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Synthesis and Structure Determination of $AgScP_2Se_6$, $AgErP_2Se_6$ and $AgTmP_2Se_6$

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Dedicated to Professor Reinhard Nesper on the Occasion of His 60th Birthday

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Abstract. $AgScP_2Se_6$, $AgErP_2Se_6$ and $AgTmP_2Se_6$ were obtained by high temperature reaction of stoichiometric amounts of the elements in evacuated silica ampoules. They crystallize in the space group $P\bar{3}1c$, $Z = 2$ with the lattice constants $a = 6.463(1)$ Å, $c = 13.349(1)$ Å ($AgScP_2Se_6$), $a = 6.578(1)$ Å, $c = 13.410(2)$ Å ($AgErP_2Se_6$), and $a = 6.567(1)$ Å, $c = 13.422(1)$ Å ($AgTmP_2Se_6$). The crystal structures of $AgScP_2Se_6$ and $AgErP_2Se_6$ were refined from merohedrally twinned crystals. No twinning was observed for $AgTmP_2Se_6$. The crystal structures are isotypic and can be described as a variant of the CdI_2 structure type. Thus, selenium atoms are hexagonally close packed. The octahedral voids of every second layer are occupied by Ag, M^{3+} (M = Sc, Er, Tm), and P_2 dumbbells in an ordered fashion. The crystal structures are isotypic to $AgScP_2S_6$ and $AgInP_2S_6$.

Introduction

Hexachalcogenohypodiphoshates have attracted some attention in the past because of their interesting physical and chemical properties. $Ni_2P_2S_6$ for example has been investigated for its potential use in high-energy lithium batteries [1–4], and $Sn_2P_2S_6$ for its strong non-linear-optical (NLO) effects [5]. Hexachalcogenohypodiphoshates form a vast family of compounds, which can roughly be divided into two major groups. The first group exhibits layered structures and the second group crystallizes in network structures. Each group can be further subdivided into subgroups based on the structure type, the elemental composition or the oxidation state of the metal ions. The most investigated subgroups are the $M_2P_2Q_6$ compounds (Q = S, Se), where M denotes a divalent metal cation as iron, nickel, cadmium, zinc, manganese, tin, lead, barium or strontium, and the group $M^{I}M^{III}P_2Q_6$, where M^{I} is a monovalent cation as sodium, potassium, silver or copper, and M^{III} is a trivalent cation as chromium, vanadium, aluminum or indium. $M_2P_2Q_6$ compounds containing transition metals crystallize with layer structures. On the other hand, divalent main-group metal containing hexachalcogenohypodiphosphates tend to form network structures. The transition metal layered structures were investigated for their capability to intercalate various guest species into the van der Waals-gaps [6–9]. Among the network structures $Sn_2P_2S_6$ is the most intriguing example; the investigations focus on its strong (NLO) properties [10–12]. In the $M^{I}M^{III}P_2Q_6$ family, the alkali metal compounds usually form network structures, e.g. $NaV_{0.84}P_2S_6$ or $KSbP_2Se_6$ [13, 14]. When M^{I} is a monovalent transition metal (Cu^{1+}, Ag^{1+}), layered structures are often observed, e.g. for $AgScP_2S_6$ [15], $AgInP_2S_6$ [16], $CuCrP_2Se_6$ and $CuInP_2Se_6$ [17]. Only a general trend is observable for structure prediction, the larger the cations, the more pronounced is the tendency to form network structures. Obviously, this is not satisfactory and more systematic structural studies need to be made and more dedicated factors for structure type formation have to be found.

Results and Discussion

$AgScP_2Se_6$, $AgErP_2Se_6$, and $AgTmP_2Se_6$ are isotypic to $AgScP_2S_6$ [15]. The crystal structures can be derived from the CdI_2 structure type. Herein, their structures will be discussed by using $AgScP_2Se_6$ as a representative. The description holds for the erbium and the thulium compound just by replacing scandium by the respective rare earth metals.

Selenium atoms form a close packed hexagonal arrangement, in which the octahedral voids of every second layer are occupied in an ordered way by silver, scandium and P_2 dumbbells. The MSe$_6$-octahedra and P_2Se_6-octahedra within a layer are connected through common edges and form a triangular lattice with an AB-type layer stacking, see Figure 1.

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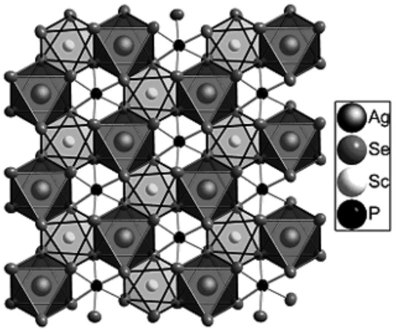

Figure 1. View on (001) of the crystal structure of $AgScP_2Se_6$. The cations in the octahedral voids of the selenium layers are trigonally ordered. Ellipsoids enclose 99 % probability.

In all compounds, the $[P_2Se_6]^{4-}$ ion has staggered conformation, which is typically observed in hexachalcogenohypodiphosphates. The torsion angles (Se−P−P−Se), selected bond angles and bond lengths *d*(P−P) and *d*(P−Se) are listed in Table 1.

Table 1. Bond lengths /Å and angles /° in the $[P_2Se_6]^{4-}$ units.

Compound	(Se−P−P−Se)	(P−P−Se)	(Se−P−Se)	*d*(P−P)	*d*(P−Se)
$AgScP_2Se_6$	172.21(6) 52.20(8) −67.81(8)	107.20(2)	111.64(2)	2.205(3)	2.192(1)
$AgErP_2Se_6$	176.87(4) 56.87(6) −63.14(5)	107.77(1)	111.11(1)	2.230(2)	2.188(1)
$AgTmP_2Se_6$	176.5(1) 56.5(1) −63.5(1)	108.00(3)	110.90(3)	2.215(6)	2.192(2)

The P−PSe_3-tetrahedra have bond angles close to the ideal tetrahedron angle with values ranging from 110.90° to 111.64° for the angles (Se−P−Se) and 107.20° to 108.00° for the angles (P−P−Se). The bond lengths *d*(P−P) are close to the usual value of 2.21 Å for P−P single bonds. The distances *d*(P−Se) are equal within the threefold standard deviations and vary between 2.188 Å in $AgErP_2Se_6$, and 2.192 Å in $AgTmP_2Se_6$ and $AgScP_2Se_6$, respectively.

The silver atoms are hexacoordinate in slightly distorted octahedra with bond lenghts *d*(Ag−Se) of 2.899 Å and 2.909 Å. The angles (Se−Ag−Se) deviate only slightly from 90°. The large displacement ellipsoids for the silver atoms are commonly observed in $AgMP_2S_6$ compounds and generally for d^{10}-ions (e.g. silver, copper, gold, zinc, cadmium, mercury). They are due to a second order Jahn−Teller-effect [18, 19].

The M^{III} atoms are also hexacoordinate. However, the octahedra $M^{III}Se_6$ show slightly larger distortions than the octahedra $AgSe_6$. The corresponding bond lengths are *d*(Sc−Se) = 2.709 Å, *d*(Tm−Se) = 2.825 Å, and *d*(Er−Se) = 2.834 Å, see Table 2. These distances compare well to those observed in binary selenides of scandium, erbium, and thulium.

Table 2. Selected bond lengths /Å and angles /° for $AgSe_6$ and $M^{III}Se_6$ octahedra.

Compound	(Se−Ag−Se)	(Se−M^{III}−Se)	*d*(Ag−Se)	*d*(M^{III}−Se)
$AgScP_2Se_6$	87.30(2) 92.31(2) 93.09(2) 179.43(2)	87.30(2) 92.31(2) 93.09(2) 179.43(2))	2.899(1)	2.709(1)
$AgErP_2Se_6$	86.36(1) 91.84(1) 95.49(1) 177.35(1)	84.61(1) 92.11(1) 98.90(1) 174.97(1)	2.909(1)	2.834(1)
$AgTmP_2Se_6$	86.30(2) 93.10(2) 95.34(2) 177.64(2)	84.35(2) 92.40(3) 99.12(3) 175.01(2)	2.909(1)	2.825(1)

The height of the van der Waals gap is about 3.15 Å, whereas the height of the selenium double layers, which are occupied by the cations, is about 3.55 Å. The cations in the *a*−*b*-layers are ordered by occupying edge-sharing octahedra, which form a triangular honeycomb lattice. Thus distances between equal cations are optimized. The crystal structure of $AgScP_2Se_6$ is displayed in Figure 1 and Figure 2.

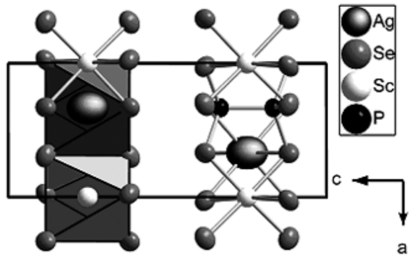

Figure 2. View on the *a*−*c* plane of $AgScP_2Se_6$. The van der Waals-gap has a height of about 3.15 Å. Coordination octahedra are drawn for one silver and one scandium atom. Ellipsoids represent 99 % probability.

Conclusions

$AgScP_2Se_6$, $AgErP_2Se_6$, and $AgTmP_2Se_6$ are three new hexaselenohypodiphosphates with a layered structure of the $AgInP_2S_6$ structure type. $AgScP_2Se_6$ has an optical bandgap of 1.55 eV. Preliminary impedance spectroscopic investigations show no silver ion conductivity.

Experimental Section

Synthesis

$AgScP_2Se_6$ was prepared by annealing stoichiometric amounts of the pure elements in evacuated silica ampoules at 650 °C for 17 days. The phase pure product was obtained as a brown powder and very small hexagonal shaped orange platelets. X-ray powder diffraction data of the bulk material confirmed its purity.

$AgErP_2Se_6$ was obtained by annealing stoichiometric amounts of the pure elements in evacuated silica ampoules at 600 °C for 4 days.

Table 3. Crystallographic data and structure refinement summary for $AgScP_2Se_6$, $AgErP_2Se_6$, and $AgTmP_2Se_6$. Lattice constants were taken from powder data refinements [24].

Empirical formula	$AgScP_2Se_6$	$AgErP_2Se_6$	$AgTmP_2Se_6$
Formula weight /g/mol	688.54	810.83	812.50
Temperature /K		298(2)	
Wavelength /Å		0.71073 (Mo K_α)	
Crystal system, space group	trigonal, $P\bar{3}1c$	trigonal, $P\bar{3}1c$	trigonal, $P\bar{3}1c$
a /Å	6.463(1)	6.578(1)	6.567(1)
c /Å	13.349(1)	13.410(2)	13.422(2)
Volume /Å^3	482.93(3)	502.6(1)	501.27(9)
Z	2	2	2
Calculated density /g/cm^3	4.735	5.358	5.383
μ /mm^{-1}	25.594	32.210	32.773
Crystal color and shape	orange-brown platelet	dark-brown platelet	dark-brown platelet
Crystal size /mm	0.04 × 0.05 × 0.015	0.12 × 0.12 × 0.03	0.11 × 0.10 × 0.07
Diffractometer Type	STOE IPDS I	STOE IPDS I	STOE IPDS I
Index ranges	$-8 \leq h \leq 8$ $-8 \leq k \leq 8$ $-17 \leq l \leq 17$	$-8 \leq h \leq 8$ $-8 \leq k \leq 8$ $-16 \leq l \leq 16$	$-8 \leq h \leq 7$ $-8 \leq k \leq 8$ $-17 \leq l \leq 17$
Min. Θ /°	3.05	3.04	3.04
Max. Θ /°	27.88	26.69	27.85
Reflections (collected / unique)	5119 / 394	6968 / 362	4480 / 407
R_{int}, R_σ	0.0841, 0.0335	0.0432, 0.0142	0.1242, 0.0538
Data / restraints / parameters	394 / 0 / 19	362 / 0 / 19	407 / 0 / 17
GooF	1.152	1.167	1.025
R_1, wR_2 (all reflections)	0.0453, 0.0764	0.0196, 0.0356	0.0580, 0.0785
Extinction coefficient	0.0087(11)	0.0019(3)	–
Twin matrix	$\bar{1}00, 0\bar{1}0, 001$	$\bar{1}00, 0\bar{1}0, 001$	–
Twin fractions	0.967(2):0.033(2)	0.742(2):0.258(2)	–

The product was a mixture of a dark brown powder and small dark-brown platelets. Phase pure $AgErP_2Se_6$ was not obtained. Powder diffraction data showed small amounts of Er_2Se_3 as a by-product.

$AgTmP_2Se_6$ results from annealing stoichiometric amounts of the pure elements in evacuated silica ampoules at 550 °C for 5 days. The product was a dark-brown powder and dark-brown small platelets. Tm_2Se_3 and $Ag_4P_2Se_6$ always were found as by-products.

Powder Diffraction

X-ray powder diffraction data were recorded with a STOE STADI P diffractometer with a Ge(111) monochromator providing Cu-$K_{\alpha1}$ radiation. Lattice constants were refined from the powder patterns and then used for the single crystal structure refinements in the last cycles, see Table 3.

Single-Crystal X-ray Diffraction

Single crystals suitable for crystal structure determination were mounted on glass fibers and checked for their quality by Weissenberg photographs. X-ray diffraction intensities were collected on a STOE IPDS at 293(2) K using Mo-K_α radiation. The measurements were performed in an incremental scanning mode. Data were corrected for Lorentz and polarization effects. Absorption was numerically corrected after an optimization of the crystal shape with the X-SHAPE [20] routine. Further details of the measurements and basic crystallographic information are collected in Table 3. The program package WinGX [21], using SHELXS-97 and SHELXL-97 [22, 23] was used for solving and refining the crystal structures. The refined atom positions and equivalent isotropic displacements parameters are printed in Table 4.

Table 4. Refined atomic parameters and equivalent isotropic displacement parameters U_{eq} of the title compounds.

Compound	Atom	Wyckoff position	x	y	z	U_{eq} /Å^2
$AgScP_2Se_6$	Ag1	2d	$^2/_3$	$^1/_3$	$^1/_4$	0.0515(5)
	Sc1	2a	0	0	$^1/_4$	0.0167(3)
	Se1	12i	0.0229(1)	0.33077(8)	0.11885(5)	0.0154(5)
	P1	4f	$^1/_3$	$^2/_3$	0.1674(2)	0.0130(5)
$AgErP_2Se_6$	Ag1	2d	$^2/_3$	$^1/_3$	$^1/_4$	0.0643(4)
	Er1	2a	0	0	$^1/_4$	0.0184(1)
	Se1	12i	0.02183(6)	0.34516(6)	0.11705(3)	0.0209(1)
	P1	4f	$^1/_3$	$^2/_3$	0.1669(1)	0.0148(3)
$AgTmP_2Se_6$	Ag1	2d	$^2/_3$	$^1/_3$	$^1/_4$	0.0688(8)
	Tm1	2a	0	0	$^1/_4$	0.0244(3)
	Se1	12i	0.0216(2)	0.3439(1)	0.11704(7)	0.0270(3)
	P1	4f	$^1/_3$	$^2/_3$	0.1675(3)	0.0206(8)

For the structure solution and refinement of $AgScP_2Se_6$ and $AgErP_2Se_6$ merohedral twinning according to a twinning matrix $\bar{1}00$, $0\bar{1}0$, 001 had to be taken into account. Thus, the *R*-values dropped from $wR_2 = 0.109$ to $wR_2 = 0.076$ ($AgScP_2Se_6$) for a twin ratio of 0.967:0.033. For $AgErP_2Se_6$ the initial *R*-value $wR_2 = 0.614$ dropped significantly to $wR_2 = 0.036$ with a refined twin ratio of 0.742:0.258. No twinning was observed for $AgTmP_2Se_6$.

UV/Vis Spectroscopy

UV/Vis data of $AgScP_2Se_6$ were collected with a Bruins instruments Omega 20 two-wave photometer in remission mode. The obtained data were transformed into absorption spectra by using the Kubelka-Munk function. The value for the band-gap was extrapolated by linear regression of the absorption edge kink. The extrapolated band-gap is 1.55 eV.

Thermal Analysis

DTA measurements were performed in sealed thin walled silica ampoules with a SETARAM TG-DTA 92−16.18. The measurements showed peritectic decomposition for the discussed compounds. Decomposition temperatures are 654 °C ($AgErP_2Se_6$), 657 °C ($AgTmP_2Se_6$), and 711 °C ($AgScP_2Se_6$), respectively. After the initial heating, a second peak is observed in all samples at 569−572 °C that is attributed to $Ag_4P_2Se_6$, which could be detected in the powder diffraction patterns.

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[24] Further details of the crystal structure investigation are available from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666, E-Mail: crysdata@fiz-karlsruhe.de referring to number CSD-420302 ($AgScP_2Se_6$), CSD-420303 ($AgErP_2Se_6$), CSD-420304 ($AgTmP_2Se_6$), name of the authors and citation of the paper.

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