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Redetermination of the quaternary phase silver dicadmium gallium tetrasulfide, $AgCd_2GaS_4$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(a–S) = 0.002 Å
R factor = 0.038
wR factor = 0.113
Data-to-parameter ratio = 28.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The structure of $AgCd_2GaS_4$, known from powder data, has been redetermined by means of single-crystal X-ray diffraction. The structure can be described as a superstructure of wurtzite. All metal atoms are in a slightly distorted tetrahedral environment formed by the S atoms. The Ag, the Ga and two S atoms are situated on positions with m symmetry, while all other atoms are in general positions.

Comment

The $(A^{I}C^{III}X_2)_{1-x}$–$(B^{II}X)_x$ systems, where A^{I} = Cu and Ag, B^{II} = Zn, Cd and Hg, C^{III} = Ga and In, and X = S, Se and Te, have been widely investigated. The existence of considerable solid solution ranges, associated with the similarity of the crystal structures of the end-member compounds, was described in most reports (Goryunova, 1968; Grima Gallardo *et al.*, 2001). Intermediate phases were also found for these systems. The formation of the quaternary $A^{I}B^{II}_2C^{III}X_4$ compounds with a component ratio of 1:2 has been observed for the $CuGaSe_2$–CdSe (Novoselova & Lazarev, 1979), $CuInSe_2$–CdSe (Garbato *et al.*, 1984; Vovk *et al.*, 2000), $AgGaS_2$–CdS (Chykhrij *et al.*, 2000; Olekseyuk *et al.*, 2001) and $AgGaSe_2$–CdSe (Olekseyuk *et al.*, 2002) systems. All compounds feature an incongruent type of melting and exhibit a broad homogeneity range. The $CuCd_2GaSe_4$ and $CuCd_2InSe_4$ phases were found to crystallize in a zinc blende structure (Novoselova & Lazarev, 1979; Garbato *et al.*, 1984; Vovk *et al.*, 2000), whereas the crystal structures of $AgCd_2GaS_4$ and $AgCd_2GaSe_4$ are orthorhombic (space group $Pmn2_1$) and can be described as a superstructure of wurtzite, based on a two-layer anion packing (Parthé *et al.*, 1969).

The crystal structure of $AgCd_2GaS_4$ was investigated previously by X-ray powder diffraction using the Rietveld full-profile method (R = 0.074; Chykhrij *et al.*, 2000). A more precise single-crystal X-ray study has now been performed in order to evidence the non-centrosymmetric character of the $AgCd_2GaS_4$ structure. The crystals are transparent over the wide spectral range 0.5–13 µm and have a potential for nonlinear optical applications. Some physical properties of $AgCd_2GaS_4$ were reported by Olekseyuk *et al.* (2005).

$AgCd_2GaS_4$ is a member of the $A^{I}B^{II}_2C^{III}X_4$ family and consists of AgS_4 tetrahedra connected by corner-sharing to CdS_4 and GaS_4 tetrahedra to form a three-dimensional framework (Fig. 1). The crystal structure of $AgCd_2GaS_4$ in projection on the ab plane is shown in Fig. 2. The Ga—S and Cd—S distances (Table 1) are in good agreement with the sums of the ionic radii [$r(Ga^{4+})$ = 0.47 Å, $r(Cd^{2+})$ = 0.78 Å and $r(S^{2-}$ = 1.84 Å (Shannon, 1976)], whereas the Ag—S distances are significantly smaller than the sum of the radii of the corresponding ions [$r(Ag^{+}$ = 1.00 Å)] and virtually equal to

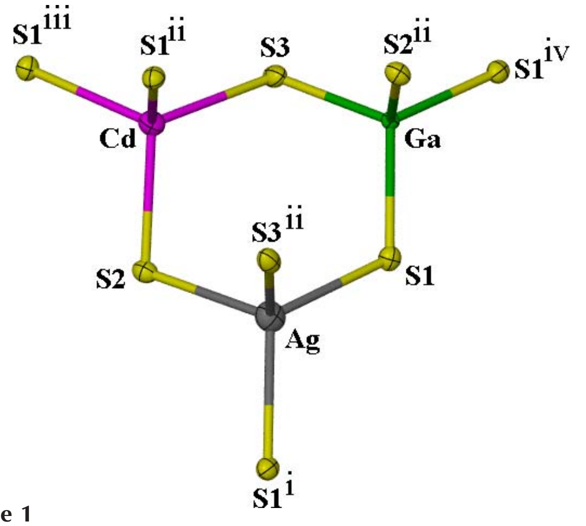

Figure 1
The tetrahedral environment of Ag, Cd and Ga atoms. Displacement ellipsoids are plotted at the 50% probability level. [Symmetry codes: (i) $-x, y, z$; (ii) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (iii) $x, 1 + y, z$; (iv) $1 - x, y, z$.]

the Cd—S distances. Chykhrij *et al.* (2000) stated that these values may indicate a possible statistical distribution of Ag and Cd ions over both crystallographic positions. However, the very close values of the atomic scattering functions for Ag and Cd do not allow the determination of the degree of statistical distribution. Contraction of the Ag—S distances may also indicate the presence of substantial covalent bonding between Ag atoms and sulfur.

Experimental

High-purity element reagents were used for synthesis (Ag: 99.999 wt%; Cd: 99.9999 wt%; Ga: 99.9997 wt%; S: 99.997 wt%). Stoichiometric amounts of the elements (charge ~20 g) were inserted into an evacuated silica ampoule, which was then sealed. The ampoule was heated in an oxygen-gas burner flame to complete conversion of elemental sulfur. In a second stage, the melt was heated to 1370 K and kept at that temperature for 4 h. The temperature was then decreased to 870 K and held for 500 h. Finally, the ampoule with the melt was cooled to room temperature in the switched-off furnace. A large polycrystalline $AgCd_2GaS_4$ ingot was crushed and a single crystalline block was selected for data collection.

Crystal data

$AgCd_2GaS_4$
$M_r = 530.63$
Orthorhombic, $Pmn2_1$
$a = 8.1395$ (9) Å
$b = 6.9394$ (8) Å
$c = 6.6014$ (7) Å
$V = 372.87$ (7) Å^3
$Z = 2$
$D_x = 4.726$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 838 reflections
$\theta = 4.3$–$35.0°$
$\mu = 12.79$ mm^{-1}
$T = 293$ (2) K
Prism, orange
0.05 × 0.03 × 0.03 mm

Data collection

Bruker–Nonius X8 Apex CCD area-detector diffractometer
φ scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{\min} = 0.550$, $T_{\max} = 0.679$
3258 measured reflections

1237 independent reflections
968 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\max} = 32.6°$
$h = -6 \rightarrow 12$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 7$

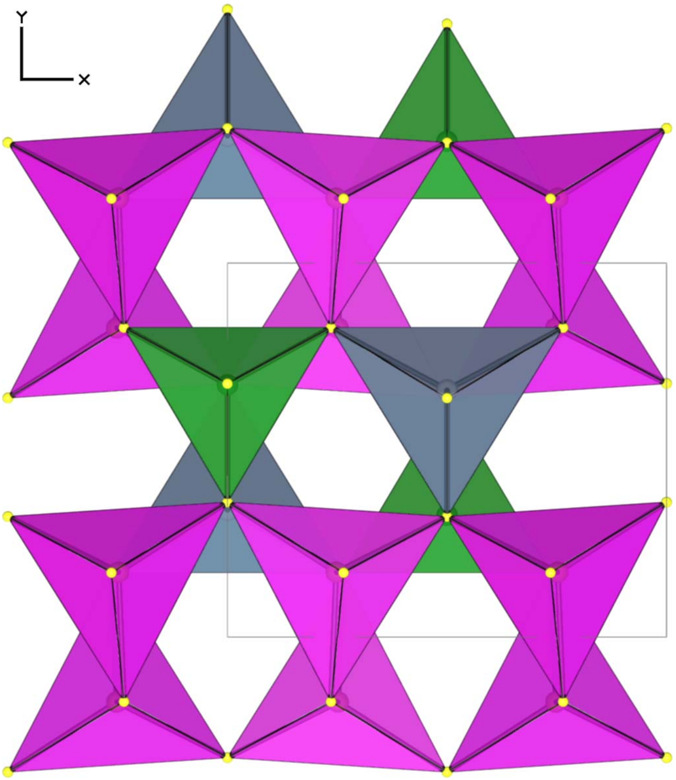

Figure 2
The crystal structure of $AgCd_2GaS_4$ in *ab* projection; AgS_4 tetrahedra are gray, CdS_4 tetrahedra are pink and GaS_4 tetrahedra are green.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.113$
$S = 1.08$
1237 reflections
44 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 3.09$ e Å^{-3}
$\Delta\rho_{\min} = -1.02$ e Å^{-3}
Extinction correction: none
Absolute structure: Flack (1983), 486 Friedel pairs
Flack parameter: 0.13 (3)

Table 1
Selected geometric parameters (Å, °).

Ag—S2	2.541 (3)	Cd—S1^{iii}	2.5232 (19)
Ag—S1^{i}	2.5535 (17)	Cd—S1^{ii}	2.538 (3)
Ag—S1	2.5535 (17)	Ga—S3	2.301 (3)
Ag—S3^{ii}	2.558 (3)	Ga—S1	2.316 (2)
Cd—S2	2.4993 (16)	Ga—S1^{iv}	2.3165 (19)
Cd—S3	2.5170 (14)	Ga—S2^{ii}	2.338 (4)
S2—Ag—S1^{i}	107.90 (7)	S2—Cd—S1^{ii}	110.51 (8)
S2—Ag—S1	107.90 (7)	S3—Cd—S1^{ii}	110.35 (8)
S1^{i}—Ag—S1	114.81 (10)	S1^{iii}—Cd—S1^{ii}	107.60 (7)
S2—Ag—S3^{ii}	108.95 (9)	S3—Ga—S1	109.26 (9)
S1^{i}—Ag—S3^{ii}	108.58 (8)	S3—Ga—S1^{iv}	109.26 (9)
S1—Ag—S3^{ii}	108.58 (8)	S1—Ga—S1^{iv}	111.82 (10)
S2—Cd—S3	109.02 (7)	S3—Ga—S2^{ii}	109.48 (11)
S2—Cd—S1^{iii}	107.78 (8)	S1—Ga—S2^{ii}	108.49 (9)
S3—Cd—S1^{iii}	111.55 (8)	S1^{iv}—Ga—S2^{ii}	108.49 (9)

Symmetry codes: (i) $-x, y, z$; (ii) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (iii) $x, y + 1, z$; (iv) $-x + 1, y, z$.

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The chosen crystal was a partial inversion twin. The highest peak and the deepest hole in the final Fourier map are located 0.01 Å from Ag and 0.92 Å from Ga, respectively.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXTL* (Bruker, 2004); molecular graphics: *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *SHELXTL* (Bruker, 2004).

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