Crystal structure of cadmium germanium selenide, Cd_4GeSe_6

K.-F. Hesse^{*,1}, M. Czank¹ and Á. Némcsics^{1,II}^I Institut für Geowissenschaften/Kristallographie, Universität Kiel, Olshausenstr.40, D-24098 Kiel, Germany^{II} Hungarian Academy of Sciences, Research Institute for Technical Physics and Materials Science, P.O.Box 49, H-1525 Budapest, Hungary

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Abstract

Cd_4GeSe_6 , monoclinic, $C1c1$ (No. 9), $a = 12.863(8)$, $b = 7.422(9)$ Å, $c = 14.78(1)$ Å, $\beta = 125.02(5)^\circ$, $V = 1155.7$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.063$, $wR_{\text{obs}}(F^2) = 0.171$, $T = 293$ K.

Source of material

Cd_4GeSe_6 (CGS) crystals were grown by chemical vapour transport method. Similar synthesis is reported in [1,2]. CdSe and GeSe_2 powders were mixed, filled in quartz ampoule and iodine was added as transport agent. First the stoichiometric material was synthesized at 1120 K for 48 h, and then the temperature was lowered and kept for three weeks at 830 K on the one end and at 750 K on the other end of the ampoule. The grown CGS material is mono- or polycrystalline with pieces of $1 \times 2 \times 2$ to $3 \times 4 \times 6$ mm³ in size.

Discussion

Nowadays there is an increased interest in research of novel compound semiconductors, because their properties can be changed in a very broad range. One of the most important group of semiconductor materials are the chalcogenides. Cd_4GeSe_6 is one representative of such materials, and it is particularly interesting because of possible photoelectrochemical solar cell application. The band gap is about 1.5 eV, which is very appropriate for solar energy conversion, but the detailed electronic structure is unknown till yet. To determine the electronic structure, accurate crystallographic characterisation (cell dimensions, bond lengths and angles) of the sample as well as the knowledge of possible structural faults is needed [3,4]. For that reason we have studied CGS by single crystal X-ray and transmission electron microscope (TEM) methods.

CGS belongs to a structural family of compounds with the general formula A_4BX_6 (where $\text{A} = \text{Cd}$ or Hg , $\text{B} = \text{Ge}$ or Si and $\text{X} = \text{S}$ or Se) [5,6]. The isotype structure of Cd_4SiS_6 has been determined by Krebs and Mandt [5]. The distorted CdSe_4 tetrahedra and the less distorted GeSe_4 tetrahedron share edges and built up a three dimensional framework. By that, two of the Se are coordinated by four Cd forming less distorted tetrahedra. The other Se have trigonal pyramidal coordination from one Ge and two Cd. The next nearest neighbours to each of these Se are either Se or Cd at about 3.4 Å. Intense TEM investigation of the real structure of CGS, i.e. bright-field, dark-field and lattice fringe imaging and diffraction experiments, have shown that the crystals are free of any fault on the microscopic scale.

Table 1. Data collection and handling.

Crystal:	black, size $0.152 \times 0.228 \times 0.432$ mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ :	286.43 cm ⁻¹
Diffractometer, scan mode:	STOE-Siemens AED 2, $\omega/2\theta$
$2\theta_{\text{max}}$:	59.78°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	1730, 1730
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1510
$N(\text{param})_{\text{refined}}$:	98
Program:	SHELXL-93 [7]

* Correspondence author (e-mail: kfh@min.uni-kiel.de)

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
Cd(1)	4a	0.7834(3)	0.1745(3)	0.9067(2)	0.0237(9)	0.0245(9)	0.024(1)	−0.0006(8)	0.0133(8)	0.0004(8)
Cd(2)	4a	1.1604(3)	0.1385(3)	1.0992(2)	0.0235(9)	0.031(1)	0.0215(9)	−0.0024(7)	0.0136(8)	−0.0008(8)
Cd(3)	4a	0.4475(3)	0.1459(3)	0.9130(2)	0.031(1)	0.0212(9)	0.026(1)	−0.0025(7)	0.0168(9)	0.0014(7)
Cd(4)	4a	0.9940(3)	0.9484(3)	0.2503(3)	0.033(1)	0.032(1)	0.029(1)	−0.0095(9)	0.0211(9)	−0.0100(9)
Ge(1)	4a	0.4718(3)	0.0188(3)	0.6613(3)	0.017(1)	0.013(1)	0.014(1)	−0.0002(9)	0.0102(9)	0.0005(9)
Se(1)	4a	0.9674(3)	−0.0026(4)	0.9127(3)	0.023(1)	0.016(1)	0.019(1)	−0.0009(9)	0.0135(9)	−0.0008(9)
Se(2)	4a	0.5842(3)	−0.0309(3)	0.8511(3)	0.020(1)	0.020(1)	0.013(1)	−0.0007(9)	0.0095(9)	0.0020(9)
Se(3)	4a	0.8419(3)	0.2303(4)	1.1105(3)	0.027(1)	0.018(1)	0.021(1)	−0.0070(9)	0.015(1)	−0.0009(9)
Se(4)	4a	1.2209(3)	0.0216(4)	1.2924(3)	0.021(1)	0.019(1)	0.019(1)	0.0015(9)	0.0124(9)	0.002(1)
Se(5)	4a	0.8435(3)	−0.2640(3)	1.0762(3)	0.020(1)	0.015(1)	0.017(1)	0.0027(9)	0.0113(9)	0.0025(9)
Se(6)	4a	0.6123(3)	−0.0093(4)	1.1111(3)	0.022(1)	0.024(1)	0.022(1)	0.004(1)	0.017(1)	0.005(1)

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