

Molten Salt Synthesis, Crystal Structure and Optical Properties of a Novel Quaternary Metal Selenide, $K_2AgIn_3Se_6$

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$K_2AgIn_3Se_6$ was synthesized by a molten-salt (alkali-metal polyselenide flux) reaction at 500 °C. The orange red granular crystal crystallizes in monoclinic space group $C2/c$ with cell parameters, $a=1.16411(7)$ nm, $b=1.16348(8)$ nm, $c=2.14179(12)$ nm, $V=2.8740(9)$ nm³, and $Z=8$. The crystal has a new two-dimensional structure containing $^{2-}_2[AgIn_3Se_6]^{2-}$ anionic layers separated by K^+ cations and the $^{2-}_2[AgIn_3Se_6]^{2-}$ layer is constructed with corner-shared $[AgSe_4]$ and $[InSe_4]$ tetrahedra. The optical band gap of $K_2AgIn_3Se_6$ was determined to be *ca.* 2.9 eV by UV/vis/NIR diffuse reflectance spectra.

Keywords potassium silver indium selenide, $K_2AgIn_3Se_6$, solid state synthesis, crystal structure

Introduction

Syntheses of the multi-component metal chalcogenides can be achieved at an intermediate temperature using the molten salt (alkali-metal polychalcogenide flux) method.¹ This method has been proven to be a successful technique for the syntheses of metal chalcogenides with interesting structures and unusual properties.²⁻⁵ Alkali metal-containing multi-component metal chalcogenides, in general, are Zintl compounds with both ionic and covalent bondings and semiconducting behaviors in character. In the past ten years, ternary alkali metal silver or indium chalcogenides, $A_xM_yQ_z$ (A =alkali metal, M =Ag or In, Q =S, Se or Te), were extensively investigated.⁶⁻⁸ However, no quaternary metal chalcogenides, $A_xAg_yIn_zQ_z$, have been reported. In this paper, synthesis, crystal structure and optical band gap of the first member in the $A_xAg_yIn_zQ_z$ family, potassium silver indium selenide, $K_2AgIn_3Se_6$ are described.

Experimental

Synthesis

All manipulations were carried out under nitrogen atmosphere.

The precursor, K_2Se_4 was prepared by a stoichiometric reaction of elemental potassium and selenium in liquid ammonia.⁹

A mixture of K_2Se_4 (79.4 mg, 0.2 mmol), Ag (21.63 mg, 0.2 mmol), In (23.51 mg, 0.2 mmol), and Se (126.67 mg, 1.6 mmol) in mole ratio 1 : 1 : 1 : 8 was

loaded into a Pyrex tube. The tube was sealed under vacuum (10^{-5} Pa), placed into a furnace, and heated at 500 °C for 5 d, and then cooled to 200 °C with a cooling rate of 2 °C/h. Subsequently, it was cooled naturally down to room temperature. The product was washed with dimethylformamide (DMF), anhydrous ethanol to move the excess K_2Se_4 , and then dried with anhydrous diethyl ether. The orange red granular crystals were isolated and appeared stable in air or water. A semi-quantitative elemental analysis for the crystal was performed with SEM/EDS to indicate a chemical formula approximate to $K_2AgIn_3Se_6$.

Determination of crystal structure

Single crystal X-ray diffraction data for $K_2AgIn_3Se_6$ were collected at room temperature [(295 ± 2) K] using a Rigaku R-Axis RAPID image plate diffractometer with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda=0.071073$ nm). The total 11930 reflections were measured, in which 3293 and 1849 reflections are unique ($R_{int}=0.0641$) and observed [$I \geq 2\sigma(I)$], respectively. The raw data were corrected for LP factors, empirical absorption. The structure was solved by direct method and refined anisotropically by full-matrix least squares on F^2 . The computations were performed using the SHELX-97 program package.¹⁰

Diffuse reflectance spectrum measurement

Optical diffuse reflectance for the powder sample was measured at room temperature with a Shimadzu UV-3100 double beam, double monochromator spec-

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trophotometer equipped with an integrating sphere 60 mm in diameter. The diffuse reflectance data were recorded in UV/vis/NIR regions. Barium sulphate powder was used as the reference (100% reflectance).

Results and discussion

Crystal structural description

The title compound crystallized in the monoclinic space group $C2/c$. Crystallographic data and processing parameters are listed in Table 1, atomic coordinates and equivalent isotropic temperature factors in Table 2, selected bond distances and angles in Table 3. The final R_1 and wR_2 values based on 1849 reflections observed are 0.0475 and 0.0975, respectively.

$K_2AgIn_3Se_6$ contains two-dimensional ${}^2_{\infty}[AgIn_3Se_6]^{2-}$ anionic layers separated by charge-compensated K^+ cations as shown in Figure 1. There are two crystallographically distinct Ag atoms, Ag(1) and Ag(2),

and three crystallographically distinct In atoms, In(1), In(2) and In(3) in the ${}^2_{\infty}[AgIn_3Se_6]^{2-}$ layer (Figure 2). All the Ag and In atoms are tetrahedrally coordinated by Se atoms, $[Ag^I Se_4]$ tetrahedra with Ag—Se distances ranging from 0.26905(19) to 0.26764(19) nm and $[In^{III} Se_4]$ tetrahedra with the mean In—Se distance of 0.25799 nm. $[Ag(1)Se_4]$, $[Ag(2)Se_4]$ and $[In(3)Se_4]$ tetrahedra are alternatively connected to form a square net extended in the (001) plane by sharing all Se atoms. While, $[In(1)Se_4]$ and $[In(2)Se_4]$ tetrahedra alternate to construct ${}^1_{\infty}[In_2Se_6]$ chains via two corner-shared Se atoms of each tetrahedron. The half chains lie in $[110]$ direction and link the square net by sharing other two corner Se atoms of each $[InSe_4]$. In the same way, the other half chains in $[1\bar{1}0]$ direction are linked to the square net on another side to build up the ${}^2_{\infty}[AgIn_3Se_6]^{2-}$ anionic layer as depicted in Figure 3. All the Se atoms in the anionic layer are coordinated by three metal centers in a trigonal pyramid geometry.

Table 1 Crystallographic data and processing parameters for $K_2AgIn_3Se_6$

Molecular formula	$K_2AgIn_3Se_6$
Molecular weight	1004.29
Color and habit	Orange red, granular
Crystal size	0.20 mm × 0.15 mm × 0.10 mm
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell parameters	$a=1.16411(7)$ nm, $b=1.16348(8)$ nm, $c=2.14179(12)$ nm, $\beta=97.832(3)^\circ$, $V=2.8738(3)$ nm ³
Z	8
$F(000)$	3488
Density (calcd)	4.642 g/cm ³
Diffractometer	Rigaku R-AXIS RAPID IP
Radiation	Graphite-monochromatized Mo $K\alpha$, $\lambda=0.071073$ nm
Temperature	295(2) K
Scan type	Scillation
Data collection rang	$0 \leq h \leq 15$, $0 \leq k \leq 15$, $-27 \leq l \leq 27$
θ_{max}	27.5°
Reflections measured	Total: 11930, Unique ($R_{int}=0.0641$): 3293, Observed [$I \geq 2\sigma(I)$]: 1849
Absorption coefficient	21.827 mm ⁻¹
T_{min} and T_{max}	0.7540, 1.3559
Refinement method	Full-matrix least-squares on F^2
No. of variables, p	111
R_1^a	0.0475 (for observed data), 0.0944 (for all data)
wR_2	0.0975 (for observed data), 0.1358 (for all data)
Goof (S)	1.054
Largest and mean Δ/σ	0.000, 0.000
Residual extrema in final difference map	-1.669 to +5.578 (e/nm ³ × 10 ⁻³)

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad wR_2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{\sum w(F_o^2)^2}}, \quad \text{Goof}(S) = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)]^2}{n - P}}, \quad w = \frac{1}{\sigma^2(F_o^2) + (0.0420P)^2}, \quad \text{where}$$

$$P = (F_o^2 - 2F_c^2)^2 / 3.$$

Table 2 Atomic coordinates and equivalent isotropic temperature factors ($\text{nm}^2 \times 10^3$) for $\text{K}_2\text{AgIn}_3\text{Se}_6$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
In(1)	0.25316(8)	0.18677(10)	0.25003(5)	0.0122(2)
In(2)	0.46541(8)	0.18566(10)	0.11168(5)	0.0149(3)
In(3)	0.21415(8)	-0.06278(10)	0.11231(5)	0.0141(3)
Ag(1)	0.0000	-0.06510(17)	0.2500	0.0272(4)
Ag(2)	0.0000	0.43799(17)	0.2500	0.0265(4)
Se(1)	0.10088(11)	0.07474(14)	0.17464(7)	0.0147(3)
Se(2)	0.14005(11)	0.29924(13)	0.32555(7)	0.0149(3)
Se(3)	0.34489(11)	0.31742(14)	0.17407(7)	0.0166(3)
Se(4)	0.38231(11)	0.05445(13)	0.32579(7)	0.0154(3)
Se(5)	0.55211(14)	0.33083(16)	0.03969(8)	0.0287(4)
Se(6)	0.34038(14)	0.04172(16)	0.03953(8)	0.0285(4)
K(1)	0.0725(3)	0.6797(4)	0.58246(18)	0.0327(9)
K(2)	0.3428(3)	0.4471(4)	0.58226(18)	0.0324(9)

^a U_{eq} defined as one third of the trace of the orthogonalized *U* tensor.

Table 3 Bond lengths (nm) and bond angles ($^\circ$) for $\text{K}_2\text{AgIn}_3\text{Se}_6$

In(1)—Se(3)	0.25635(18)	In(3)—Se(6)	0.25869(18)
In(1)—Se(4)	0.25688(18)	In(3)—Se(5) ^c	0.25905(19)
In(1)—Se(2)	0.25772(17)	Ag(1)—Se(3) ^f	0.26406(19)
In(1)—Se(1)	0.25824(18)	Ag(1)—Se(3) ^b	0.26406(19)
In(2)—Se(3)	0.25720(18)	Ag(1)—Se(1)	0.26735(19)
In(2)—Se(4) ^a	0.25729(18)	Ag(1)—Se(1) ^d	0.26735(19)
In(2)—Se(5)	0.25832(18)	Ag(2)—Se(4) ^e	0.26371(18)
In(2)—Se(6)	0.25880(19)	Ag(2)—Se(4) ^f	0.26371(18)
In(3)—Se(1)	0.25614(18)	Ag(2)—Se(2) ^d	0.26764(19)
In(3)—Se(2) ^b	0.25716(18)	Ag(2)—Se(2)	0.26764(19)
Se(1)—K(1)	0.3463(4)	Se(1)—K(2)	0.3374(4)
Se(2)—K(1)	0.3375(4)	Se(2)—K(2)	0.3471(4)
Se(3)—K(1)	0.3495(4)	Se(3)—K(2)	0.3370(4)
Se(4)—K(1)	0.3358(4)	Se(4)—K(2)	0.3486(4)
Se(5)—K(1)	0.3317(4)	Se(5)—K(2)	0.3320(4)
Se(6)—K(1)	0.3340(4)	Se(6)—K(2)	0.3324(4)
Se(3)-In(1)-Se(4)	119.85(5)	Se(3) ^b -Ag(1)-Se(1) ^d	105.25(4)
Se(3)-In(1)-Se(2)	112.94(7)	Se(1)-Ag(1)-Se(1) ^d	105.03(10)
Se(4)-In(1)-Se(2)	102.30(6)	Se(4) ^e -Ag(2)-Se(4) ^f	118.16(10)
Se(3)-In(1)-Se(1)	102.26(6)	Se(4) ^e -Ag(2)-Se(2) ^d	105.22(4)
Se(4)-In(1)-Se(1)	112.66(7)	Se(4) ^f -Ag(2)-Se(2) ^d	110.93(4)
Se(2)-In(1)-Se(1)	106.43(5)	Se(4) ^e -Ag(2)-Se(2)	110.93(4)
Se(3)-In(2)-Se(4) ^a	117.98(6)	Se(4) ^f -Ag(2)-Se(2)	105.22(4)
Se(3)-In(2)-Se(5)	101.86(7)	Se(2) ^d -Ag(2)-Se(2)	105.81(9)
Se(4) ^a -In(2)-Se(5)	113.65(6)	In(3)-Se(1)-In(1)	106.43(6)
Se(3)-In(2)-Se(6)	113.19(6)	In(3)-Se(1)-Ag(1)	103.54(7)
Se(4) ^a -In(2)-Se(6)	102.61(7)	In(1)-Se(1)-Ag(1)	104.49(6)
Se(5)-In(2)-Se(6)	107.48(6)	In(3) ^e -Se(2)-In(1)	106.51(5)
Se(1)-In(3)-Se(2) ^b	118.07(6)	In(3) ^e -Se(2)-Ag(2)	103.95(7)

Continued

Se(1)-In(3)-Se(6)	113.30(7)	In(1)-Se(2)-Ag(2)	104.36(6)
Se(2) ^b -In(3)-Se(6)	102.49(6)	In(1)-Se(3)-In(2)	106.27(7)
Se(1)-In(3)-Se(5) ^c	103.12(6)	In(1)-Se(3)-Ag(1) ^g	103.01(6)
Se(2) ^b -In(3)-Se(5) ^c	112.81(7)	In(2)-Se(3)-Ag(1) ^g	104.65(5)
Se(6)-In(3)-Se(5) ^c	106.84(6)	In(1)-Se(4)-In(2) ^d	106.00(6)
Se(3) ^c -Ag(1)-Se(3) ^b	117.65(10)	In(1)-Se(4)-Ag(2) ^h	103.16(6)
Se(3) ^c -Ag(1)-Se(1)	105.25(4)	In(2) ^a -Se(4)-Ag(2) ^h	104.27(5)
Se(3) ^b -Ag(1)-Se(1)	111.53(4)	In(2)-Se(5)-In(3) ^g	105.41(6)
Se(3) ^c -Ag(1)-Se(1) ^d	111.53(4)	In(3)-Se(6)-In(2)	105.29(7)

Symmetry transformation codes: *a* (1 - *x*, *y*, 0.5 - *z*); *b* (0.5 - *x*, -0.5 + *y*, 0.5 - *z*); *c* (-0.5 + *x*, -0.5 + *y*, *z*); *d* (-*x*, *y*, 0.5 - *z*); *e* (0.5 - *x*, 0.5 + *y*, 0.5 - *z*); *f* (-0.5 + *x*, 0.5 + *y*, *z*); *g* (0.5 + *x*, 0.5 + *y*, *z*); *h* (0.5 + *x*, -0.5 + *y*, *z*).

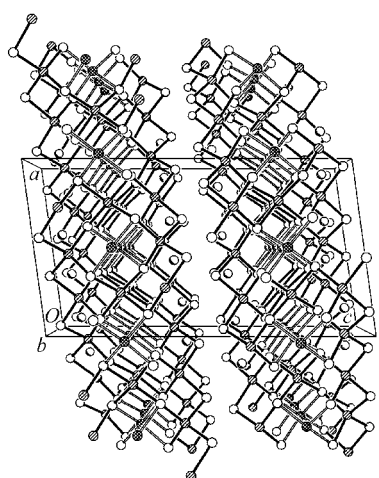


Figure 1 A packing view along the *b*-axis with double shaded circles for Ag, single shaded circles for In and open circles for Se atoms. The unit cell is outlined.

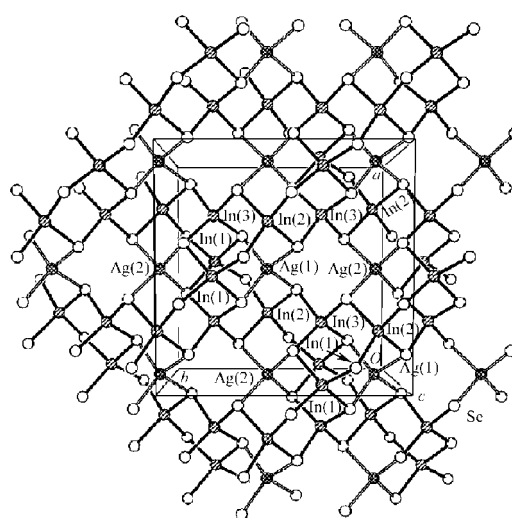


Figure 3 Structure of the ${}^2_{\infty}[\text{AgIn}_3\text{Se}_6]^{2-}$ layer.

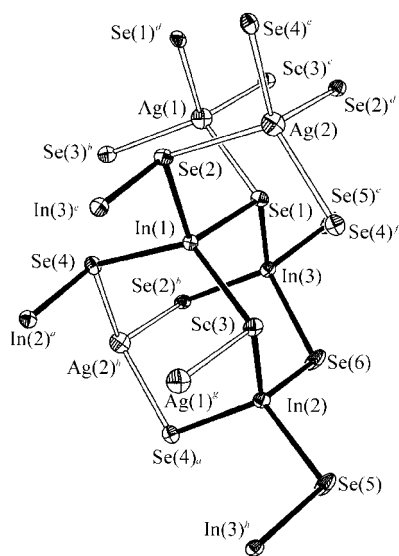


Figure 2 ORTEP drawing for dimer of $[\text{AgIn}_3\text{Se}_6]^{2-}$ with 50% probability ellipsoids, showing the atomic numbering scheme.

The ${}^2_{\infty}[\text{AgIn}_3\text{Se}_6]^{2-}$ anionic layers parallel to the (001) plane are packed along the *c*-axis direction to set

up the 3-D crystal structure by electrostatic interaction between ${}^2_{\infty}[\text{AgIn}_3\text{Se}_6]^{2-}$ anion and K cation (Figure 1). There are two crystallographically distinct K atoms, K(1) and K(2) in the crystal. Both of K(1) and K(2) atoms are coordinated by seven Se atoms in a coordination polyhedron shaped like one-capped triangular prism with K—Se distances ranging from 0.3317(4) to 0.3495(4) nm as shown in Figure 4 (a) and (b), respectively.

Optical band gap

The measurement of diffuse reflectivity can be used to obtain the value of band gap which agrees rather well with the value obtained by absorption measurement from single crystal of the same compound.¹¹ Absorption data were calculated from the reflectance data using the Kubelka-Munk function, $\alpha/S = (1 - R_{\infty})^2 / 2R_{\infty}$, where R_{∞} is the reflectance of an infinitely thick layer at a given wavelength, α the absorption coefficient and S the scattering coefficient.¹² The band gap (E_g) was determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a Kubelka-Munk function (α/S) vs energy E plot.¹³ The (α/S) vs. E plot of $\text{K}_2\text{AgIn}_3\text{Se}_6$, as shown in Figure 5, exhibits steep absorption edge from which the

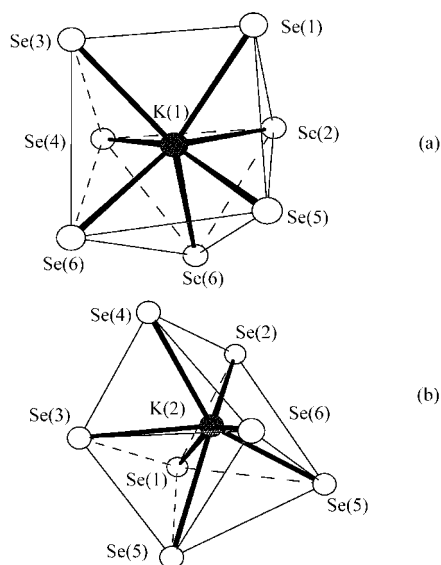


Figure 4 Coordination polyhedra (a) around K(1) and (b) around K(2).

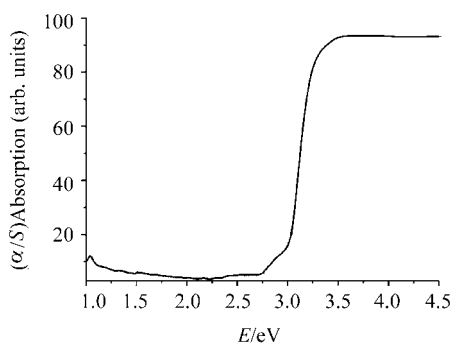


Figure 5 α/S vs. E plot of $K_2AgIn_3Se_6$.

band gap can be assessed at 2.9 eV. The reflectance spectrum measurement revealed the presence of optical band gap and the nature of semiconductor with a large energy gap for the novel compound, $K_2AgIn_3Se_6$.

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