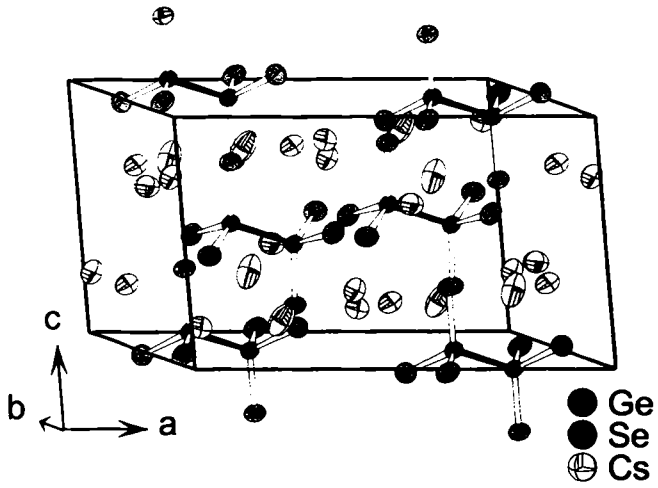
© by Oldenbourg Wissenschaftsverlag, München

Crystal structure of hexacesium hexaselenidodigermanate(III), $Cs_6Ge_2Se_6$

J. Schlirf* and H. J. Deiseroth

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

Received July 25, 2000, CSD-No. 409512



Abstract

$Cs_6Ge_2Se_6$, monoclinic, $C12/c1$ (No. 15), a = 16.280(3) Å, b = 13.528(3) Å, c = 9.621(2) Å, β = 96.70(3)°, V = 2104.4 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F^2)$ = 0.060, 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 $GeSe_2$ (molar ratio 6 : 2). The reaction was carried out at 630 K in a quartz glass ampule. Together with additional Se (molar composition 6 Cs : 2 Ge : 6 Se), the raw product was heated to 1273 K. After quenching in icewater, homogenization and subsequent annealing at 953 K for two weeks the reaction yielded air sensitive, transparent, orange single crystals of $Cs_6Ge_2Se_6$.

Discussion

With $Cs_6Ge_2Se_6$ another crystalline solid could be prepared using the "azide-method" [1]. $Cs_6Ge_2Se_6$ crystallizes isotypically to $K_6Ge_2Te_6$ [2]. The hitherto known compounds with the composition $M_6M'_2X_6$, M = Na (M' = Si, X = Te; M' = Ge, X = Se, Te), K (M' = Ge, X = S, Se, Te; M' = Sn, X = Se, Te), $Rb_6Sn_2Te_6$ and M = Cs (M' = Ge, X = Te; M' = Sn, X = Se, Te) [2, 3 and cited literature] crystallize in three different structure types characterized by isolated M'_2X_6 units with covalent M'—M'-bondings. In $Cs_6Ge_2Se_6$, the alkali metals are distorted octahedral and distorted trigonal prismatic coordinated by selenium (d(Cs—Se) = 3.49 Å – 3.96 Å, see fig.). The ethane analogous Ge_2Se_6 unit contains two trigonal $GeSe_3$-pyramides (d(Ge—Se) = 2.36 Å – 2.38 Å) in staggered conformation connected by a covalent Ge—Ge bond (d(Ge—Ge) = 2.54 Å).

Table 1. Data collection and handling.

Crystal:	orange, transparent, polygonal isometric, size 0.16 × 0.16 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	234.36 cm^{-1}
Diffractometer, scan mode:	STOE IPDS, φ
$2\theta_{max}$:	55.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11351, 2525
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2102
$N(param)_{refined}$:	66
Programs:	SHELXS-97 [4], SHELXL-97 [5], DIAMOND [6])

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}
Cs(1)	8f	0.77802(2)	–0.02458(3)	–0.19190(5)	0.0392(2)	0.0330(2)	0.0640(3)	–0.0084(2)	0.0241(2)	–0.0184(2)
Cs(2)	8f	0.59492(2)	–0.20100(3)	0.12209(4)	0.0317(2)	0.0512(2)	0.0267(2)	0.0045(2)	0.0027(1)	0.0023(2)
Cs(3)	4e	1/2	0.09239(4)	1/4	0.0315(2)	0.0387(3)	0.0256(2)	0	0.0086(2)	0
Cs(4)	4e	1/2	0.57846(4)	3/4	0.0266(2)	0.0286(2)	0.0331(2)	0	0.0078(2)	0
Se(1)	8f	0.68376(3)	0.26385(4)	0.28565(5)	0.0264(2)	0.0272(3)	0.0175(2)	0.0014(2)	0.0044(2)	0.0000(2)
Se(2)	8f	0.62156(3)	0.08581(4)	–0.02693(6)	0.0289(2)	0.0236(3)	0.0263(3)	–0.0052(2)	0.0089(2)	–0.0055(2)
Se(3)	8f	0.59077(3)	0.36589(4)	–0.07126(6)	0.0273(2)	0.0275(3)	0.0236(2)	0.0059(2)	0.0028(2)	0.0046(2)
Ge	8f	0.67842(3)	0.24344(4)	0.03914(5)	0.0177(2)	0.0191(2)	0.0163(2)	–0.0003(2)	0.0041(2)	–0.0003(2)

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

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

References

1. Reiner, C.: Gemischte Alkalimetallthioindate und Chalkogenide mit heteronuklearen Clustern der Tetrele und der Triele, Dissertation, Universität Siegen , Germay 1999.
2. Dittmar, G.: Die Kristallstrukturen von $K_6[Ge_2Te_6]$ und $K_6[Sn_2Te_6]$ und ihre kristall-chemische Beziehung zum $K_6[Si_2Te_6]$-Typ. Z. Anorg. Allg. Chem. **453** (1978) 68-78.
3. Friede, B.; Jansen, M.: Darstellung und Kristallstruktur von Hexacaesium-hexatellurido-digermanat(III) ($Cs_6Ge_2Te_6$). Z. Naturforsch. **54b** (1999) 1095-1097.
4. Sheldrick, G. M.: SHELXS-97, Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
5. Sheldrick, G. M.: SHELXL-97, Program for Crystal Structure Refinement. University of Göttingen, Germany 1997.
6. Brandenburg, K.: Diamond (Version 2.1a). Crystal Impact GbR, Germany 1996-1999.