Crystal structure of samarium selenide, $SmSe_{1.90}$

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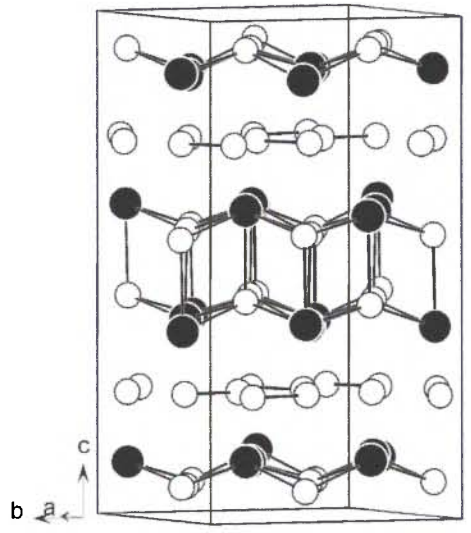

Fig. 1. Unit cell of $SmSe_{1.9}$; Sm atoms black, Se atoms open circles.

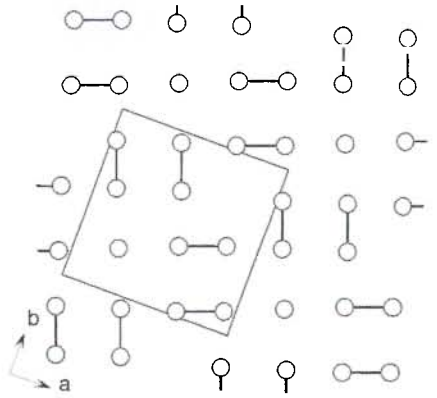

Fig. 2. Projection of one of the Se sheets.

Abstract

$Se_{1.90}Sm$, tetragonal, $P4_2/n$ (No. 86), $a = 9.143(1)$ Å, $c = 16.624(3)$ A, $V = 1389.7$ Å^3, $Z = 20$, $R_{gt}(F) = 0.027$, $wR_{ref}(F^2) = 0.067$, $T = 293$ K.

Source of material

Stoichiometric amounts of samarium (powder, Alfa, 99.99%) and selenium (powder, Fluka, 99.99%) are filled in a quartz-glass ampoule. After sealing under vacuum, the ampoule is heated slowly to 1223 K and remains at this temperature for one week. After cooling, the powder is transferred into another quartz-glass ampoule, iodine is added as transport agent and the sealed ampoule is placed in a two zone furnace. Chemical transport is carried out in a temperature gradient from 1123 K – 923 K for two weeks. Small black platelets with metallic luster are obtained in the colder zone. ICP analysis of the crystals gave the composition $SmSe_{1.90(1)}$.

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Discussion

$SmSe_{1.90}$ crystallizes in the $CeSe_{1.9}$ structure type, which has been discovered in the late eighties [1]. Since then, some sulfides and selenides, especially of the lighter rare earth elements have been described in this structure type [2-4]. $CeSe_{1.9}$ is a 10-fold superstructure of the ZrSSi type, which we consider to be the aristotype of rare earth dichalcogenides $LnX_{2-\delta}$ (X = S, Se, Te) and related compounds. This structure type consists of puckered [LnX] double slabs, which are sandwiched by square-planar [X] sheets. Different superstructures have been noticed due to different chalcogen deficiencies in the [X] sheets. In superstructures of the $CeSe_{1.9}$ type, one out of ten X atoms of the square-planar sheet is missing. Figure 1 shows the stacking of the [SmSe] double slabs and the deficient square-planar [Se] sheets of $SmSe_{1.90}$, which reveal the close relation to the aristotype. In Figure 2, a projection of the chalcogen sheet is depicted. Due to the occurrence of vacancies, single Se^{2-} anions and Se_2^{2-} dumbbells are found. The Se—Se distances in the dumbbells are 2.45 Å. The Se_2^{2-} dimers are arranged in pinwheel-like patterns resulting in eight membered rings around the vacancies. The Se—Se distances between the dumbbells in the eight-membered ring 2.87 Å are somewhat shorter than distances between dumbbell Se atoms and single Se^{2-} anions (3.12 Å). Two different coordination spheres are found for samarium. Two of the three crystallographically independent Sm atoms are surrounded by 9 selenium in a capped tetragonal antiprism. The third one, with coordination number 8, is in the centre of a di-capped trigonal prism. According to conductivity measurements, $SmSe_{1.90}$ is an insulator [6].

Table 1. Data collection and handling.

Crystal:	black-metallic platelet, size 0.03 × 0.06 × 0.08 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	456.36 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS, 289 exposures, $\varphi = 0.9°$
$2\theta_{max}$:	59.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	20007, 2019
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1390
$N(param)_{refined}$:	67
Programs:	SHELXS-97 [7], SHELXL-97 [8], DIAMOND [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sm(1)	4*e*	3/4	1/4	0.38413(3)	0.0030(2)	0.0037(2)	0.0024(2)	0.0001(2)	0	0
Sm(2)	8*g*	0.04292(3)	0.34803(3)	0.11960(2)	0.0042(2)	0.0034(2)	0.0031(1)	–0.0001(1)	–0.00113(8)	–0.00032(9)
Sm(3)	8*g*	0.05332(3)	0.35298(3)	0.60559(2)	0.0036(2)	0.0041(2)	0.0026(1)	0.0001(1)	0.00067(8)	–0.00004(8)
Se(1)	8*g*	0.12134(6)	0.56569(6)	0.25054(3)	0.0083(2)	0.0080(2)	0.0019(3)	–0.0004(2)	–0.0002(2)	0.0000(2)
Se(2)	4*e*	3/4	1/4	0.06478(5)	0.0031(4)	0.0037(4)	0.0011(3)	0.0002(3)	0	0
Se(3)	8*g*	0.14918(5)	0.05248(5)	0.56306(3)	0.0036(3)	0.0034(3)	0.0015(2)	–0.0002(3)	–0.0001(2)	0.0001(2)
Se(4)	8*g*	0.15221(5)	0.04883(5)	0.07146(3)	0.0036(3)	0.0038(3)	0.0012(2)	0.0003(3)	0.0003(2)	–0.0000(2)
Se(5)	8*g*	0.67865(7)	0.02795(6)	0.24995(3)	0.0115(2)	0.0098(2)	0.0018(3)	–0.0004(2)	0.0003(2)	0.0001(3)
Se(6)	2*a*	1/4	1/4	1/4	0.0070(3)	0.0070(3)	0.0014(4)	0	0	0

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