Crystal structure of tetrasodium tetraselenidosilicate(IV), Na_4SiSe_4

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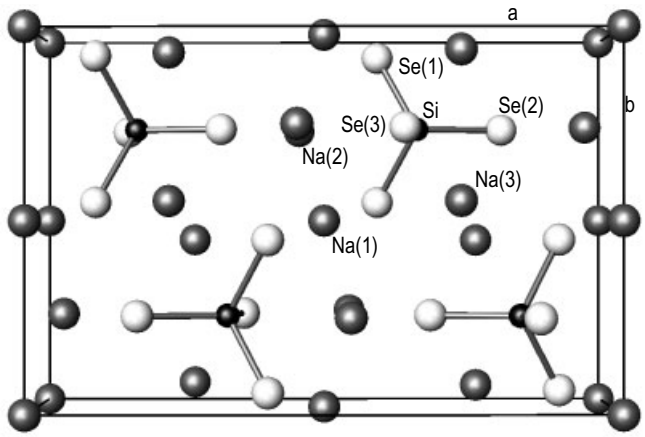

Abstract

Na_4Se_4Si, orthorhombic, *Pnma* (No. 62), $a = 14.182(5)$ Å, $b = 9.208(3)$ Å, $c = 7.122(3)$ Å, $V = 930.0$ Å^3, $Z = 4$, $R_{gt}(F) = 0.066$, $wR_{ref}(F) = 0.059$, $T = 294$ K.

Source of material

Colourless single crystals of Na_4SiSe_4 were obtained by reacting an intimate mixture of 829.5 mg Na_2Se (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 Na_4SiSe_4 is characterized by the formation of discrete tetrahedral $SiSe_4^{4-}$ anions ($\bar{d}$(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 occupy the octahedral interstices of a rather distorted cubic close chalcogen packing. Na(1) is in the centre of a strongly elongated octahedron d(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 $SiSe_4$ tetrahedra by the alkali cations there is only one interanionic Se···Se contact (d(Se1—Se1) = 3.654 (5) Å below 4.48 Å. Na_4SiSe_4 is besides Cs_4SiSe_4 [1] (Ba_4SiAs_4 type [2]) so far the only alkali ortho selenidosilicate. Its atomic arrangement corresponds to that of K_4SnSe_4 [3]. This structure type is also observed with the chalcogenostannates Rb_4SnSe_4, K_4SnTe_4 and Rb_4SnTe_4 [4]. The germanium homologue Na_4GeSe_4, however, crystallizes with an idiosyncratic yet closely related structure [5].

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.05 × 0.05 × 0.08 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	160.07 cm^{-1}
Diffractometer, scan mode:	Enraf Nonius CAD4, $\omega/2\theta$
$2\theta_{max}$:	53.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1189, 1189
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 340
$N(param)_{refined}$:	49
Programs:	SIR92 [6], Crystal Structure [7], DIFABS [8], ATOMS [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}
Na(1)	4*a*	0	0	0	0.14(2)	0.10(2)	0.05(1)	–0.07(2)	–0.05(1)	0.03(1)
Na(2)	4*c*	0.4546(9)	1/4	–0.007(3)	0.016(7)	0.05(1)	0.08(2)	0	–0.004(8)	0
Na(3)	8*d*	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)	4*c*	0.1649(6)	1/4	0.219(2)	0.022(4)	0.016(5)	0.037(7)	0	0.002(5)	0
Se(1)	8*d*	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)	4*d*	0.3174(2)	1/4	0.3157(8)	0.018(2)	0.043(3)	0.057(3)	0	–0.002(2)	0
Se(3)	4*d*	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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