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Structure Determination of Lanthanum Seleno-Silicate, $La_4Se_3Si_2O_7$

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$La_4Se_3Si_2O_7$ crystallizes in a tetragonal symmetry, space group $I4_1/amd$, with $a = 12.2846(18)$Å and $c = 14.6992(10)$Å. The final R value obtained after full matrix least squares refinement was 0.025 for 789 unique reflections. The structure contains isolated $[Si_2O_7]$ units (double tetrahedra) which are formed by condensation of two $[SiO_4]$ tetrahedra connected by a sharing corner. These $[Si_2O_7]$ units bridge all other polyhedra built around two kinds of lanthanum atoms. La(1) is coordinated to three O and three Se atoms while La(2) is coordinated by six O and three Se atoms.

Introduction

In all crystalline silicates, the $[SiO_4]$ tetrahedra are either isolated or share corners with other tetrahedra. Only one phase (fibrous SiO_2 as reported by Weiss and Weiss (*1*)) is known to have edge-sharing $[SiO_4]$ tetrahedra. The $[SiO_4]$ tetrahedra can also be linked with other oxygenated polyhedra. This is the case in various lamellar silicates. Here we find complex sheets built of slabs of edge-sharing $[AlO_6]$ or $[MgO_6]$ octahedra located between slabs $[SiO_4]$ tetrahedral slabs.

Here we report on a new phase in which $[Si_2O_7]$ polyhedra share the three-dimensional network with $[LaO_3Se_3]$ and $[LaO_6Se_3]$ polyhedra.

A larger family of those compounds does exist because we could show the similarity of the structure determined in the present work with an already obtained sulfur compound.

Experimental

The $La_4Se_3Si_2O_7$ phase was obtained as a by-product in the preparation of the misfit selenide $(LaSe)_{1.14}(NbSe_2)_2$ by using La, Nb, Se as starting elements in a 1 : 2 : 5 ratio (*2*). These elements were sealed in an evacuated quartz tube ($\approx 10^{-2}$ torr) (protected by a thin carbon film). It was heated in a furnace at 1050°C for 8 days. The furnace was then cooled to room temperature within a day. In addition to the misfit ternary phase some small, octahedral, transparent crystals were found. They could easily be separated from the major black product.

Semiquantitative chemical analyses (energy dispersive) were carried out using an electron microprobe mounted on a scanning electron microscope. The analysis results averaged over four crystals (% at. La : 43.2 ± 0.4, Si : 26.1 ± 0.5, Se : 30.8 ± 0.3) agree well with the title formula (theor. % La : 44.4, Si : 22.2, Se : 33.3). The oxygen content was deduced from the charge equilibrium (electrical neutrality). The chemical composition was confirmed exactly by the crystal structure determination.

No sensible powder pattern could be recorded because the described product was a by-product of the synthesis. A truncated octahedral crystal was mounted on an Enraf–Nonius CAD4 diffractometer. The

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TABLE I

CRYSTAL DATA AND EXPERIMENTAL DETAILS FOR $La_4Se_3Si_2O_7$

Space group	$I4_1/amd$ (No. 141), origin at center ($2/m$) at 0, $-\frac{1}{4}$, $\frac{1}{8}$ from ($\bar{4}m2$)
a (Å)	12.2846(18)
c (Å)	14.6992(10)
V (Å^3)	2218.3(4)
Z	8
ρ_{calc} (g/cm^3)	5.753
μ (cm^{-1})	251.5
(Absorption correction: empirical from psi-scans)	
Temperature of measurement	293K
Scan mode	ω; $\Delta\omega = 1.0 + 0.35 \tan\theta$
Data collected	$+h, +k, +l$
Condition for observed reflections	$I > 3\sigma(I)$
No. of data collected	1564
No. of unique reflections	789
No. of refined parameters	37
$R = 0.025$	
$R_w = 0.027$	
Weighting scheme No. 1; $W^{-1} = [\sigma(I)^2 + (p * F^2)^2]\ /4 * F^2$	
	$p = 0.03$
Secondary extinction	$g = 2.28 \times 10^{-7}$

unit-cell dimensions were determined on the basis of 25 well-centered reflections by using the CELLDIM program ($12° < \theta < 30°$).

Preliminary classical X-ray investigations (Weissenberg camera) indicated a tetragonal symmetry with systematic existing conditions consistent with an I centered lattice. Additional existence conditions [for $hk0: h(k) = 2n$, and $hhl: (l = 2n)$; $2h + l = 4n$ reflections] led to the unique space group $I\,4_1/amd$ (No. 141). Intensities were collected with graphite monochromated Mo$K\alpha$ radiation using a pure ω scan mode. The intensities were corrected for Lorentz and polarization effects. Details of the data collection are summarized in Table I.

TABLE IIa

POSITIONAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS

Atom	Position	x	y	z	B_{eq},B^*_{iso}(Å^2)
La(1)	16(h)	0	0.99027(4)	0.66559(3)	0.580(7)
La(2)	16(g)	0.17201(3)	$x + \frac{1}{4}$	$\frac{7}{8}$	0.428(4)
Si	16(h)	0	0.6264(2)	−0.0942(2)	0.46(4)
Se(1)	4(a)	0	$\frac{1}{4}$	$\frac{7}{8}$	0.75(2)
Se(2)	4(b)	0	$\frac{1}{4}$	$\frac{3}{8}$	0.93(2)
Se(3)	16(f)	0.35290(7)	$\frac{1}{2}$	0	0.79(1)
O(1)	32(i)	0.1161(4)	0.6099(4)	−0.0416(3)	0.78(7)*
O(2)	8(e)	0	$\frac{1}{4}$	0.6125(6)	0.9(1)*
O(3)	16(h)	0	0.5271(5)	0.8294(4)	0.7(1)*

Note. Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent (B_{eq}) displacement parameter defined as $\frac{4}{3} * [a^{*2}\,\beta_{11} + b^{*2}\,\beta_{22} + c^{*2}\,\beta_{33} + a^*b^*(\cos\gamma)\,\beta_{12} + a^*c^*(\cos\beta)\,\beta_{13} + b^*c^*(\cos\alpha)\,\beta_{23}]$.

TABLE IIb

DISPLACEMENT PARAMETERS $Uij(*10^4)$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	63(2)	95(2)	63(2)	0	0	−9(2)
La(2)	53.0(9)	U_{11}	57(1)	3(2)	−1(1)	$-U_{13}$
Si	60(9)	25(9)	88(9)	0	0	−5(8)
Se(1)	69(4)	U_{11}	147(7)	0	0	0
Se(2)	79(4)	U_{11}	194(8)	0	0	0
Se(3)	60(3)	167(4)	74(3)	0	0	−32(4)

Structure Determination

The structure was solved by interpretation of the Patterson map. The lightest atoms (Si, O) were located through difference Fourier synthesis. Full matrix least squares refinements were performed using neutral atomic scattering factor (corrected for anomalous dispersion). A semiempirical absorption correction was applied based on the psi-scans of four reflections (minimum transmission: 68.5%, maximum transmission: 99.22%). The refinements converged to reliability factors of $R = 0.039$ and $R_w = 0.041$ by taking an isotropic thermal motion for all atoms into account. In the following least-squares cycles with anisotropic thermal parameters for La, Se, and Si atoms, the refinements led to R factors of $R = 0.026$ and $R_w = 0.029$. After application of an absorption correction procedure by DIFABS (*2*) and rejection of three obviously wrongly measured reflections a final least squares refinement converged to $R = 0.025$ and $R_w = 0.027$ for 789 reflections and 37 variable parameters. Final atomic coordinates and thermal parameters are listed in Tables II (a and b). The final difference Fourier map shows one residual peak (2.2 e^- Å^{-3}) corresponding to an 8(e) type site (0, $\frac{1}{4}$, 0.3295). This residual peak is only slightly shifted from the Se(2) position (4b: 0, $\frac{1}{4}$, $\frac{3}{8}$). It therefore seemed reasonable to split the Se(2) position into a statistical occupancy (50%) of the 8(e) type site. Unfortunately, refinement attempts did not converge under those assumptions.

Description of the Structure

A structure description can be done by using three types of polyhedra: $[Si_2O_7]$, $[LaO_3Se_3]$, and $[LaO_6Se_3]$.

(Si_2O_7) Double Tetrahedra

In this configuration silicon atoms are surrounded by four O atoms in a tetragonal orientation. Each time two of these tetrahedra are linked together by a corner sharing O(2) atom thereby forming isolated (Si_2O_7) units. The Si–O distances within one unit agree well with distances commonly reported for "disilicate" compounds (*4*) (see Table III).

"LaO_3Se_3" Polyhedra

The La(1) atoms are coordinated by six nearest neighbors (Se(2), 2 Se(3), 2 O(1), O(3)) located at the corners of a distorted

TABLE III

INTERATOMIC DISTANCES UP TO 3.2 Å AND THEIR STANDARD DEVIATIONS

Around Si atom	
Si–2 O(1): 1.635(5)	Si–Si: 3.038(5)
Si–O(2): 1.647(4)	
Si–O(3): 1.657(7)	∢Si–O(2)–Si: 134.6(6)°
Around La(1) atom	
La(1)–2 Se(3): 3.0339(7)	
La(1)–Se(2): 3.0113(6)	
La(1)–2 O(1): 2.544(5)	
La(1)–O(3): 2.418(6)	
Around La(2) atom	
La(2)–Se(1): 2.9883(3)	
La(2)–2 Se(3): 3.0384(7)	
La(2)–2 O(1): 2.702(5)	
La(2)–2 O(1): 2.573(5)	
La(2)–2 O(3): 2.565(4)	

"trigonal prism." Each triangular basis of this configuration is occupied by atoms of the same type (Se or O) (Se(2), 2 Se(3) and 2 O(1), O(3), respectively). The triangular bases deviate from parallelism by an angle of about 11° as shown in Fig. 1. Interatomic distances found within this "trigonal prism" are reported in Table III. Four of these polyhedra are linked by sharing a common Se(2) to form a repetitive unit. Such a unit has four Se(3)–Se(3) edges which are common between adjacent units. Moreover, opposite polyhedra inside the single unit (the four linked "trigonal prisms") create two new units at a higher z level, and two more new units at a lower z level (Fig. 2).

"LaO_6Se_3" Polyhedra

The La(2) atoms are coordinated by nine atoms (4 O(1), 2 O(3), 1 Se(1), 2 Se(3)). The polyhedron around each La(2) atoms is a tricapped prism in which the two prism faces are capped by one O(3) and two O(1) respectively (Fig. 3). The interatomic La(2)–O and La(2)–Se distances of the configuration are reported in Table III. The La(2)–O distances are considerably longer than the La(1)–O distances whereas the La(2)–Se distances can be compared to the La(1)–Se distances (Table III). These values are in agreement with those frequently given for Ln–Se and Ln–O (Ln = La, Ce, Pr, Nd) distances in a similar environment (5) (6).

Four of these polyhedra are linked by sharing a common O(3)–Se(1) edge oriented parallel to the **a** axis (or **b** axis respectively). In addition, along **c** these polyhedra share common triangular faces built with 2 O(1), Se(3) atoms (shaded triangular bases on the left side of the Fig. 3).

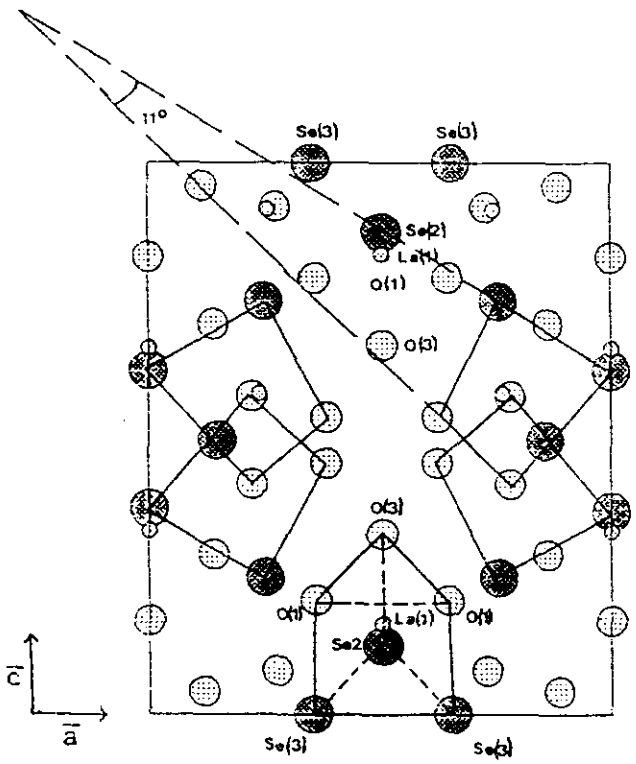

FIG. 1. Projection along [010] direction of $[LaO_3Se_3]$polyhedra (environment of La(1) atom). The angle between the two triangular faces is about 11°.

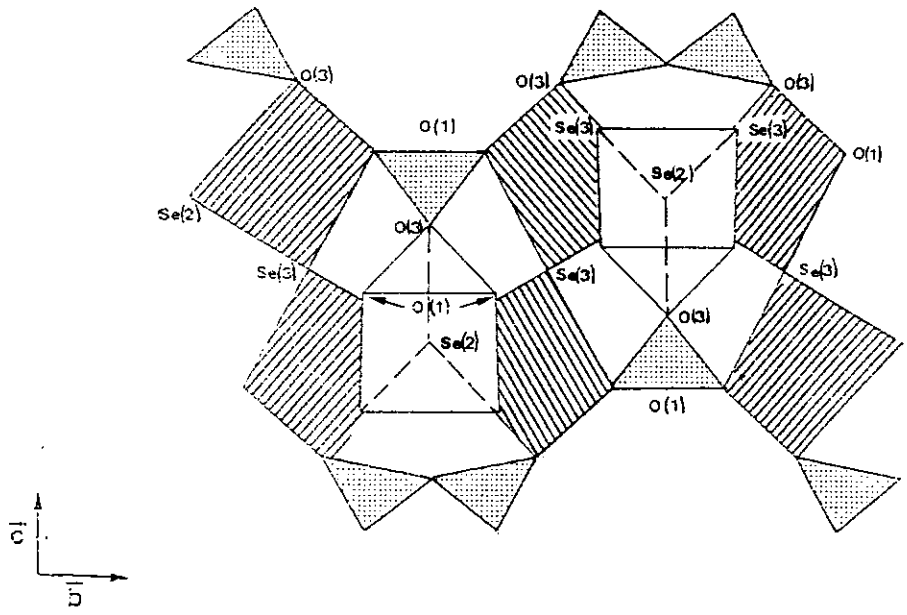

FIG. 2. Projection along [100] direction of $[LaO_3Se_3]$ and $[Si_2O_7]$ polyhedra.

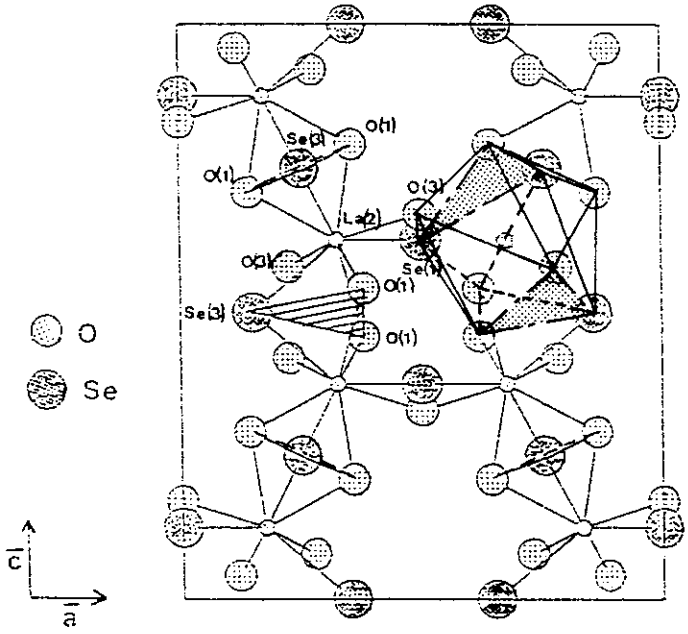

FIG. 3. Coordination of La(2) atoms (tricapped prism drawn on the right side of the figure), linkage of $[LaO_6Se_3]$ polyhedra (environment of La(2) atom) projected on (**a**, **c**) plane.

Three-Dimensional Structure

The structure can be described as an "intergrowth" of these three kinds of polyhedra as shown above.

The $[Si_2O_7]$ entity is bridging four La(1) polyhedra:

—two of them by sharing O(1) corners along the O(1)–O(1) edge of two La(1) polyhedra at the same z level and belonging to two distinct units.

—the two others located at a lower z level via O(3) atoms (see Fig. 2).

The $[Si_2O_7]$ entity also connects four La(2) polyhedra through a common O(1)–O(3) edge (Fig. 4).

Eventually La(1) polyhedra share Se(3)–O(1) and O(1)–O(3) common edges with the tricapped La(2) polyhedra (Fig. 5). The La(1) block fills the cavities A formed by La(2) polyhedra framework (Fig. 4). There is no space left between different coordination polyhedra making the structure very compact (Fig. 5).

Discussion and Conclusion

The main feature of the $La_4Se_3Si_2O_7$ structure are $[SiO_4]$ units connected by a common oxygen atom therefore forming isolated $[Si_2O_7]$ units. These $[Si_2O_7]$ polyhedra have

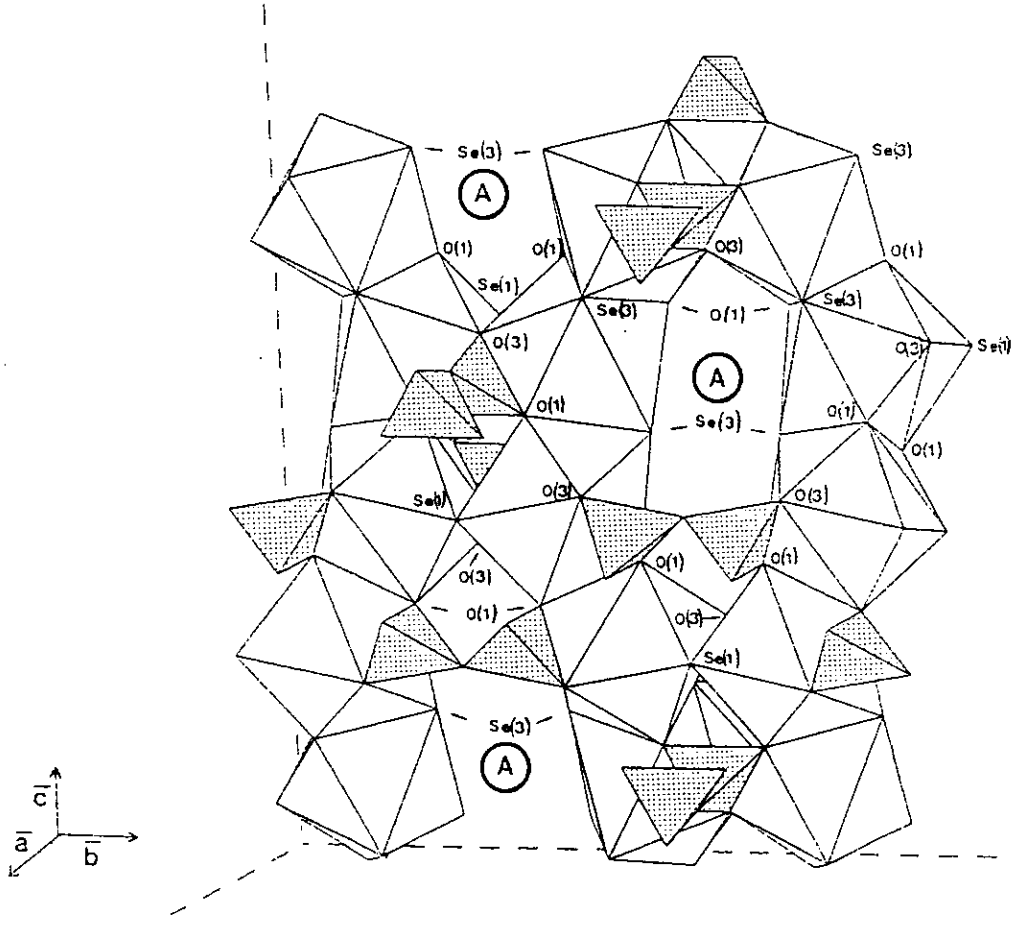

FIG. 4. Three-dimensional building of $[Si_2O_7]$ and $[LaO_6Se_3]$ polyhedra.

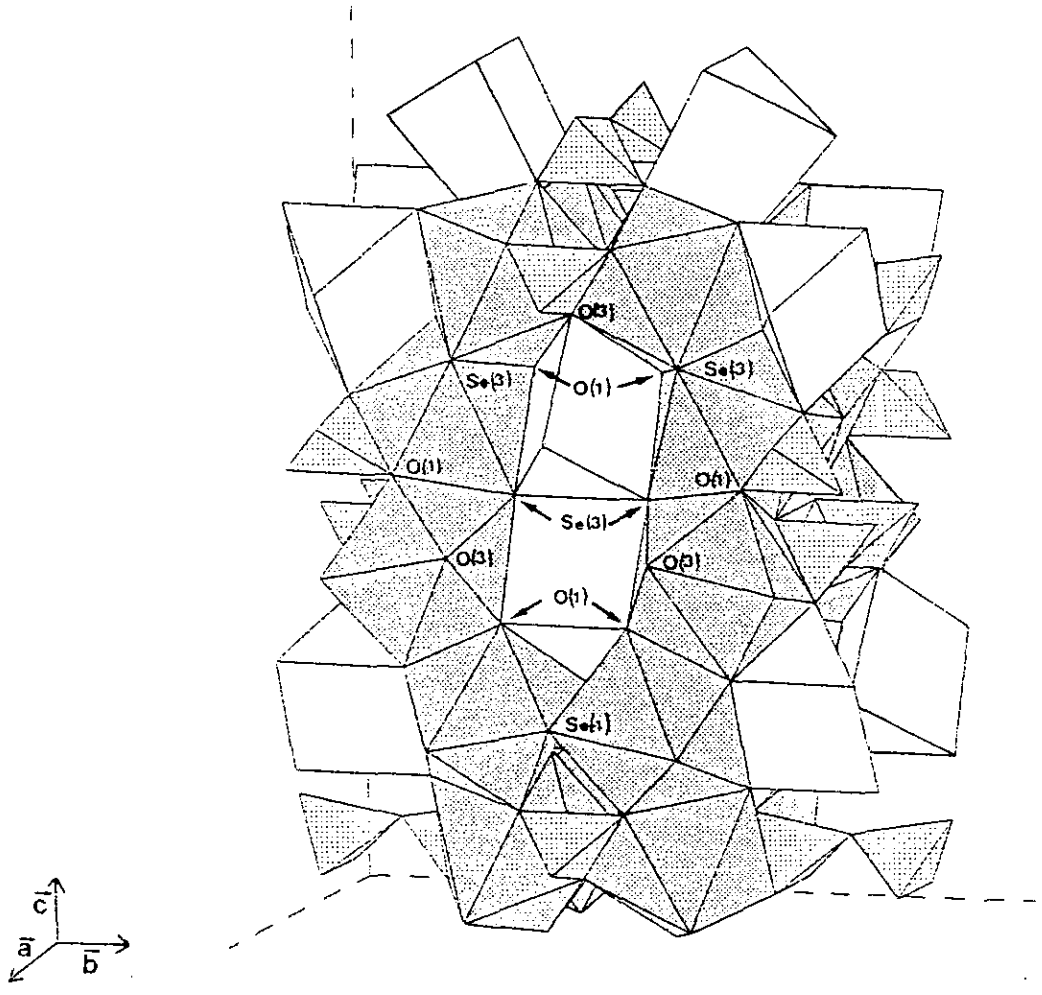

FIG. 5. Complete structure.

the *mm* symmetry with bond lengths (d(Si–O)$_{av.}$ = 1.643Å and d(Si–Si) = 3.038Å) and bond angles ($\sphericalangle$O–Si–O)$_{av}$ = 111.7° and $\sphericalangle$Si–O–Si = 134.6°) being in agreement with the classical values reported by Liebau (1.57Å < d(Si–O) < 1.72Å, 98° < $\sphericalangle$O–Si–O < 122°, and 120° < $\sphericalangle$Si–O–Si < 180°) (*4*). These $[Si_2O_7]$ polyhedra are bridging all other polyhedra.

In search for homologue derivatives, we found one isotypic phase $Sm_4S_3Si_2O_7$ which was reported by Siegrist *et al.* (*7*). This demonstrates well that a larger family of compounds could be made by substituting the La by other rare-earth elements for sulfide or selenide derivatives. Attempts to synthesize some of these new phases "directly" will be undertaken.

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