Reinvestigation of the low-temperature form of Ag$_2$Se (naumannite) based on single-crystal data

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The crystal structure of the low-temperature form of synthetic naumannite [disilver(I) selenide], Ag$_2$Se, has been reinvestigated based on single-crystal data. In comparison with previous powder diffraction studies, anisotropic displacement parameters are additionally reported. The structure is composed of Se layers and two crystallographically independent Ag atoms. One Ag atom lies close to the Se layer and is surrounded by four Se atoms in a distorted tetrahedral coordination, while the second Ag atom lies between the Se layers and exhibits a [3 + 1] coordination defined by three close Se atoms, forming a trigonal plane, and one remote Se atom.

Related literature

The crystal structure of the low-temperature form of Ag$_2$Se has been previously refined by using X-ray (Wiegers, 1971) and synchrotron (Billetter & Ruschewitz, 2008) powder diffraction. For the structure of the cubic high-temperature form of Ag$_2$Se, see: Oliveria *et al.* (1988). For general background, see: Frueh (1958). For ionic radii, see: Shannon (1976).

Experimental

Crystal data

Ag$_2$Se	a = 4.3359 (8) Å
M_r = 294.7	b = 7.070 (1) Å
Orthorhombic, $P2_12_12_1$	c = 7.774 (1) Å

V = 238.34 (7) Å^3	μ = 31.27 mm^{-1}
Z = 4	T = 290 K
Mo $K\alpha$ radiation	0.30 × 0.04 × 0.02 mm

Data collection

Rigaku R-AXIS RAPID diffractometer	1981 measured reflections
Absorption correction: multi-scan (*NUMABS*; Higashi, 2000)	464 independent reflections
T_{min} = 0.053, T_{max} = 0.278	447 reflections with $I > 2\sigma(I)$
	R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031	$\Delta\rho_{max}$ = 1.19 e Å^{-3}
$wR(F^2)$ = 0.080	$\Delta\rho_{min}$ = −1.07 e Å^{-3}
S = 1.14	Absolute structure: Flack (1983), 167 Friedel pairs
464 reflections	
29 parameters	Flack parameter: 0.34 (4)

Table 1
Selected bond lengths (Å).

Ag1—Se^i	2.6800 (14)	Ag2—Se^{iii}	2.6538 (14)
Ag1—Se^{ii}	2.7058 (16)	Ag2—Se	2.7560 (15)
Ag1—Se^{iii}	2.8282 (14)	Ag2—Se^v	2.8036 (16)
Ag1—Se^{iv}	2.9076 (16)	Ag2—Se^{vi}	3.2112 (16)

Symmetry codes: (i) $-x + \frac{1}{2}, -y + 1, z + \frac{1}{2}$; (ii) $x + 1, y - 1, z$; (iii) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + \frac{3}{2}, -y + 1, z + \frac{1}{2}$; (v) $-x + \frac{1}{2}, -y + 2, z + \frac{1}{2}$; (vi) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *RAPID-AUTO* (Rigaku, 2006); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: locally modified version of *ORTEP* (Johnson, 1965); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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S1. Comment

Structural studies of the low-temperature form (transition point is 406 K) of the mineral naumannite, Ag$_2$Se, based on powder diffraction data have been reported previously by Wiegers (1971; X-ray data) and Billetter & Ruschewitz (2008; synchrotron data). In case of the related phase Ag$_2$S, single crystals of the high-temperature form (space group $Im\bar{3}m$) are known to convert to polycrystalline powder of the low-temperature form on cooling (Frueh, 1958), and the same conversion has been assumed for the Se analogue (Wiegers, 1971). Consequently, structure determinations of the low-temperature form of Ag$_2$Se have been carried out only by using powder diffraction methods. In an attempt to prepare new mixed-metal selenides using AgCl as a flux, we were able to isolate single crystals of the low-temperature form of Ag$_2$Se and report here the results of the structure analysis. In comparison with the previous powder diffraction studies, anisotropic displacement parameters are additionally reported.

The general structural features of AgSe$_2$ are the same as reported previously (Wiegers, 1971; Billetter & Ruschewitz, 2008). The structure of the low-temperature form of Ag$_2$Se is closely related to the cubic high-temperature phase, where the Se atoms form a body-centered cubic packing, while the silver atoms are statistically distributed over interstitial sites (Oliveria *et al.*, 1988). As a result, layers composed of Se atoms perpendicular to the *b* axis are retained in the low-temperature structure (Fig. 1). There are two crystallographically independent Ag atoms. Ag1 atoms lie close to this layer and are surrounded by four Se atoms in a distorted tetrahedral fashion (Se—Ag1—Se, 91.55 (3)–136.30 (5) °). The Ag1—Se distances range from 2.6800 (14) Å to 2.9076 (16) Å. Ag2 atoms are located between the layers and the coordination can be described as [3+1]. Three Se atoms built up a triangle that is bound to the Ag2 atom (Se—Ag2—Se, 94.00 (3)–141.46 (5) °), the coordination of which is augmented by a forth Se atom at a considerably longer distance of 3.2112 (16) Å. The observed Ag—Se distances are in agreement with the sum of the ionic radii of each element (Shannon, 1976) except for the very long Ag—Se bond. The distances and angles as calculated from single-crystal diffraction data differ slightly from those calculated previously from powder diffraction data. For example, the reported Ag1—Se distances are 2.62, 2.71, 2.79, 2.86 Å (Wiegers, 1971) and 2.658 (4), 2.668 (5), 2.861 (5), 2.937 (5) Å (Billetter & Ruschewitz, 2008) Å, and the Ag2—Se distances are 2.72, 2.74, 2.81, 3.28 Å (Wiegers, 1971) and 2.686 (5), 2.764 (5), 2.797 (4), 3.182 (5) Å (Billetter & Ruschewitz, 2008), respectively, with lattice parameters of *a* = 4.333 (Wiegers, 1971); 4.3373 (2) Å (Billetter & Ruschewitz, 2008), *b* = 7.062; 7.0702 (3) Å; *c* = 7.764; 7.7730 (4) Å.

S2. Experimental

Single crystals of the low-temperature form of Ag$_2$Se were isolated during attemts to prepare new mixed-metal phases of Hf/Zr selenides. A combination of the pure elements, Zr powder, Hf powder, Se powder were mixed in a fused silica tube in a molar ratio of Zr: Hf: Se = 1:1:3 with AgCl. The mass ratio of the reactants and the halide flux was 1:2. The tube was evacuated to 0.133 Pa, sealed and heated gradually (20 K/h) to 600 K, where it was kept for 72 h. The tube was cooled to

200 K at 3 K/h and then was quenched to room temperature. The excess halide flux was removed with distilled water and black needle shaped crystals were obtained. The crystals are stable in air and water. A qualitative XRF analysis of the crystals showed only the presence of Ag and Se.

S3. Refinement

Refinement with TWIN and BASF instruction for the final positional parameters gave a value of 0.34 (4) for the Flack parameter (Flack, 1983). The highest peak and the deepest hole in the final Fourier map are located 1.71 Å and 0.99 Å, respectively, from atom Ag1.
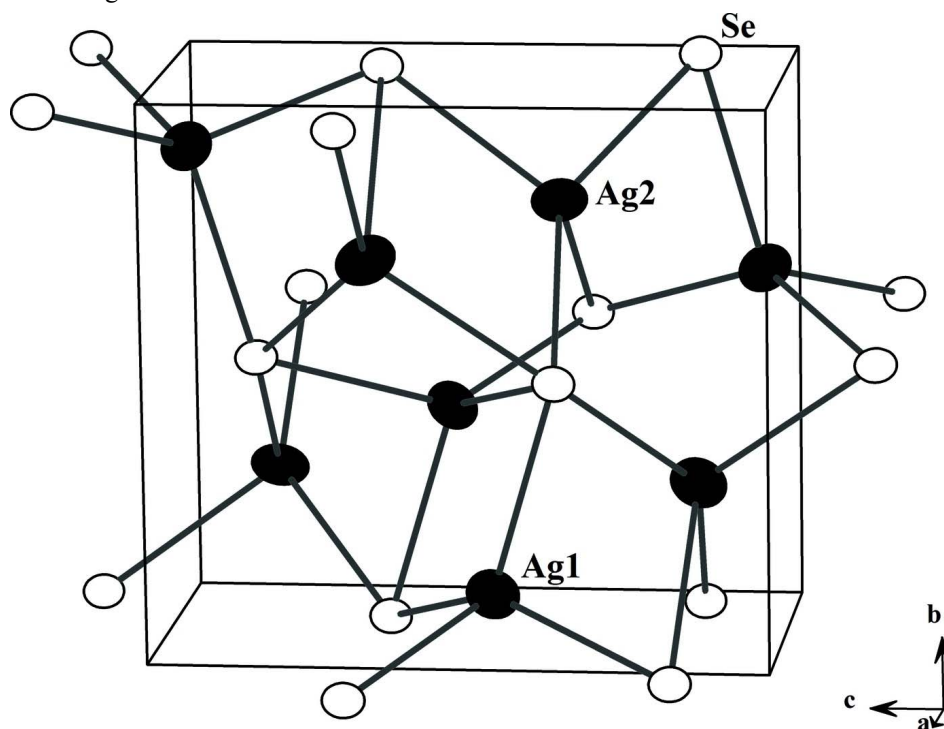

Figure 1

View of Ag_2Se (50% probability displacement ellipsoids)

disilver(I) selenide

Crystal data

Ag_2Se	$F(000) = 512$
$M_r = 294.7$	$D_x = 8.213$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: P 2ac 2ab	Cell parameters from 1738 reflections
$a = 4.3359$ (8) Å	$\theta = 3.4–27.5°$
$b = 7.070$ (1) Å	$\mu = 31.27$ mm^{-1}
$c = 7.774$ (1) Å	$T = 290$ K
$V = 238.34$ (7) Å^3	Needle, black
$Z = 4$	$0.30 \times 0.04 \times 0.02$ mm

Data collection

Rigaku R-AXIS RAPID diffractometer	464 independent reflections
ω scans	447 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*NUMABS*; Higashi, 2000)	$R_{int} = 0.057$
	$\theta_{max} = 26.0°$, $\theta_{min} = 3.9°$
$T_{min} = 0.053$, $T_{max} = 0.278$	$h = -5{\rightarrow}5$
1981 measured reflections	$k = -8{\rightarrow}8$
	$l = -9{\rightarrow}9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 1.0072P]$ where $P = (F_o^2 + 2F_c^2)/3$
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.031$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.080$	$\Delta\rho_{max} = 1.19$ e Å^{-3}
$S = 1.14$	$\Delta\rho_{min} = -1.07$ e Å^{-3}
464 reflections	Absolute structure: Flack (1983), 167 Friedel pairs
29 parameters	
0 restraints	Absolute structure parameter: 0.34 (4)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Ag1	0.8537 (2)	0.11503 (14)	0.45100 (14)	0.0398 (3)
Ag2	0.4745 (3)	0.77441 (14)	0.36152 (14)	0.0447 (4)
Se	0.1124 (2)	0.99787 (14)	0.15274 (14)	0.0242 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ag1	0.0381 (6)	0.0378 (6)	0.0436 (6)	−0.0010 (5)	0.0080 (5)	0.0060 (4)
Ag2	0.0462 (7)	0.0338 (6)	0.0540 (7)	0.0131 (4)	−0.0100 (5)	−0.0057 (5)
Se	0.0249 (5)	0.0190 (6)	0.0286 (6)	0.0001 (4)	−0.0011 (4)	−0.0006 (4)

Geometric parameters (Å, º)

Ag1—Se[i]	2.6800 (14)	Ag2—Se[ix]	3.2112 (16)
Ag1—Se[ii]	2.7058 (16)	Ag2—Ag1[x]	2.9979 (16)
Ag1—Se[iii]	2.8282 (14)	Ag2—Ag1[xi]	3.0330 (14)
Ag1—Se[iv]	2.9076 (16)	Ag2—Ag2[xii]	3.0749 (16)
Ag1—Ag1[v]	2.9872 (15)	Ag2—Ag2[xiii]	3.0749 (16)
Ag1—Ag1[vi]	2.9872 (15)	Ag2—Ag1[vi]	3.1591 (16)
Ag1—Ag2[vii]	2.9979 (15)	Ag2—Ag1[xiv]	3.3692 (17)
Ag1—Ag2[iii]	3.0330 (14)	Se—Ag2[xi]	2.6538 (14)
Ag1—Ag2[v]	3.1591 (16)	Se—Ag1[xv]	2.6800 (14)
Ag1—Ag2[iv]	3.3692 (17)	Se—Ag1[xvi]	2.7058 (16)

Ag2—Se^iii	2.6538 (14)	Se—Ag2^xvii	2.8036 (16)
Ag2—Se	2.7560 (15)	Se—Ag1^xi	2.8282 (14)
Ag2—Se^viii	2.8036 (16)	Se—Ag1^xiv	2.9076 (16)
Se^i—Ag1—Se^ii	136.30 (5)	Se^viii—Ag2—Ag1^x	54.90 (4)
Se^i—Ag1—Se^iii	119.41 (5)	Se^iii—Ag2—Ag1^xi	90.54 (4)
Se^ii—Ag1—Se^iii	91.55 (3)	Se—Ag2—Ag1^xi	58.26 (4)
Se^i—Ag1—Se^iv	101.71 (5)	Se^viii—Ag2—Ag1^xi	142.86 (5)
Se^ii—Ag1—Se^iv	92.76 (3)	Ag1^x—Ag2—Ag1^xi	137.88 (5)
Se^iii—Ag1—Se^iv	112.04 (5)	Se^iii—Ag2—Ag2^xii	58.04 (3)
Se^iii—Ag2—Se^ix	94.87 (4)	Se—Ag2—Ag2^xii	151.45 (6)
Se—Ag2—Se^ix	82.95 (3)	Se^viii—Ag2—Ag2^xii	66.03 (5)
Se^viii—Ag2—Se^ix	105.72 (5)	Ag1^x—Ag2—Ag2^xii	62.68 (4)
Se^i—Ag1—Ag1^v	126.05 (6)	Ag1^xi—Ag2—Ag2^xii	148.22 (5)
Se^ii—Ag1—Ag1^v	96.50 (4)	Se^iii—Ag2—Ag2^xiii	114.98 (6)
Se^iii—Ag1—Ag1^v	54.80 (4)	Se—Ag2—Ag2^xiii	94.31 (4)
Se^iv—Ag1—Ag1^v	57.32 (3)	Se^viii—Ag2—Ag2^xiii	53.43 (4)
Se^i—Ag1—Ag1^vi	59.58 (3)	Ag1^x—Ag2—Ag2^xiii	108.32 (6)
Se^ii—Ag1—Ag1^vi	135.65 (6)	Ag1^xi—Ag2—Ag2^xiii	100.86 (4)
Se^iii—Ag1—Ag1^vi	59.92 (5)	Ag2^xii—Ag2—Ag2^xiii	89.67 (6)
Se^iv—Ag1—Ag1^vi	127.99 (6)	Se^iii—Ag2—Ag1^vi	59.27 (4)
Ag1^v—Ag1—Ag1^vi	93.06 (6)	Se—Ag2—Ag1^vi	132.61 (5)
Se^i—Ag1—Ag2^vii	58.86 (4)	Se^viii—Ag2—Ag1^vi	96.07 (5)
Se^ii—Ag1—Ag2^vii	77.44 (4)	Ag1^x—Ag2—Ag1^vi	133.16 (4)
Se^iii—Ag1—Ag2^vii	136.98 (5)	Ag1^xi—Ag2—Ag1^vi	88.17 (3)
Se^iv—Ag1—Ag2^vii	109.95 (4)	Ag2^xii—Ag2—Ag1^vi	72.30 (4)
Ag1^v—Ag1—Ag2^vii	166.05 (5)	Ag2^xiii—Ag2—Ag1^vi	57.47 (4)
Ag1^vi—Ag1—Ag2^vii	100.04 (3)	Se^iii—Ag2—Ag1^xiv	88.98 (4)
Se^i—Ag1—Ag2^iii	103.04 (4)	Se—Ag2—Ag1^xiv	55.60 (4)
Se^ii—Ag1—Ag2^iii	67.77 (4)	Se^viii—Ag2—Ag1^xiv	131.41 (5)
Se^iii—Ag1—Ag2^iii	55.96 (3)	Ag1^x—Ag2—Ag1^xiv	84.96 (4)
Se^iv—Ag1—Ag2^iii	155.18 (5)	Ag1^xi—Ag2—Ag1^xiv	55.32 (3)
Ag1^v—Ag1—Ag2^iii	107.91 (5)	Ag2^xii—Ag2—Ag1^xiv	122.24 (4)
Ag1^vi—Ag1—Ag2^iii	68.06 (4)	Ag2^xiii—Ag2—Ag1^xiv	147.69 (4)
Ag2^vii—Ag1—Ag2^iii	81.67 (3)	Ag1^vi—Ag2—Ag1^xiv	132.52 (4)
Se^i—Ag1—Ag2^v	66.13 (4)	Ag2^xi—Se—Ag1^xv	134.75 (5)
Se^ii—Ag1—Ag2^v	93.43 (4)	Ag2^xi—Se—Ag1^xvi	95.17 (4)
Se^iii—Ag1—Ag2^v	163.17 (5)	Ag1^xv—Se—Ag1^xvi	106.26 (4)
Se^iv—Ag1—Ag2^v	51.68 (3)	Ag2^xi—Se—Ag2	93.59 (4)
Ag1^v—Ag1—Ag2^v	108.60 (5)	Ag1^xv—Se—Ag2	127.12 (5)
Ag1^vi—Ag1—Ag2^v	124.02 (5)	Ag1^xvi—Se—Ag2	84.66 (5)
Ag2^vii—Ag1—Ag2^v	59.85 (3)	Ag2^xi—Se—Ag2^xvii	68.53 (4)
Ag2^iii—Ag1—Ag2^v	140.46 (4)	Ag1^xv—Se—Ag2^xvii	66.24 (4)
Se^i—Ag1—Ag2^iv	71.43 (4)	Ag1^xvi—Se—Ag2^xvii	117.42 (5)
Se^ii—Ag1—Ag2^iv	142.30 (5)	Ag2—Se—Ag2^xvii	151.82 (5)
Se^iii—Ag1—Ag2^iv	92.10 (4)	Ag2^xi—Se—Ag1^xi	131.16 (5)
Se^iv—Ag1—Ag2^iv	51.45 (3)	Ag1^xv—Se—Ag1^xi	65.62 (4)
Ag1^v—Ag1—Ag2^iv	56.62 (4)	Ag1^xvi—Se—Ag1^xi	123.98 (5)

Ag1^{vi}—Ag1—Ag2^{iv}	76.74 (5)	Ag2—Se—Ag1^{xi}	65.78 (4)
Ag2^{vii}—Ag1—Ag2^{iv}	121.83 (4)	Ag2^{xvii}—Se—Ag1^{xi}	109.05 (5)
Ag2^{iii}—Ag1—Ag2^{iv}	140.93 (4)	Ag2^{xi}—Se—Ag1^{xiv}	69.05 (4)
Ag2^{v}—Ag1—Ag2^{iv}	74.25 (3)	Ag1^{xv}—Se—Ag1^{xiv}	101.71 (5)
Se^{iii}—Ag2—Se	141.46 (5)	Ag1^{xvi}—Se—Ag1^{xiv}	151.20 (5)
Se^{iii}—Ag2—Se^{viii}	123.20 (5)	Ag2—Se—Ag1^{xiv}	72.95 (4)
Se—Ag2—Se^{viii}	94.00 (3)	Ag2^{xvii}—Se—Ag1^{xiv}	80.16 (4)
Se^{iii}—Ag2—Ag1^{x}	103.38 (5)	Ag1^{xi}—Se—Ag1^{xiv}	62.75 (4)
Se—Ag2—Ag1^{x}	89.34 (4)		

Symmetry codes: (i) −x+1/2, −y+1, z+1/2; (ii) x+1, y−1, z; (iii) −x+1, y−1/2, −z+1/2; (iv) −x+3/2, −y+1, z+1/2; (v) x+1/2, −y+1/2, −z+1; (vi) x−1/2, −y+1/2, −z+1; (vii) x, y−1, z; (viii) −x+1/2, −y+2, z+1/2; (ix) −x, y−1/2, −z+1/2; (x) x, y+1, z; (xi) −x+1, y+1/2, −z+1/2; (xii) x+1/2, −y+3/2, −z+1; (xiii) x−1/2, −y+3/2, −z+1; (xiv) −x+3/2, −y+1, z−1/2; (xv) −x+1/2, −y+1, z−1/2; (xvi) x−1, y+1, z; (xvii) −x+1/2, −y+2, z−1/2.