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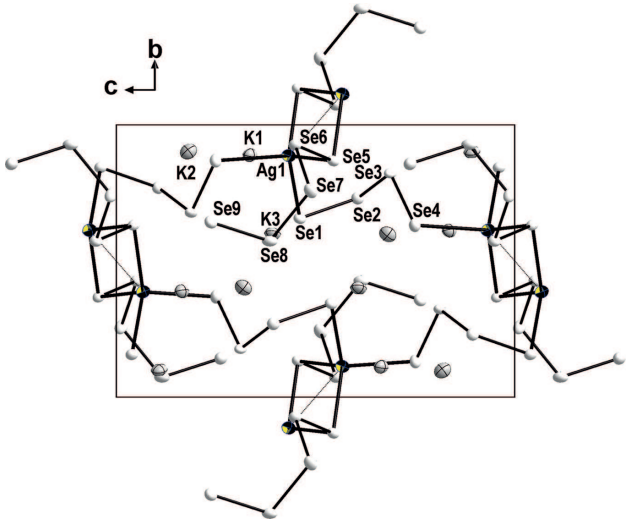
Crystal structure of semiconducting potassium poly[(μ_2-tetraselenido-κ^2Se^1:Se^4)(μ_2-pentaselenido-κ^1Se^1:Se^1)argentate(I)], K_3AgSe_9



https://doi.org/10.1515/ncrs-2018-0046
Received January 25, 2018; accepted April 12, 2018; available online May 7, 2018

Abstract

K_3AgSe_9, monoclinic, $P2_1/c$ (no. 14), $a = 11.094(2)$ Å, $b = 9.7164(15)$ Å, $c = 14.223(3)$ Å, $\beta = 90.738(9)°$, $V = 1533.0(5)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0377$, $wR_{ref}(F^2) = 0.0832$, $T = 223(2)$ K.

CCDC no.: 1836642

The title crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

$AgCH_3CO_2$ (0.020 g, 0.12 mmol), K_2Se_4 (0.139 g, 0.36 mmol) and Et_3MeNI (0.057 g, 0.24 mmol) were charged to a Pyrex tube with diameter of 9 mm under an argon atmosphere and about 0.5 mL MeOH was added as solvent. While the solvent was being frozen, the Pyrex tube was evacuated and sealed with the use of a flame. The sealed tube was placed in an oven and heated at 80 °C for a day, then cooled to room temperature. Dark purple plate crystals were isolated by filtration and washed with MeOH and diethyl ether several times. Crystals of K_3AgSe_9 were obtained in 48% yield, based on Ag.

Table 1: Data collection and handling.

Crystal:	Dark purple, plate
Size:	0.15 × 0.13 × 0.03 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	23.46 mm^{-1}
Diffractometer, scan mode:	Bruker Photon 100, φ and ω
θ_{max}, completeness:	28.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	41091, 3831, 0.106
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2980
$N(param)_{refined}$:	119
Programs:	Bruker [10], SHELX [11], WinGX[12], Diamond[13]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Ag1	0.54031(5)	0.11327(5)	0.43267(4)	0.02399(14)
Se1	0.67540(6)	0.34352(7)	0.46068(5)	0.02037(16)
Se2	0.75540(6)	0.26942(7)	0.60569(5)	0.02058(16)
Se3	0.59317(7)	0.17762(7)	0.68781(5)	0.02424(18)
Se4	0.48996(7)	0.36846(7)	0.74938(5)	0.02283(17)
Se5	0.34453(6)	0.13219(7)	0.54408(5)	0.01779(15)
Se6	0.17487(6)	0.07314(7)	0.44892(5)	0.02057(16)
Se7	0.03363(7)	0.24222(8)	0.48766(5)	0.02407(17)
Se8	0.07222(7)	0.42699(7)	0.38518(5)	0.02502(18)
Se9	0.00050(7)	0.35731(8)	0.23753(5)	0.02699(18)
K1	0.82136(15)	0.38859(16)	0.83566(11)	0.0267(3)
K2	0.19708(16)	0.40214(17)	0.68115(12)	0.0304(4)
K3	0.62075(16)	0.59985(16)	0.60773(12)	0.0287(4)

Comment

Compared to other polychalcogenidometallates, polyselenidoargentates have been relatively less explored. A few known polyselenidoargentates are $[Ag(Se_4)]_n^{n-}$,

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$[Ag(Se_4)]_4^{4-}$, $[Ag(Se_5)]_n^{n-}$, and $[Ag_4(Se_4)_3]^{2-}$ as stabilized with symmetric organic cations such as R_4N^+ (R = Me, Et, *n*-Pr) and Ph_4P^+ [1, 2]. Most of the previously known polyselenidoargentates were synthesized by the solution method. To explore new polyselenidoargentates we adopted a solventothermal synthetic method and asymmetric organic cations such as Et_3MeN^+. A ternary silver selenide, K_3AgSe_9 has been obtained and found to contain a new polyselenidoargentate, $[Ag(Se_4)(Se_5)]^{3-}$ as stabilized with K^+ cations. So far, structurally characterized ternary silver selenides are as follows: KAgSe [3], KAg_3Se_2 [4], $K_2Ag_4Se_3$ [5], $RbAg_5Se_3$ [6], $M_2Ag_{12}Se_7$ (M = K, Tl) [7, 8], $MAgSe_4$ (M = Rb, Cs) [9]. These ternary silver selenides consist of Se^{2-} monoselenides, except $MAgSe_4$ with $(Se_4)^{2-}$ tetraselenide ligands.

The $[Ag(Se_4)(Se_5)]^{3-}$ anion in the title compound K_3AgSe_9 was revealed to be of a 2D layered structure. All the other known polyselenidoargentates are either molecular or 1D chain. The 2D layered $[Ag(Se_4)(Se_5)]^{3-}$ complex features to be of a novel structure and possesses a dangling pentaselenide, $(Se_5)^{2-}$ ligand. Both bridging $(Se_4)^{2-}$ and dangling $(Se_5)^{2-}$ ligands connect Ag metal centers to form a 24-membered rings, which are finally linked into the polymeric $[Ag(Se_4)(Se_5)]_n^{3n-}$ layer. In the 24-membered ring, there are six Ag atoms, sixteen Se atoms from four bridging $(Se_4)^{2-}$ ligands, and two Se atoms from two dangling $(Se_5)^{2-}$ ligands. Rhombuses made of two Ag metal centers and two Se atoms from two different $(Se_5)^{2-}$ ligands, are also present in the $[Ag(Se_4)(Se_5)]_n^{3n-}$ layer. The $[Ag(Se_4)(Se_5)]_n^{3n-}$ layer is quite corrugated and three different K^+ cations fill the empty space inside and between the layers. Around each of the three potassium cations, seven Se atoms are present inside the range of 3.7 Å, and the closest Se atoms are Se1 (3.306(2) Å) for K1, Se4 (3.397(2) Å) for K2, and Se1 (3.312(2) Å) for K3, respectively.

The Ag1 atom in K_3AgSe_9 has distorted tetrahedral geometry, with one shorter bond to Se4 at 2.668(1) Å, and three marginally longer bonds to Se5, Se5′ and Se1 with the average bond distance of 2.71(3) Å. Bond angles ranging from 101.39(3) to 116.43(3)° also exemplify the distorted coordination around Ag1. There exists a weak interaction between d^{10} metal centers as indicated by the Ag1–Ag1 distance of 3.057(1) Å. Bonds between Se atoms show distances from 2.334(1) to 2.377(1) Å and an average distance of 2.35(1) Å. K_3AgSe_9 is a semiconducting material with the bandgap of about 1.55 eV, measured by the UV/Vis reflectance spectroscopy. TGA results show that K_3AgSe_9 is stable up to 180 °C but decomposes thereafter to lose K and Se and to become simple binary $AgSe_x$ compounds upon being heated to 900 °C under an argon atmosphere.

Acknowledgements: This work was supported by the Incheon National University Research Grant in 2015.

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