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$K_2MM'_3Se_6$ (M = Cu, Ag; M′ = Ga, In), A New Series of Metal Chalcogenides with Chain–Sublayer–Chain Slabs: $_{\infty}{}^{1}[M'Se_4]$–$_{\infty}{}^{2}[(MSe_4)(M'Se_4)]$–$_{\infty}{}^{1}[M'Se_4]$

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A new series of novel isostructural metal chalcogenides, $K_2CuIn_3Se_6$ (**1**), $K_2CuGa_3Se_6$ (**2**), and $K_2AgIn_3Se_6$ (**3**), were obtained by a reactive flux technique and structurally characterized. Compounds **1**, **2**, and **3** crystallize in the space group *C*2/*c* of the monoclinic system with eight formula units in a cell: *a* = 11.445(2) Å, *b* = 11.495(2) Å, *c* = 21.263(4) Å, β = 97.68(3)°, *V* = 2772(1) $Å^3$, R1/wR2 = 0.0676/0.1652 for **1**; *a* = 11.031(2) Å, *b* = 11.050(4) Å, *c* = 20.808(7) Å, β = 97.71(2)°, *V* = 2513(1) $Å^3$, R1/wR2 = 0.0301/0.0511 for **2**; and *a* = 11.633(1) Å, *b* = 11.587(1) Å, *c* = 21.355(1) Å, β = 98.010(8)°, *V* = 2850.4(4) $Å^3$, R1/wR2 = 0.0471/0.0732 for **3**. These isostructural compounds are characterized by a chain–sublayer–chain slab structure. The sublayer, composed of alternative corner-sharing mixed-metal tetrahedra, is sandwiched by parallel corner-sharing tetrahedral chains. Optical absorption spectra of compounds **1**, **2**, and **3** reveal the presence of a sharp optical gap of 1.68, 1.72, and 1.64 eV, respectively, suggesting that these materials are semiconductors and suitable for efficient absorption of solar radiation in solar cell applications. IR spectra show no obvious absorption in the range 800–4000 cm^{-1}.

Introduction

The transition and main group metal chalcogenides show rich structural chemistry and useful physical and chemical properties for potential applications in nonlinear optics,[1] optical storage,[2] solar energy conversion,[3] thermal electrics,[4] and so forth. In contrast to binary and ternary metal chalcogenides, quaternary metal chalcogenides are less extensively investigated. A number of quaternary metal chalcogenides, formulated as $A_xM_yM'_zQ_t$ (A = alkali metals; M,M′ = metals; Q = chalcogen), have been reported recently for group 14[5] and 15[6] elements, but to our knowledge, the existing examples for group 13 elements are limited, amounting to only $KCd_4Ga_5S_{12}$, $KGaSnS_4$, $KInGeS_4$, $NaNdGa_4S_8$,

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$CsFe_{0.25}Ga_{0.75}S_2$, $NaLaGa_3S_{14}$, $CsHg_4Ga_5Se_{12}$, and $NaAgGa_6Te_{10}$.[7] Recently, we have been interested in the use of alkali metal polychalcogenides as mineralizers or reactive fluxes to prepare transition metal polychalcogenides.[8] In this paper, we report a new series of quaternary chalcogenides containing group 13 elements, $K_2CuIn_3Se_6$ (**1**), $K_2CuGa_3Se_6$ (**2**), and $K_2AgIn_3Se_6$ (**3**) from the K_2Se_4 flux.

Experimental Section

All operations were carried out under a nitrogen atmosphere. All chemicals were commercially available and used as received. K_2Se_4 was prepared by dissolving the stoichiometric amount of elements in liquid ammonia. Semiquantitive microscope analyses were performed on an EPM-810Q electron probe microscope. The ZAF matrix correction procedure was used to calculate elemental concentrations. IR spectra were recorded using KBr pellets with a Nicolet Magana 750 FT-IR infrared spectrometer (4000−400 cm^{-1}). TGA measurement was performed on a DT-40 thermal analysis system under nitrogen protection. An empty Pt crucible was used as reference.

Synthesis. $K_2CuIn_3Se_6$ (**1**) was prepared by the reaction of K_2Se_4 (0.394 g, 1 mmol), In grains (0.115 g, 1 mmol), Cu powder (0.064 g, 1 mmol), and Se powder (0.395 g, 5 mmol) in a Pyrex ampule. The ampule was flame-sealed under vacuum, heated in a furnace at 500 °C for 4 days, and then cooled to 150 °C at 4 °C h^{-1}. The excess K_xSe_y flux was removed with DMF. Dark red plate crystals were isolated with an estimated yield of ca. 20%. The semiquantitative elemental analysis of compound **1** by SEM/EDS indicates a composition of $K_{1.2}Cu_{1.0}In_{3.2}Se_{5.8}$. The TGA curve of compound **1** shows no weight changes until 300 °C.

Compounds **2** and **3** were prepared using the same procedure with the replacement of In with Ga and Cu with Ag, respectively.

UV−Vis Spectroscopy. Optical diffuse reflectance spectra were measured at room temperature with a Lambda 35 UV−vis spectrophotometer. The instrument was equipped with an integrating sphere and controlled by a personal computer. The samples were ground into fine powder and pressed onto a thin glass slide holder. The $BaSO_4$ plate was used as reference. The absorption spectra were calculated from reflection spectra by the Kubelka−Munk function: $\alpha/S = (1 - R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm, and R is the reflectance.

X-ray Crystallography. Single crystals of compounds **1**, **2**, and **3** were mounted, respectively, at the apex of a glass fiber for X-ray diffraction data collection. Data sets of compounds **1**, **2**, and **3** were collected on Enraf-Nonius CAD4, Rigaku AFC5R and Rigaku Raxiscs3 diffractometers, respectively. Graphite-monochromated Mo Kα radiation was used, and all data sets were collected at room temperature. Empirical absorption corrections based on a series of ψ scans were applied for compounds **1** and **2**. The structures were solved by the direct methods using the Siemens *SHELXTL* version 5 package of crystallographic software.[9] The difference Fourier maps based on these atomic positions yield all other non-hydrogen atoms. The structure was refined using a full-matrix least-squares refinement on F^2. All atoms were refined anisotropically. The distribution of Cu and In atoms in compound **1** is well-ordered on the basis of clearly distinguishable bond distances of Cu−Se and In−Se. This structural model is used to establish the structures of its analogues **2** and **3**, although there is no substantial difference between the bond distances of Cu−Se and Ga−Se for **2**, and Ag−Se and In−Se for **3**, respectively. The crystallographic data and detailed information of structure solution and refinement for compounds **1**, **2**, and **3** are listed in Table 1. The selected bond lengths and angles are given in Table 2.

Table 1. Crystal Data for Compounds **1**, **2**, and **3**

	1	**2**	**3**
chemical formula	$K_2CuIn_3Se_6$	$K_2CuGa_3Se_6$	$K_2AgIn_3Se_6$
fw	959.96	824.66	1004.29
space group	$C2/c$	$C2/c$	$C2/c$
a (Å)	11.445(2)	11.031(2)	11.633(1)
b (Å)	11.495(2)	11.050(4)	11.587(1)
c (Å)	21.263(4)	20.808(7)	21.355(1)
β (deg)	97.68(3)	97.71(2)	98.01(1)
V (Å^3)	2772(1)	2513(1)	2850.4(4)
Z	8	8	8
diffractometer	Enraf-Nonius CAD4	Rigaku AFC5R	Rigaku Raxiscs3
λ (Mo kα, Å)	0.71073	0.71073	0.71073
D_{calcd} (g/cm^3)	4.600	4.359	4.681
μ (cm^{-1})	227.5	260.2	220.1
obsd reflns	2724	1382	2461
indep reflns	3994	2297	3255
R1[a]	0.0676	0.0301	0.0471
wR2[b]	0.1652	0.0511	0.0732

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Results and Discussion

Compounds **1**, **2**, and **3** are isostructural, and only compound **1** is discussed in detail here. The structural novelty of $K_2CuIn_3Se_6$ derives from the fact that its anionic superlayers (or slabs) consist of a sublayer sandwiched by parallel corner-sharing tetrahedral chains, as shown in Figure 1a. The sublayer is composed of tetrahedral [$CuSe_4$] and [$InSe_4$] units that are linked to each other alternately by sharing all four corners extended along the a and b directions (Figure 1b). The parallel corner-sharing [$InSe_4$] tetrahedral chains running above the sublayer are perpendicular to those below the sublayer. The metal tetrahedra in compound **1** are slightly distorted from the ideal ones with the average bond distances of Cu−Se and In−Se being 2.466 and 2.572 Å, respectively, which are comparable with those found in $KInSe_2$ [10] and $CuInSe_2$.[11] The K^+ cations are located in the grooves formed by the parallel corner-sharing [$InSe_4$] tetrahedral chains and the sublayer. The crystal structure of the compound can be considered as a stack of alternate anionic superlayers and K^+ cationic layers. Thus, the K···Se interactions between the adjacent layers are important for stabilizing the structure,

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Table 2. Selected Bond Lengths and Angles for Compounds **1**, **2**, and **3**[a]

Compound **1**					
In(1)−Se(2)^{i}	2.5700(8)	In(2)−Se(1)^{iv}	2.5859(8)	In(4)−Se(5)	2.5695(9)
In(1)−Se(2)^{ii}	2.5700(8)	In(3)−Se(3)^{v}	2.5627(9)	In(4)−Se(6)	2.5727(8)
In(1)−Se(6)^{iii}	2.5794(7)	In(3)−Se(5)^{iv}	2.5668(9)	Cu(1)−Se(4)	2.452(1)
In(1)−Se(6)	2.5794(7)	In(3)−Se(4)	2.5709(8)	Cu(1)−Se(2)^{iv}	2.453(1)
In(2)−Se(4)^{iv}	2.5680(8)	In(3)−Se(2)	2.5713(8)	Cu(1)−Se(6)	2.479(1)
In(2)−Se(4)	2.5681(8)	In(4)−Se(3)	2.5654(9)	Cu(1)−Se(1)^{v}	2.479(1)
In(2)−Se(1)^{iv}	2.5859(8)	In(4)−Se(1)	2.5688(8)		
Se(2)^{i}−In(1)−Se(2)^{ii}	115.89(3)	Se(4)−In(2)−Se(1)	109.82(2)	Se(1)−In(4)−Se(5)	111.61(3)
Se(2)^{i}−In(1)−Se(6)^{iii}	108.92(2)	Se(1)^{iv}−In(2)−Se(1)	103.00(3)	Se(3)−In(4)−Se(6)	111.16(3)
Se(2)^{ii}−In(1)−Se(6)^{iii}	109.53(2)	Se(3)^{v}−In(3)−Se(5)^{iv}	104.30(3)	Se(1)−In(4)−Se(6)	116.17(2)
Se(2)^{i}−In(1)−Se(6)	109.53(2)	Se(3)^{v}−In(3)−Se(4)	106.55(3)	Se(5)−In(4)−Se(6)	106.13(3)
Se(2)^{ii}−In(1)−Se(6)	108.92(2)	Se(5)^{iv}−In(3)−Se(4)	111.45(3)	Se(4)−Cu(1)−Se(2)^{iv}	118.32(3)
Se(6)^{iii}−In(1)−Se(6)	103.31(3)	Se(3)^{v}−In(3)−Se(2)	111.18(3)	Se(4)−Cu(1)−Se(6)	111.30(4)
Se(4)^{iv}−In(2)−Se(4)	115.60(3)	Se(5)^{iv}−In(3)−Se(2)	106.74(3)	Se(2)^{iv}−Cu(1)−Se(6)	105.30(3)
Se(4)^{iv}−In(2)−Se(1)^{iv}	109.82(2)	Se(4)−In(3)−Se(2)	116.04(2)	Se(4)−Cu(1)−Se(1)^{v}	105.16(3)
Se(4)−In(2)−Se(1)^{iv}	108.93(2)	Se(3)−In(4)−Se(1)	106.61(3)	Se(2)^{iv}−Cu(1)−Se(1)^{v}	111.04(4)
Se(4)^{iv}−In(2)−Se(1)	108.93(2)	Se(3)−In(4)−Se(5)	104.62(3)	Se(6)−Cu(1)−Se(1)^{v}	105.06(3)
Compound **2**					
Ga(1)−Se(2)^{i}	2.4076(6)	Ga(2)−Se(1)	2.4219(6)	Ga(4)−Se(5)	2.4333(6)
Ga(1)−Se(2)^{ii}	2.4076(6)	Ga(3)−Se(4)	2.3740(6)	Ga(4)−Se(3)	2.4395(6)
Ga(1)−Se(6)	2.4324(6)	Ga(3)−Se(2)	2.3868(6)	Cu(1)−Se(4)	2.4201(7)
Ga(1)−Se(6)^{iii}	2.4324(6)	Ga(3)−Se(3)^{v}	2.4224(6)	Cu(1)−Se(1)^{v}	2.4315(6)
Ga(2)−Se(4)	2.4097(6)	Ga(3)−Se(5)^{iv}	2.4336(6)	Cu(1)−Se(2)^{iv}	2.4367(7)
Ga(2)−Se(4)^{iv}	2.4097(5)	Ga(4)−Se(6)	2.3795(6)	Cu(1)−Se(6)	2.4400(6)
Ga(2)−Se(1)^{iv}	2.4219(6)	Ga(4)−Se(1)	2.3908(6)		
Se(2)^{i}−Ga(1)−Se(2)^{ii}	116.01(3)	Se(4)−Ga(2)−Se(4)^{iv}	116.31(3)	Se(4)−Ga(3)−Se(2)	116.82(2)
Se(2)^{i}−Ga(1)−Se(6)	110.76(2)	Se(4)−Ga(2)−Se(1)^{iv}	106.98(2)	Se(4)−Ga(3)−Se(3)^{v}	104.62(2)
Se(2)^{ii}−Ga(1)−Se(6)	106.74(2)	Se(4)^{iv}−Ga(2)−Se(1)^{iv}	110.50(2)	Se(2)−Ga(3)−Se(3)^{v}	111.43(3)
Se(2)^{i}−Ga(1)−Se(6)^{iii}	106.74(2)	Se(4)−Ga(2)−Se(1)	110.50(2)	Se(4)−Ga(3)−Se(5)^{iv}	111.73(3)
Se(2)^{ii}−Ga(1)−Se(6)^{iii}	110.76(2)	Se(4)^{iv}−Ga(2)−Se(1)	106.98(2)	Se(2)−Ga(3)−Se(5)^{iv}	104.25(2)
Se(6)−Ga(1)−Se(6)^{iii}	105.36(3)	Se(1)^{iv}−Ga(2)−Se(1)	105.02(3)	Se(3)^{v}−Ga(3)−Se(5)^{iv}	107.83(2)
Se(6)−Ga(4)−Se(1)	116.39(2)	Se(1)−Ga(4)−Se(3)	105.18(3)	Se(1)^{v}−Cu(1)−Se(2)^{iv}	110.05(3)
Se(6)−Ga(4)−Se(5)	105.64(3)	Se(5)−Ga(4)−Se(3)	106.73(2)	Se(4)−Cu(1)−Se(6)	110.51(3)
Se(1)−Ga(4)−Se(5)	111.40(2)	Se(4)−Cu(1)−Se(1)^{v}	107.95(2)	Se(1)^{v}−Cu(1)−Se(6)	106.93(2)
Se(6)−Ga(4)−Se(3)	111.19(2)	Se(4)−Cu(1)−Se(2)^{iv}	114.07(2)	Se(2)^{iv}−Cu(1)−Se(6)	107.11(2)
Compound **3**					
In(1)−Se(2)^{i}	2.639(1)	In(2)−Se(1)	2.670(1)	In(4)−Se(3)	2.584(1)
In(1)−Se(2)^{ii}	2.639(1)	In(3)−Se(4)	2.560(1)	In(4)−Se(5)	2.589(1)
In(1)−Se(6)	2.668(1)	In(3)−Se(2)	2.565(1)	Ag(1)−Se(2)^{iv}	2.559(1)
In(1)−Se(6)^{iii}	2.668(1)	In(3)−Se(3)^{v}	2.577(1)	Ag(1)−Se(4)	2.566(1)
In(2)−Se(4)^{iv}	2.638(1)	In(3)−Se(5)^{iv}	2.583(1)	Ag(1)−Se(6)	2.575(1)
In(2)−Se(4)	2.638(1)	In(4)−Se(6)	2.557(1)	Ag(1)−Se(1)^{v}	2.5754(9)
In(2)−Se(1)^{iv}	2.670(1)	In(4)−Se(1)	2.561(1)		
Se(2)^{i}−In(1)−Se(2)^{ii}	117.79(6)	Se(4)−In(2)−Se(1)	110.95(2)	Se(1)−In(4)−Se(3)	112.88(4)
Se(2)^{i}−In(1)−Se(6)	111.44(2)	Se(1)^{iv}−In(2)−Se(1)	105.73(6)	Se(6)−In(4)−Se(5)	113.48(4)
Se(2)^{ii}−In(1)−Se(6)	105.20(2)	Se(4)−In(3)−Se(2)	118.45(3)	Se(1)−In(4)−Se(5)	102.34(3)
Se(2)^{i}−In(1)−Se(6)^{iii}	105.20(2)	Se(4)−In(3)−Se(3)^{v}	113.54(3)	Se(3)−In(4)−Se(5)	106.73(3)
Se(2)^{ii}−In(1)−Se(6)^{iii}	111.44(2)	Se(2)−In(3)−Se(3)^{v}	101.90(4)	Se(2)^{iv}−Ag(1)−Se(4)	119.98(3)
Se(6)−In(1)−Se(6)^{iii}	105.17(6)	Se(4)−In(3)−Se(5)^{iv}	102.49(4)	Se(2)^{iv}−Ag(1)−Se(6)	102.15(3)
Se(4)^{iv}−In(2)−Se(4)	118.52(6)	Se(2)−In(3)−Se(5)^{iv}	112.92(3)	Se(4)−Ag(1)−Se(6)	112.78(4)
Se(4)^{iv}−In(2)−Se(1)^{iv}	110.95(2)	Se(3)^{v}−In(3)−Se(5)^{iv}	107.43(3)	Se(2)^{iv}−Ag(1)−Se(1)^{v}	113.31(4)
Se(4)−In(2)−Se(1)^{iv}	105.05(2)	Se(6)−In(4)−Se(1)	118.48(3)	Se(4)−Ag(1)−Se(1)^{v}	102.06(3)
Se(4)^{iv}−In(2)−Se(1)	105.05(2)	Se(6)−In(4)−Se(3)	102.69(3)	Se(6)−Ag(1)−Se(1)^{v}	106.12(3)

[a] Symmetry transformations used to generate equivalent atoms follow. Compound **1**: i, $x - {}^{1}/_{2}, y + {}^{1}/_{2}, z$; ii, $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{3}/_{2}$; iii $-x, y, -z + {}^{3}/_{2}$; iv, $-x + 1, y, -z + {}^{3}/_{2}$; v, $-x + {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{3}/_{2}$. Compound **2**: i, $x - {}^{1}/_{2}, y + {}^{1}/_{2}, z$; ii, $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{3}/_{2}$; iii, $-x, y, -z + {}^{3}/_{2}$; iv, $-x + 1, y, -z + {}^{3}/_{2}$; v, $-x + {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{3}/_{2}$. Compound **3**: i, $x - {}^{1}/_{2}, y + {}^{1}/_{2}, z$; ii, $-x + {}^{1}/_{2}, y + {}^{1}/_{2}, -z + {}^{3}/_{2}$; iii, $-x, y, -z + {}^{3}/_{2}$; iv, $-x + 1, y, -z + {}^{3}/_{2}$; v, $-x + {}^{1}/_{2}, y - {}^{1}/_{2}, -z + {}^{3}/_{2}$.

resulting in the tendency of crystals to cleave into very thin mica-like sheets.

It is structurally evident that the Cu/In distribution in compound **1** is ordered from the clearly distinguishable Cu−Se and In−Se distances in the metal-centered tetrahedra. But the same conclusion cannot be extended to the isostructural compounds **2** and **3** because of the similarity in both X-ray scattering factors, and there is no substantial difference between the bond distances of Cu−Se and Ga−Se for **2**, and Ag−Se and In−Se for **3**, respectively. The tetrahedral coordination environments around Cu and Ga for **2** and Ag and In for **3** are nearly identical, which would imply a crystallographic possibility for a disordered model of Cu and Ga for **2** and Ag and In for **3**, respectively. However, the refinement on the model of disordered structure for **2** and **3** cannot improve the *R* factors obviously, so the ordered structure model adopted by their analogue **1** were finally used. In this case, a model with disordered metal atoms for

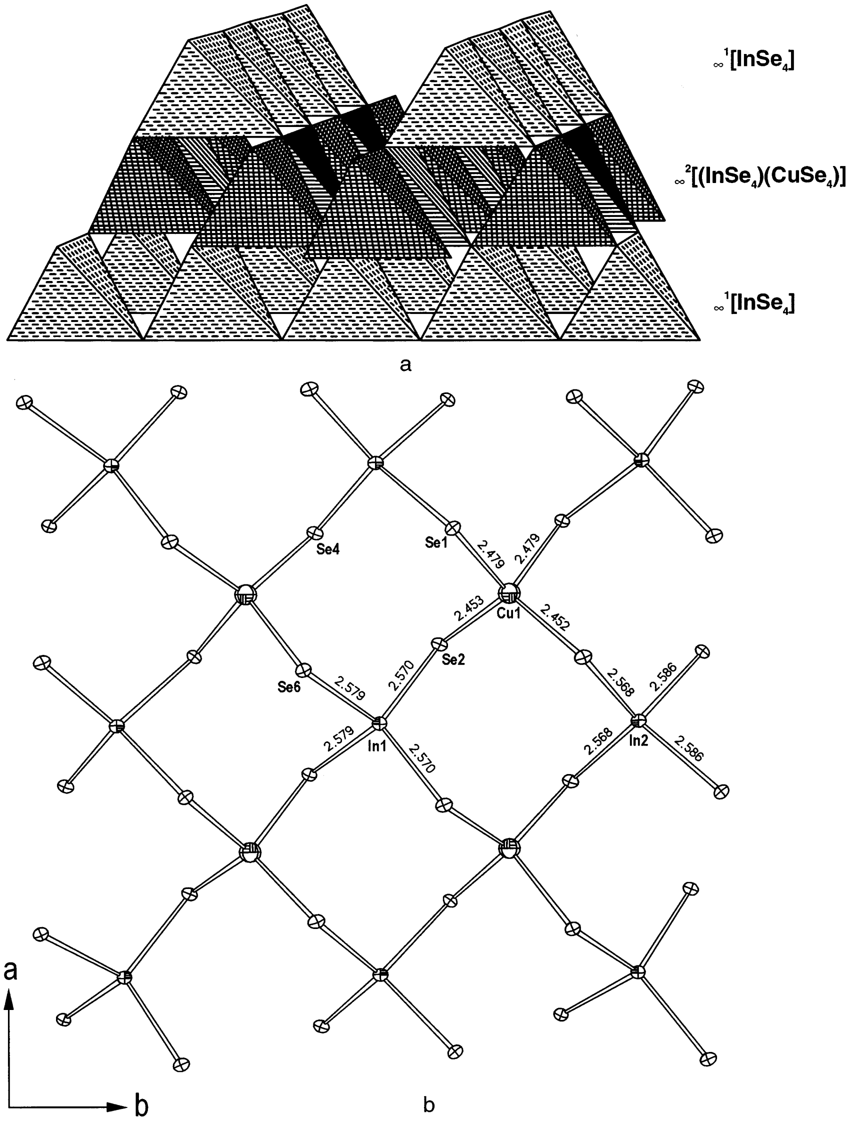

Figure 1. (a) Polyhedral perspective of compound **1** shows the sublayer sandwiched by parallel corner-sharing [InSe$_4$] tetrahedra chains. (b) The sublayer $_\infty^2$[(InSe$_4$)(CuSe$_4$)] in compound **1** viewed along the [001] direction with 50% thermal ellipsoids.

2 and **3** should be equally valid. On the basis of neutrality, the formal oxidation states in these compounds can be formulated as follows: K, +1; Cu/Ag, +1; Ga/In, +3; and Se, −2.

Unlike $Rb_2Cu_2Sn_2S_6$,[5e] the only example of a similar structure with sublayers consisting of corner-sharing [CuS$_4$] tetrahedra, the present sublayer structure features an alternately packed corner-sharing [CuSe$_4$] and [InSe$_4$] mixed-metal tetrahedral sheet. The architecture of such sublayer sandwiched by [InSe$_4$] tetrahedral chains is found for the first time among the quaternary layered metal chalcogenides.[4b,5b,5d,5f,6,12] The difference between the present compounds and the previously reported $Rb_2Cu_2Sn_2S_6$ lies in the position of Cu/M atoms that occupy five Wyckoff sites. In compound **1**, only one of the five sites is occupied by Cu while three of five are occupied by Cu atoms in the Sn compound. The parallel corner-sharing tetrahedral chains of both structures are composed of Sn- and In-centered tetrahedra for $Rb_2Cu_2Sn_2S_6$ and **1**, respectively.

Analogous to the K−Cu−M−Q (M = Nb, Ta),[13] the structural dimensionality of the present compounds also decreases with the increase of the alkali metal content. The three-dimensional chalcopyrite $CuInSe_2$ (expressed as $Cu_3In_3Se_6$) converts to the present two-dimensional layer structure for $K_2CuIn_3Se_6$ when $^2/_3$ of the Cu atoms in $CuInSe_2$ are replaced by K atoms; it can further convert to the $KInSe_2$ structure with a simple two-dimensional layer when all of the Cu atoms are replaced by K atoms.

Optical absorption spectra[14] of compounds **1**, **2**, and **3** reveal the presence of a sharp optical gap of 1.68, 1.72, and 1.64 eV (Figure 2), respectively, which suggests that these materials are semiconductors and is consistent with the dark

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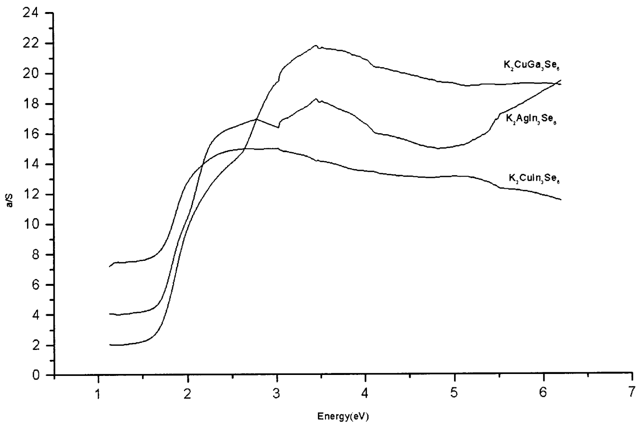

Figure 2. Optical absorption spectra of compound **1**, **2**, and **3**.

Table 3. Summary of the Optical Band Gaps (eV) of Some Quaternary Metal Chalcogenides

compound	E_g (eV)	compound	E_g(eV)
K_2CuVS_4 [17]	1.82	$Cs_2CuNbSe_4$ [17]	2.19
Rb_2CuVS_4 [17]	1.85	Rb_2AgNbS_4 [18]	2.76
K_2AgVS_4 [18]	1.85	$K_2Cu_2Sn_2S_6$ [5e]	1.47
Rb_2AgVS_4 [18]	1.83	$Rb_2Cu_2Sn_2S_6$ [5e]	1.44
Cs_2AgVS_4 [18]	1.77	$K_2Cu_2Sn_2Se_6$ [5e]	1.04
K_2CuNbS_4 [17]	2.82	$Rb_2Cu_2Sn_2Se_6$ [5e]	1.04
Rb_2CuNbS_4 [17]	2.64	$K_2CuIn_3Se_6$	1.68
$K_2CuNbSe_4$ [17]	2.14	$K_2CuGa_3Se_6$	1.72
$Rb_2CuNbSe_4$ [17]	2.19	$K_2AgIn_3Se_6$	1.64

red color of the crystals. The optical band gaps of some quaternary metal chalcogenides are tabulated in Table 3. It is worth noting that, for the same structural types, the optical band gap changes only slightly for changes in the types of alkali metals and coinage metals, whereas the band gap changes are relatively large when the type of group 15 elements and chalcogens is changed. These observations suggest that the optical absorption of quaternary metal chalcogenides is likely originated from the charge transfer from Q^{2-} ligand valence band to M^V(or M^{III}) conduction band.[5e,15]

The energy band gaps of the present compounds are comparable to those of CdTe (1.5 eV), GaAs (1.4 eV), and the structurally related chalcopyrite $CuInS_2$ (1.55 eV), but larger than that of the structurally related chalcopyrite $CuInSe_2$ (1.04 eV), all of which are highly efficient photovoltaic materials.[16−18] The present compounds are potential materials for the efficient absorption of solar radiation in solar cell applications. The IR spectra of the present compounds show no obvious absorption in the range 4000−800 cm^{-1}, indicating the absence of direct Se···Se bonds, consistent with their single-crystal structures. The absence of IR absorption may render these compounds useful as IR transparent materials in the region.

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Supporting Information Available: Additional figure and X-ray crystallographic files in CIF format for the structure determination of complexes **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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