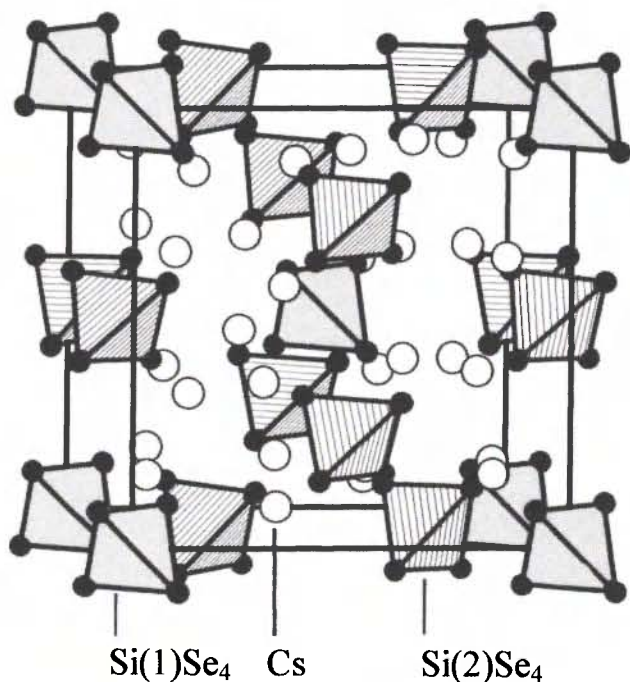


Crystal structure of cesium ortho-selenosilicate, Cs_4SiSe_4

J. Schlirf*, H. J. Deiseroth and T. Nilges

Universität Siegen, Anorganische Chemie, D-57068 Siegen, Germany

Received February 10, 2000, CSD-No. 409480



Abstract

$\text{Cs}_4\text{Se}_4\text{Si}$, cubic, $P43n$ (No. 218), $a = 14.147(3)$ Å, $V = 2831.3$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.021$, $wR_{\text{ref}}(F^2) = 0.047$, $T = 293$ K.

Source of material

The title compound was prepared starting from an inhomogeneous sample obtained by thermal decomposition of CsN_3 mixed with SiSe_2 (molar ratio 6 : 2) at 680 K in a quartz glass ampoule. Together with additional Se, corresponding to a molar composition 6 Cs : 2 Si : 6 Se, the raw product was heated to 1170 K. After quenching in icewater, homogenization and subse-

quent annealing at 850 K for 17 days the reaction yielded air sensitive, pale yellow single crystals of Cs_4SiSe_4 (size up to 0.5 mm). A hitherto unidentified additional phase must be present, but could not be identified until now.

Discussion

Compounds with the composition $\text{M}_4\text{M}'\text{X}_4$ (M = alkali metal) are well known for the lighter alkali metals Li ($\text{M}' = \text{Ge}$, $\text{X} = \text{S}$), Na ($\text{M}' = \text{Ge}$, $\text{X} = \text{Se}$; $\text{M}' = \text{Sn}$, $\text{X} = \text{S}$, Se , Te) and K ($\text{M}' = \text{Sn}$, $\text{X} = \text{Se}$) [1]. They crystallize in five different structure types with isolated $\text{M}'\text{X}_4$ -tetrahedra and coordination numbers between 4 and 6 for the alkali metals. Cs_4SiSe_4 represents the first cesium compound of this series to crystallize isotypically to Ba_4SiAs_4 [2]. In this structure cesium atoms are embedded in a matrix of SiSe_4 -tetrahedra ($d(\text{Si}—\text{Se}) = 227$ pm – 228 pm) and show a distorted octahedral coordination of selenium atoms ($d(\text{Cs}—\text{Se}) = 361$ pm – 375 pm). The spatial distribution of the Si(1) and Si(2) atoms as centers of the SiSe_4 -tetrahedra is topologically equivalent to the A15 structure type (Cr_3Si) with Si(1) Se_4 corresponding to Si and Si(2) Se_4 corresponding to Cr.

Table 1. Data collection and handling.

Crystal:	pale yellow, transparent, wedge shaped fragment, size $0.15 \times 0.2 \times 0.36$ mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ :	205.33 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, $\omega/2\theta$
$2\theta_{\text{max}}$:	59.9°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	11230, 1383
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1281
$N(\text{param})_{\text{refined}}$:	29
Programs:	SHELXS-97 [3], SHELXL-97 [4], DIAMOND [5]

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cs(1)	24i	0.84672(2)	0.58292(2)	0.63682(2)	0.0313(2)	0.0315(2)	0.0331(2)	−0.0019(1)	0.0030(1)	0.0022(1)
Cs(2)	8e	0.84600(2)	x	x	0.0326(1)	U_{11}	U_{11}	−0.0025(1)	U_{12}	U_{12}
Si(1)	2a	1/2	1/2	1/2	0.0188(8)	U_{11}	U_{11}	0	0	0
Si(2)	6c	3/4	1/2	0	0.018(1)	0.0178(7)	U_{22}	0	0	0
Se(1)	24i	0.83867(4)	0.58972(4)	0.89947(4)	0.0291(2)	0.0281(2)	0.0255(2)	−0.0049(2)	0.0043(2)	0.0061(2)
Se(2)	8e	0.59279(3)	x	x	0.0288(2)	U_{11}	U_{11}	−0.0054(2)	U_{12}	U_{12}

* Correspondence author (e-mail: schlirf@chemie.uni-siegen.de)

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

References

1. Matsushita, Y.; Kanatzidis, M. G.: Synthesis and Structure of Li_4GeS_4 . *Z. Naturforsch.* **B53** (1998) 23-30.
2. Eisenmann, B.; Jordan, H.; Schäfer, H.: Zintlphasen mit isolierten SiAs_4 - bzw. GeAs_4 -Anionen: Darstellung und Struktur von Ba_4SiAs_4 und Ba_4GeAs_4 sowie Sr_4SiAs_4 und Sr_4GeAs_4 . *Z. Anorg. Allg. Chem.* **475** (1981) 74-80.
3. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr.* **A46** (1990) 467-473.
4. Sheldrick, G. M.: SHELXL-97. Program for the refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Brandenburg, K.: DIAMOND. Crystal Impact GbR, Germany 1996-1999.