Instrumental Achievements

Crystal Structure of Samarium Sesquisulfide, α -Sm₂S₃

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The crystal structure of α -Ln₂S₃ type compounds (Ln: rare earth elements) was first reported for α -Gd₂S₃ by Prewitt and Sleight.¹ Though structure determinations were also carried out for lanthanum (Besançon and Laruelle²), and neodymium (Eliseev *et al.*³), *R* values were relatively high: *R*=0.11 or *R*=0.131, respectively. α -Ln₂S₃ is a low temperature phase and is stable at room temperature. Since α -Ln₂S₃ is the most basic compound among rare earth sulfides, the structure should be clearly understood. So a structure analysis of α -Sm₂S₃ was undertaken in order to obtain accurate structural information.

A selected single crystal was prepared by the silica tube method. A powder mixture of Sm and S in a molar ratio of 1:1 was sealed in an evacuated silica tube. This tube was heated for 30 d at 1100°C. A single crystal of 0.08×0.13×0.13 mm was used for X-ray structure determination. Crystal data and experimental conditions are given in Table 1. Intensities of 1114 independent reflections were measured in the 2 θ range of 1.5° through 70° using graphite-monochromated Mo K α radiation (λ =0.70926 Å). Lattice parameters were determined by a least-squares treatment of 2 θ values of 25 reflections (45°<2 θ <60°). The intensity data were corrected for Lorentz and polarization factors; no absorption or extinction corrections were made. The crystal structure factor *F*_c was calculated using the atomic coordinates of isostructural α -La₂S₃ (Besançon and Laruelle²) with overall temperature factors of 2.0, the obtained *R* value was 26.9% which was regarded as good for an initial model. Then, atomic parameters, scale and temperature factors were refined by the least-squares method. The final atomic positions and thermal parameters are given in Table 2. The selected bond lengths and angles are listed in Table 3. Figure 1 is a view of the structure down the *b* axis.

The structure consists of Sm(1)S₇ and Sm(2)S₈ polyhedra. Sm(2) is coordinated by eight sulfur atoms in a bicapped trigonal prism at an average distance of 2.914 Å having two longer Sm-S distances: 3.077 and 3.042 Å. The trigonal prism stands along the *b* axis.

Table 1 Crystal data and experimental conditions

Formula: α -Sm ₂ S ₃
Formula weight=396.90
Crystal system: orthorhombic
Space group: <i>P</i> _{nma} <i>Z</i> = 4
<i>a</i> =7.376(1) Å
<i>b</i> =3.9622(5) Å
<i>c</i> =15.352(2) Å
<i>V</i> =448.7 Å ³
<i>D</i> _x =5.88 g/cm ³
μ for Mo K α radiation=271.7 cm ⁻¹
<i>R</i> =0.051, <i>R</i> _w =0.068
No. of reflections used = 1042
Measurement: Rigaku AFC-5
Structure determination: Fourier method (GSFFR)
Program system: RFINE2
Refinement: full-matrix least-squares

Table 2 Atomic coordinates and temperature factors

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} /Å ²
Sm(1)	0.76572(9)	0.25	0.54378(4)	0.551
Sm(2)	0.14189(8)	0.25	0.20400(4)	0.486
S(1)	0.0686(4)	0.25	0.3915(2)	0.579
S(2)	0.1488(4)	0.25	0.7812(2)	0.481
S(3)	0.3738(4)	0.25	0.5669(2)	0.601

$$B_{eq}=4(\beta_{11}a^2+\beta_{22}b^2+\beta_{33}c^2)/3.$$

The Sm(1)S₇ polyhedron forms a distorted 7-coordinated octahedron at an average distance of 2.834 Å, with one longer Sm-S distance of 2.945 Å. These two coordination forms, though the former eightfold coordination is more common, are typical ones for the light rare earths up to dysprosium. The structure of α -Sm₂S₃ is a flat cell, whose thickness is about 4 Å, corresponding to the period of the *b* axis. The height of the prisms

Table 3 Selected bond lengths (Å) and bond angles (°)

Sm(1)S ₇ polyhedron				
Sm(1)-S(1)	2.945(3) Å	S(1) ⁱ -Sm(1)-S(1) ^{iv}	95.37(8)°	x2
Sm(1)-S(1)'	2.772(2) x2	S(1) ⁱ -Sm(1)-S(3) ^{iv}	75.07(8)	x2
Sm(1)-S(2)	2.822(3)	S(1) ^{iv} -Sm(1)-S(1) ^{iv}	91.24(9)	x2
Sm(1)-S(3)	2.913(3)	S(1) ^{iv} -Sm(1)-S(2) ⁱⁱ	80.92(8)	x2
Sm(1)-S(3)'	2.806(2) x2	S(1) ^{iv} -Sm(1)-S(3) ^{iv}	86.14(7)	x2
Mean	2.834	S(2) ⁱⁱ -Sm(1)-S(3) ⁱ	65.21(9)	
		S(3) ⁱ -Sm(1)-S(3) ^{iv}	73.13(8)	
		S(3) ^{iv} -Sm(1)-S(3) ^{iv}	89.84(9)	
Sm(2)S ₈ bicapped trigonal				
Sm(2)-S(1)	3.042(3) Å	S(1) ⁱ -Sm(2)-S(2) ⁱⁱⁱ	77.05(7)°	x2
Sm(2)-S(1)''	3.077(3)	S(1) ⁱ -Sm(2)-S(2) ^{iv}	71.93(7)	x2
Sm(2)-S(2)'	2.777(2) x2	S(1) ⁱⁱ -Sm(2)-S(2) ⁱⁱⁱ	73.42(7)	x2
Sm(2)-S(2)''	2.928(2) x2	S(1) ⁱⁱ -Sm(2)-S(3) ⁱⁱⁱ	71.85(7)	x2
Sm(2)-S(3)	2.893(2) x2	S(2) ⁱⁱⁱ -Sm(2)-S(2) ⁱⁱⁱ	91.01(9)	
Mean	2.914	S(2) ⁱⁱⁱ -Sm(2)-S(2) ^{iv}	83.76(3)	x2
		S(2) ⁱⁱⁱ -Sm(2)-S(3) ⁱⁱⁱ	81.04(7)	x2
		S(2) ^{iv} -Sm(2)-S(2) ^{iv}	85.15(8)	
		S(2) ^{iv} -Sm(2)-S(3) ⁱⁱⁱ	64.14(8)	
		S(3) ⁱⁱⁱ -Sm(2)-S(3) ⁱⁱⁱ	86.45(9)	

Symmetry code: i, x, y, z ; ii, $1/2+x, 1/2-y, 1/2-z$; iii, $1/2-x, -y, 1/2+z$; iv, $-x, 1/2+y, -z$. x2 indicate that two crystallographically equivalent bonds or angles are involved in the same polyhedron.

determines the lattice period.

Each Sm(2)S₈ polyhedron is slightly zigzag, but linked to each other in the direction of the a axis by sharing two triangle faces composed of one vertical edge of the prism and a cap of the polyhedron. Simultaneously, Sm(2)S₈ polyhedra are piled up along the b axis by sharing two trigonal basal planes of the prism. As a result, the Sm(2)S₈ polyhedra form two-dimensional layers parallel to the ab plane. The Sm(1) atom connects Sm(2)S₈

Fig. 1 ORTEP drawing of the crystal structure of α -Sm₂S₃ projected along the b axis.

polyhedra by entering the 7-coordinated octahedral space between these layers. Each Sm(1)S₇ polyhedron shares two pairs of opposite edges along the ab plane. Namely, two layers of Sm(1)S₇ and Sm(2)S₈ alternately stack parallel to the ab plane. The shape of Sm(2)S₈ polyhedron leads to a small vacant space at the residual side of the prism. So the Sm(1)S₇ polyhedron cannot share the faces with each other, but only the edges. It is clear that the structure is not a simple close-packed one, and the coordination polyhedra form a complex three-dimension structure.

References

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