CRYSTAL STRUCTURE OF THE SIMPLEST SILICATES OF La AND Sm

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Abstract

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The use of rare-earth-element silicates in high-refractory technology, in semiconductor technology, and also as matrix crystals in quantum radio electronics has determined the increased interest in them on the part of chemists, physicists, and crystallographers both in our country and abroad ([1-8] and others). The most complete studies of phase diagrams of the system La_2O_3–SiO_2 were carried out at Pennsylvania University (USA) and at the Institute of Silicate Chemistry of the Academy of Sciences of the USSR (Leningrad); in the latter, in particular, compounds of composition $La_2O_3 \cdot SiO_2$, $La_2O_3 \cdot 2SiO_2$, $Sm_2O_3 \cdot SiO_2$, $Sm_2O_3 \cdot 2SiO_2$ were synthesized. Single-crystal fragments of these silicates, kindly provided by N. A. Toropov and I. A. Bondar' , served as the object of our study.

In the course of X-ray photography it was established that the unit cells of the supposed $La_2O_3 \cdot SiO_2$ and $La_2O_3 \cdot 2SiO_2$ are completely identical and, consequently, these compounds are simply identical. An analogous result was obtained for the silicates with Sm.

Comparison of powder patterns of La- and Sm-silicates with powder patterns of britholite (a rare-earth silicate—the structural analogue of apatite) revealed their striking similarity. This closeness was confirmed when the parameters of the hexagonal cells of the synthetic compounds were fixed:

Apatite $Ca_5[PO_4]_3F$	$a = 9.43$ Å,	$c = 6.88$ Å [9];
Britholite $Ca_2Ce_3[SiO_4]_3F$	$a = 9.63$ Å,	$c = 7.03$ Å [9];
La-silicate	$a = 9.55$ Å,	$c = 7.14$ Å
Sm-silicate	$a = 9.33$ Å,	$c = 6.85$ Å

The result obtained forced us to accept for the synthesized compounds a chemical formula close to the formula of britholite, $La_{5-x}[SiO_4]_3O$, and equal to the sum of the two initially proposed ones plus the minimal amount of more free La_2O_3:

$$La_2O_3 \cdot SiO_2 + La_2O_3 \cdot 2SiO_2 + {}^1/_3La_2O_3 =$$

$$= La_2SiO_5 + La_2Si_2O_7 + {}^1/_3La_2O_3 = La_{4.33}[SiO_4]_3O \ * .$$

Such a derivation of the formula seemed insufficiently reliable, and therefore, subsequently, in solving the structure, three possible variants of the formula were checked: 1) with 5 La atoms, and then one of them must be divalent; 2) with 4 La^{3+}, and then instead of the apatite F we would have a neutral H_2O particle; and, finally, 3) the one just written, with a statistical distribution of La^{3+} over 5 positions.

The experimental set of intensities was obtained from Weissenberg photographs of zero layer lines (MoKα radiation). With Laue symmetry $6/m$, the presence of only serial extinctions makes possible two Fedorov groups: $C_{6h}^2 = P6_3/m$ and $C_6^6 = P6_3$. Since minerals of the apatite group belong to the first of them, at the initial stage of analysis the silicates under study were also assigned to the holohedral group $P6_3/m$.

* Everything said above applies equally to Sm silicates.

The intensity of the reflections on the radiographs was measured by blackening marks (step ${}^4/_2$). In view of the small sizes of the crystals ($0.4 \times 0.2 \times 0.2$ mm for the La silicate and $0.3 \times 0.2 \times 0.1$ mm for the Sm silicate), no absorption correction was introduced. On the Patterson syntheses $p(xy)$, heavy La (and Sm) atoms immediately appeared in positions close to the positions of Ca (Sr, TR) in the structures of the apatite series: 6 rare-earth atoms are located in a 6-fold position (on the symmetry plane, if present) and 4 on the threefold axes.

Table 1

Coordinates of atoms in the structure of two rare-earth silicates with the apatite structure

$La_{4.67}[SiO_4]_3O$				$Sm_{4.67}[SiO_4]_3O$				$Ca_5[PO_4]_3F$			
atom	x/a	y/b	z/c	atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
La_I	0.233	−0.013	1/4	Sm_I	0.232	−0.009	1/4	Ca_I	0.246	0.993	1/4
La_{II}	1/3	2/3	0	Sm_{II}	1/3	2/3	0	Ca_{II}	1/3	2/3	0
Si	0.400	0.368	1/4	Si	0.394	0.370	1/4	P	0.400	0.369	1/4
O_1	0.333	0.485	1/4	O_1	0.319	0.493	1/4	O_1	0.329	0.484	1/4
O_2	0.592	0.468	1/4	O_2	0.595	0.470	1/4	O_2	0.589	0.466	1/4
O_3	0.346	0.246	0.073	O_3	0.342	0.244	0.065	O_3	0.348	0.259	0.073
O_4	0	0	1/4	O_4	0	0	1/4	O_4	0	0	1/4

Table 2

Interatomic distances in La and Sm silicates (in Å)

Polyhedron	La silicate						Sm silicate					
	Atom	O_1	O_2	O_3	O_3'	O_4	Atom	O_1	O_2	O_3	O_3'	O_4
Tetrahedron SiO_4	Si	1.54	1.59	1.62			Si	1.62	1.62	1.63		
Tetrahedron SiO_4	O_3	2.67	2.58	2.53			O_3	2.66	2.58	2.53		
Seven-vertex polyhedron	La_I	2.75	2.48	2.50	2.49	2.29	Sm_I	2.67	2.41	2.34	2.41	2.21
Nine-vertex polyhedron	La_{II}	2.49	2.51	2.79			Sm_{II}	2.32	2.37	2.74		

The coordinates x and y of the lighter Si and O atoms were established from electron-density syntheses $\sigma(xy)$. The third coordinates of the La, Si, and O atoms were found from the side projections $p(yz)$ and $\sigma(yz)$.

Refinement of the atomic coordinates of the resulting model by the least-squares method led to the following values of the discrepancy factors: for the La silicate, 13.5% (B_{hk0} = 0.8 Å^2 and B_{0kl} = 0.6 Å^2); and for the Sm silicate, 12.5% (B = 0.5 Å^2).

The corresponding R-factors for models following from chemical formulas with 5 and 4 La atoms exceeded those just given for $La_{5-x}[SiO_4]_3O$ by 10 and 15%.

At the final stage of the analysis, the formula $La_{4.67}[SiO_4]_3O$ was adopted (all La trivalent). The smallest R-factor, 11.3–11.5% for the La silicate and 10.2% for the Sm silicate, was obtained within the space group $P6_3/m$ for the following model: 6 La (or Sm) atoms on mirror planes; $3^1/_3$ (instead of the remaining 4) La (Sm) atoms are distributed statistically on two threefold axes.

The final coordinates are given in Table 1 (in the last column the coordinates of the apatite structure according to ([13]) are repeated).

Interatomic distances for the La and Sm silicates are given in Table 2. The Si–O distances in the Si tetrahedron for the La silicate do not go beyond 1.54–1.62 Å (average 1.59 Å); O–O 2.53–2.67 Å; for the Sm silicate: Si–O = 1.62–1.63 Å (average 1.62 Å); O–O = 2.53–2.69 Å. In the semi-vertex around the 6-fold axis the distances are: La–O = 2.29–2.75 Å; in the nine-vertex on the 3-fold axis La

–O = 2.49-2.79 Å; for the Sm silicate the Sm–O distances are 2.21-2.67 Å and 2.32-2.74 Å, respectively.

The low discrepancy coefficients of the two structures and the good interatomic distances make it possible to assert with considerable confidence that the structural motif of apatite is also preserved for the silicates of the rare-earth elements (La and Sm), with complete replacement of divalent Ca by trivalent La (Sm), P by Si, and simultaneous replacement on the 6_3 axis of two F^{1-} anions by two O^{2-} anions.

Such isomorphous substitution in the apatite structural type does not seem unexpected in light of recent structural studies on strontium and rare-earth apatites ([10]-[12]).

Direct structural confirmation of the existence of compounds of composition $La(Sm)_{4\cdot67}[SiO_4]_3O$ makes it possible to suppose that they will take their place in the phase diagrams of the systems La_2O_3–SiO_2 and Sm_2O_3–SiO_2.

One may note the clearly expressed proportionality of the hexagonal parameters of the three apatite-type structures to the ionic radii of the corresponding principal cations: La : Ca : Sm.

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Note: Figure translations are in progress. See original paper for figures.