ii}	90.0
S2^{vi}—Ca1—S2^{vii}	90.000 (1)	Ca1^{iv}—S2—Ca1^{ii}	90.0
S1—Ca1—S2^{viii}	89.91 (9)	Ca1^{v}—S2—Ca1^{ii}	179.82 (17)
S2—Ca1—S2^{viii}	90.000 (1)	Ca1—S2—Bi1^{ii}	90.0
S2^{vi}—Ca1—S2^{viii}	90.0	Bi1^{iv}—S2—Bi1^{ii}	90.0
S2^{vii}—Ca1—S2^{viii}	179.82 (17)	Ca1^{iv}—S2—Bi1^{ii}	90.0
S1—Ca1—S2^{ix}	180.0	Ca1^{v}—S2—Bi1^{ii}	179.82 (17)
S2—Ca1—S2^{ix}	90.09 (9)	Ca1^{ii}—S2—Bi1^{ii}	0.00 (2)
S2^{vi}—Ca1—S2^{ix}	90.09 (9)	Ca1—S2—Bi1^{v}	90.0
S2^{vii}—Ca1—S2^{ix}	90.09 (9)	Bi1^{iv}—S2—Bi1^{v}	90.0
S2^{viii}—Ca1—S2^{ix}	90.09 (9)	Ca1^{iv}—S2—Bi1^{v}	90.0
S1—Ca1—Ca1^{ii}	90.0	Ca1^{v}—S2—Bi1^{v}	0.00 (2)
S2—Ca1—Ca1^{ii}	45.0	Ca1^{ii}—S2—Bi1^{v}	179.82 (17)
S2^{vi}—Ca1—Ca1^{ii}	135.0	Bi1^{ii}—S2—Bi1^{v}	179.82 (17)
S2^{vii}—Ca1—Ca1^{ii}	45.0	Ca1—S2—Ca1^{ix}	89.91 (9)
S2^{viii}—Ca1—Ca1^{ii}	135.0	Bi1^{iv}—S2—Ca1^{ix}	89.9
S2^{ix}—Ca1—Ca1^{ii}	90.0	Ca1^{iv}—S2—Ca1^{ix}	89.91 (9)
S1—Ca1—Ca1^{vii}	90.0	Ca1^{v}—S2—Ca1^{ix}	89.91 (9)
S2—Ca1—Ca1^{vii}	135.0	Ca1^{ii}—S2—Ca1^{ix}	89.91 (9)

S2^{vi}—Ca1—Ca1^{vii}	45.0	Bi1^{ii}—S2—Ca1^{ix}	89.9
S2^{vii}—Ca1—Ca1^{vii}	45.0	Bi1^{v}—S2—Ca1^{ix}	89.9

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