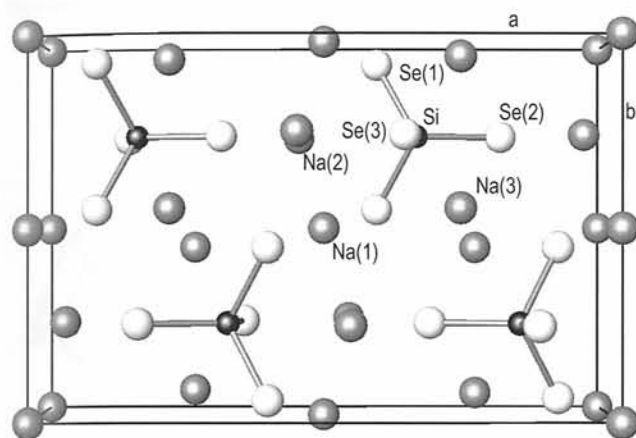


Crystal structure of tetrasodium tetraselenidosilicate(IV), Na₄SiSe₄

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occupy the octahedral interstices of a rather distorted cubic close packed chalcogen packing. Na(1) is in the centre of a strongly elongated octahedron $d(\text{Na1—Se})$: 2.816(3) Å (2×), 3.121(3) Å (2×) and 3.705(3) Å (2×) – leading to elevated displacement parameters U_{11} and U_{22} – while the other two Na⁺ ions are in off centred positions attaining skew square pyramidal chalcogen coordinations with mean Na—Se distances of 3.01(1) Å and 3.02(1) Å, respectively. Due to the effective separation of the SiSe₄ tetrahedra by the alkali cations there is only one interanionic Se...Se contact ($d(\text{Se1—Se1}) = 3.654(5)$ Å below 4.48 Å. Na₄SiSe₄ is besides Cs₄SiSe₄ [1] (Ba₄SiAs₄ type [2]) so far the only alkali ortho selenidosilicate. Its atomic arrangement corresponds to that of K₄SnSe₄ [3]. This structure type is also observed with the chalcogenostannates Rb₄SnSe₄, K₄SnTe₄ and Rb₄SnTe₄ [4]. The germanium homologue Na₄GeSe₄, however, crystallizes with an idiosyncratic yet closely related structure [5].

Abstract

Na₄Se₄Si, orthorhombic, *Pnma* (No. 62), $a = 14.182(5)$ Å, $b = 9.208(3)$ Å, $c = 7.122(3)$ Å, $V = 930.0$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.066$, $wR_{\text{ref}}(F) = 0.059$, $T = 294$ K.

Source of material

Colourless single crystals of Na₄SiSe₄ were obtained by reacting an intimate mixture of 829.5 mg Na₂Se (prepared from the elements in liquid ammonia), 124.4 mg 99.9999% Si and 525.0 mg 99.999% Se (approximate molar ratio 3:2:3) in a sealed and evacuated silica tube. The sample was gradually heated to 973 K, annealed for 12 h at this temperature and finally allowed to cool to ambient temperature at a controlled rate of 3 K/h.

Discussion

The crystal structure of Na₄SiSe₄ is characterized by the formation of discrete tetrahedral SiSe₄^{4−} anions ($d(\text{Si—Se}) = 2.259(9)$ Å) with *C_s* symmetry. With one triangular plane almost parallel to (001) the tetrahedra pointing in opposite directions are arranged in alternating sheets parallel to (100). Three independent Na⁺ ions

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.05 × 0.05 × 0.08 mm
Wavelength:	Mo <i>K</i> _α radiation (0.7107 Å)
μ :	160.07 cm ^{−1}
Diffractionmeter, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	53.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	1189, 1189
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 340
$N(\text{param})_{\text{refined}}$:	49
Programs:	SIR92 [6], Crystal Structure [7], DIFABS [8], ATOMS [9]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na(1)	4a	0	0	0	0.14(2)	0.10(2)	0.05(1)	−0.07(2)	−0.05(1)	0.03(1)
Na(2)	4c	0.4546(9)	1/4	−0.007(3)	0.016(7)	0.05(1)	0.08(2)	0	−0.004(8)	0
Na(3)	8d	0.2678(6)	0.947(1)	0.140(2)	0.036(5)	0.044(6)	0.049(7)	0.011(6)	0.007(5)	−0.022(8)
Si(1)	4c	0.1649(6)	1/4	0.219(2)	0.022(4)	0.016(5)	0.037(7)	0	0.002(5)	0
Se(1)	8d	0.0955(2)	0.4497(3)	0.3405(4)	0.026(1)	0.033(1)	0.032(1)	0.002(1)	−0.000(2)	−0.003(2)
Se(2)	4d	0.3174(2)	1/4	0.3157(8)	0.018(2)	0.043(3)	0.057(3)	0	−0.002(2)	0
Se(3)	4d	0.1410(3)	1/4	−0.0931(6)	0.048(2)	0.040(2)	0.028(2)	0	0.008(2)	0

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