Layered Ternary and Quaternary Metal Chalcogenides☆

Michael A. Pell and James A. Ibers*

Department of Chemistry, Northwestern University,
Evanston, Illinois, 60208-3113, USA
Telefax: (internat.) +1(847)491-2976
E-mail: ibers@chem.nwu.edu

Received July 15, 1996

Keywords: Chalcogenides / Reactive flux / Layered compounds / Structures / Physical properties

The syntheses, crystal structures, and physical properties of some recently discovered layered ternary and quaternary chalcogenides are reviewed. One component of these systems is an alkali metal or thallium; another is a d-, f-, or p-block metal.

Differences among metal oxide and metal chalcogenide structures (chalcogen = Q = S, Se, Te) are striking. These differences include polyhedra other than tetrahedra and octahedra as building blocks in most chalcogenide structures; the absence of closest packing in many chalcogenide structures; the occurrence of trigonal-prismatic coordination for the second- and third-row early transition metals; the presence of Q–Q bonds, that is Q_n^{2-} species, $n \geqslant 2$, in many chalcogenides; and finally the wide range of possible Q–Q bond lengths, especially for the tellurides. But perhaps the most striking feature of the metal chalcogenides is their tendency to crystallize in low-dimensional structures. The chalcogens are less electronegative than their group 16 congener, oxygen, and as such M–Q bonds are far less ionic than M–O bonds (M = metal). In oxides, dominant O···O repulsions promote instabilities in one- and two-dimensional compounds. In chalcogenides, however, Q···Q repulsions are small and one- and two-dimensional structures are stabilized by Q···Q van der Waals attractions[1]. Because of these differences, metal chalcogenides, in particular the tellurides, show a very rich structural chemistry that is fundamentally different from that of the oxides. Low-dimensional materials are of more than structural interest. Novel chemical or physical properties are most often found in materials with unusual structures[2,3]. This paradigm has spurred research in the area of metal chalcogenides. The low-dimensional, highly anisotropic nature of these materials may give rise to interesting physical properties, including superconductivity and charge density wave formation.

To keep this review concise, we restrict ourselves to two-dimensional or layered metal chalcogenides, mentioning one-dimensional materials only in passing. A layered (or laminar) structure, by strict definition, consists of neutral sandwiches stacked one upon the other with no chemical bonding between sandwiches[4]. Adherence to this definition would force us to replace the word "layer" by "slab" throughout this review. In the wake of recent activity in

Michael Pell (right) was born in Montréal in 1970. He received his B.Sc. from McGill University in 1992 and came to Northwestern University as a graduate student in the Ibers group in 1993. He received his Ph.D. degree in 1996 and will be an NSERC Postdoctoral Fellow with Prof. Reinhard Nesper at ETH-Zürich late in 1996. James A. Ibers was born in Los Angeles in 1930. He received his Ph.D. from Caltech in 1954. After a period in industry and at Brookhaven he became Professor of Chemistry at Northwestern in 1964. His research interests include the solution and solid-state chemistry of metal chalcogenides.

MICROREVIEWS: This feature introduces Berichte's readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

0009–2940/97/0101–0001 $ 15.00+.25/0

solid-state chalcogenide chemistry, a more flexible definition of a layered structure has evolved; there is a tacit understanding that a "layered structure" is one where intralayer bonding is more significant than interlayer bonding. In many metal tellurides, as opposed to most metal sulfides and metal selenides, interlayer attractions are significant and are manifested by Te···Te distances that are significantly shorter than van der Waals interactions[5,6]. Nevertheless, such compounds are termed layered.

The binary chalcogenides of the early transition metals are predominantly layered compounds (even in the formal sense). By 1965, it was realized that these binary chalcogenides could be intercalated with a variety of species, including alkali metals[7]. The alkali-metal cations residing in the van der Waals gaps in these materials further stabilize their two-dimensional arrangements. Thus, whereas most binary transition-metal oxides exhibit the three-dimensional rutile structure, two-dimensional Na_xMO_2 phases isostructural with Na_xMS_2 intercalation compounds may be prepared[8]. Again, to keep this review concise, materials synthesized by intercalation of existing layered chalcogenides will not be considered here.

In this review we discuss some recently discovered layered ternary $A_xM_yQ_z$ and quaternary $A_xM_yM'_{y'}Q_z$ chalcogenides, where A is an alkali metal or Tl, M is a d-, f-, or p-block metal, and Q is a chalcogen (S, Se, or Te). For a systematic presentation of some of the more classical layered chalcogenides that contain an alkali metal, the reader is referred to a review by Bronger[9]. Although all of the materials to be discussed here are formed from ionic packing, we elect to describe their structures in terms of coordination polyhedra. This description facilitates comparison among different structures. It also emphasizes the importance of coordination preferences of specific metal cations and the role these have played in our design of target phases[10]. We illustrate this below. Also, the orbital energies of molecular polyhedra provide building blocks for the characterization of the electronic band and structures in extended solids; such band structures are useful for the correlation of physical properties and crystal structure[11,12].

The Reactive Flux

Alkali-metal sulfide and polysulfide fluxes have been used for over 150 years to aid in crystal growth[13,14]. The potential of these binary alkali-metal chalcogenides as starting materials, however, was first demonstrated in our laboratory in 1987 by the reaction of K_2S with S and Ti at 375 °C to yield the one-dimensional compound $K_4Ti_3S_{14}$[15]. As the flux components were incorporated into the reaction product, K_2S/S was dubbed a "reactive flux". We extended the reactive-flux technique to the synthesis of selenides[16] and tellurides[17], the latter through the use of a low-melting $CuTe_y$ reactive flux. Since the initial demonstration with K_2S/S, a host of reactive binary low-melting alkali-metal polychalcogenide fluxes (Table 1) have been used intensively by us and by others[18−24] in the synthesis of ternary and quaternary chalcogenide phases. In fact, this technique has been the subject of two extensive reviews by Kanatzidis[25,26]. Traditional solid-state techniques require high temperatures to achieve fusion of particles. Low-melting reactive fluxes furnish a solvent that facilitates particle mixing and allows the investigation of systems at lower temperatures. Access to phases thermodynamically unstable at high temperatures is thus provided. Another important feature of these reactive-flux materials is that they provide a convenient source of alkali metal. Alkali metals react with fused silica at high temperature, are dangerously moisture-sensitive, and, owing to their texture, are difficult to weigh out precisely. A reactive flux may be prepared as an easily handled powder by the reaction of alkali metal and chalcogen in liquid ammonia. Analogous to an alkali-metal or alkaline-earth halide flux, the product crystals embedded in the solidified flux may be extracted by washing the flux away with water or other solvents.

Table 1. A_2Q_y Melting points (°C)[a]

Formula	Q	Alkali Metal		
		Na	K	Cs
A_2Q	S	978	948	–
	Se	876	800	770
	Te	953	900	820
A_2Q_3	S	–	252	217
	Se	313	380	338
	Te	–	429	395
A_2Q_5	S	258	206	212
	Se	–	195	242
	Te	–	–	235

[a] Data are from ref.[80].

Quaternary A/Cu/M/Q (M = Group IV Metal) Systems

1:1:1:3 Phases

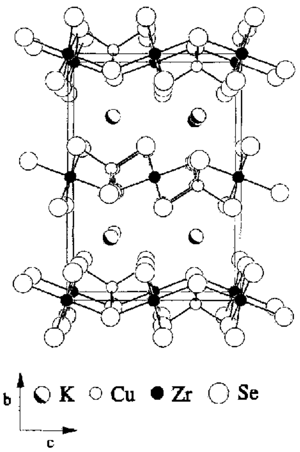
The investigation of the A/Cu/M/Q (A = Na, K, Cs, Tl; M = Ti, Zr; Q = S, Se, Te) system has uncovered a diverse group of structures with varying charge-transport properties (Table 2). Several different two-dimensional structure types built from layers of edge-sharing Ti^{4+} or Zr^{4+} octahedra (*oct*) and Cu^+ tetrahedra (*tet*) have been discovered. The layers in these materials are separated by A^+ cations. It is the ordering of the polyhedra within the layers of these 1:1:1:3 phases that is remarkable. The slabs in $NaCuZrS_3$[27], $KCuZrS_3$[28], $KCuZrSe_3$[28], $KCuZrTe_3$[28], and $TlCuZrTe_3$[29] comprise alternating Cu^+ tetrahedra and Zr^{4+} octahedra in the fashion *oct tet oct tet oct tet* and are separated by A^+ cations coordinated to seven Q^{2-} anions in a monocapped trigonal-prismatic arrangement (Figure 1). Electrical conductivity is greatly influenced by the A^+ cation and Q^{2-} anion: $KCuZrS_3$ is an insulator, $KCuZrSe_3$ undergoes a metal-to-semiconductor transition at 50 K, $KCuZrTe_3$ is a metal, and $TlCuZrTe_3$ is a semiconductor.

The slabs in $NaCuTiS_3$[27], $NaCuZrSe_3$[27], $NaCuZrTe_3$[27], and $TlCuTiTe_3$[29] comprise alternating *pairs* of polyhedra (in the fashion *oct oct tet tet oct oct*) separated by eight-coordinate bicapped trigonal-prismatic A^+ cations.

Table 2. Layered Cu/group IV structures

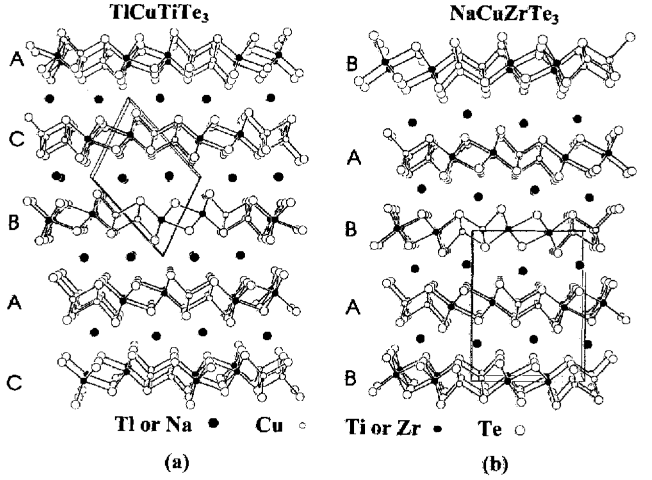
Compound	Space group	Ordering of polyhedra	Conductivity	Ref.
$KCuZrS_3$	*Cmcm*	*oct tet oct tet oct tet*	insulator	[28,29,42]
$KCuZrSe_3$			metal to semiconductor at 50 K	
$KCuZrTe_3$			metal	
$NaCuZrS_3$				
$TlCuZrTe_3$			semiconductor	
$NaCuTiS_3$	*Pnma*	*oct oct tet tet oct oct*		[27]
$NaCuZrSe_3$				
$NaCuZrTe_3$				
$TlCuTiTe_3$	*$P2_1/m$*	*oct oct tet tet oct oct*	semiconductor	[29]
$Na_2Cu_2ZrS_4$	*C2/m*	*oct tet tet oct tet tet*		[30]

Figure 1. Unit cell of $KCuZrSe_3$ viewed along [100]



The stacking of the layers in $TlCuTiTe_3$ is different from that in $NaCuTiS_3$, $NaCuZrSe_3$, and $NaCuZrTe_3$ (Figure 2). In the Tl compound the layer repeat is three units; the layers stack in an *ABCABC* sequence. In the Na compounds the layer repeat is two units; an *ABABAB* sequence is observed.

Figure 2. Layer stacking in (a) $TlCuTiTe_3$ and (b) $NaCuZrTe_3$. Whereas the layers in both materials feature polyhedra alternating in a *tet tet oct oct tet tet* sequence, the layer stacking repeat is different



The transport properties of the Na compounds have not been measured; $TlCuTiTe_3$ is a semiconductor.

2:2:1:4 Phases

$Na_2Cu_2ZrS_4$ contains $^2_\infty[Cu_2ZrS_4^{2-}]$ layers formed from *pairs* of Cu^+ tetrahedra alternating with *single* Zr^{4+} octahedra (in the fashion *oct tet tet oct tet tet*) (Figure 3)[30]. This compound is clearly related to the 1:1:1:3 phases. The layers in $Na_2Cu_2ZrS_4$ are separated by seven-coordinate monocapped trigonal-prismatic Na^+ cations. Given that Ag^+ exhibits more coordination geometries that does Cu^+, we investigated the substitution of Ag^+ for Cu^+. This resulted in the compound $Cs_2Ag_2ZrTe_4$[31]. Its structure comprises $^2_\infty[Ag_2ZrTe_4^{2-}]$ layers separated by Cs^+ cations. $Cs_2Ag_2ZrTe_4$ is neither isostructural with $Na_2Cu_2ZrS_4$ nor is it related to the 1:1:1:3 phases. The Cs^+ coordination in $Cs_2Ag_2ZrTe_4$ is square prismatic, differing from the trigonal-prismatic coordination of the K, Na, and Tl compounds. The $^2_\infty[Ag_2ZrTe_4^{2-}]$ layers are composed of $^1_\infty[AgZrTe_4^{3-}]$ chains stitched together by Ag^+ cations (Figure 4). Both the Ag^+ and Zr^{4+} cations exhibit tetrahedral coordination. This represents the first example of tetrahedral coordination of Zr by a chalcogen. It appears that only one oxide structure exhibits an analogous Zr coordination; isolated ZrO_4^{4-} tetrahedra are found in the structure of Cs_4ZrO_4[32].

Figure 3. Unit cell of $Na_2Cu_2ZrS_4$ viewed along [010]

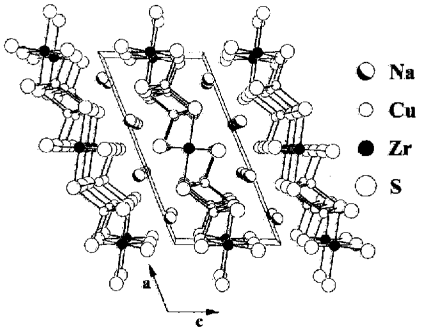
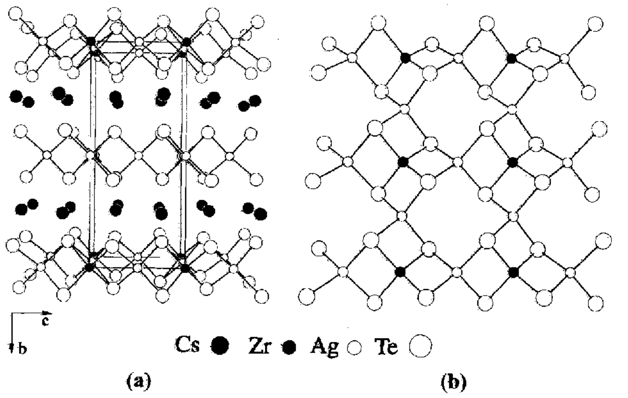


Figure 4. (a) Unit cell of $Cs_2Ag_2ZrTe_4$ viewed along [100]. (b) View of $^2_\infty[Ag_2ZrTe_4^{2-}]$ layer showing the tetrahedral coordination of Ag^+ and Zr^{4+}

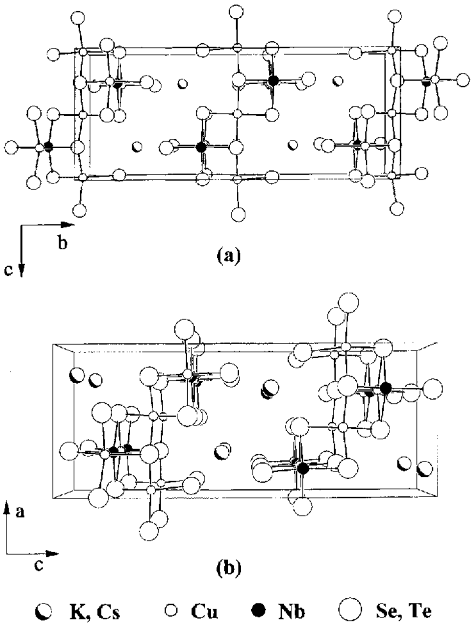


Quaternary ACu_2MQ_4 (M = Nb, Ta) Systems

The series Cu_3NbSe_4[33], KCu_2NbSe_4[34], $K_2CuNbSe_4$[35], and K_3NbSe_4[36] nicely illustrates two features of importance in our research, the first being the effect on dimensionality of alkali-metal substitution[37]. Cu_3NbSe_4 has a three-dimensional structure comprising the edge- and corner-sharing of $CuSe_4$ and $NbSe_4$ tetrahedra, KCu_2NbSe_4, which we describe below, has a two-dimensional structure. $K_2CuNbSe_4$ has a one-dimensional structure comprising infinite chains of edge-sharing, alternating $CuSe_4$ and $NbSe_4$ tetrahedra separated from one another by K^+ ions, and K_3NbSe_4 comprises isolated $[NbSe_4]^{3-}$ and K^+ ions. We have illustrated previously[37] this trend of decreasing dimensionality of a solid-state chalcogenide with increasing alkali-metal content. The second feature illustrated by this series of compounds is the coordination preferences of metals[10]. Cu is usually in the +1 state in chalcogenides; alkali metals are always in the +1 state. But Cu^+ strongly prefers to be four coordinate whereas alkali metals strongly favor six or higher coordination in chalcogenides. Thus we often attempt the substitution of alkali metal for Cu in solid-state syntheses, for such a substitution will lead to lower dimensionality and a different structure with concomitant different physical properties.

KCu_2NbQ_4 (Q = S, Se) contains $^{2}_{\infty}[Cu_2NbQ_4^-]$ layers separated by regular tricapped trigonal-prismatic K^+ cations[34] (Figure 5a). Both Cu^+ and Nb^{5+} cations exhibit tetrahedral coordination. Edge- and corner-sharing of these tetrahedra results in undulating layers. KCu_2NbQ_4 crystallizes with a C-centered lattice; the layers are eclipsed. The structures of $CsCu_2MTe_4$ (M = Nb, Ta) (Figure 5b)[38] demonstrate how substitutional effects influence crystal packing. In $CsCu_2MTe_4$, the tricapped trigonal-prismatic environments about the Cs^+ cations are highly distorted, the layers are slipped, and the lattice-type is primitive. $CsCu_2NbTe_4$ has a conductivity less than $2.5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ and $CsCu_2TaTe_4$ has a conductivity less than $2.2 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ at room temperature.

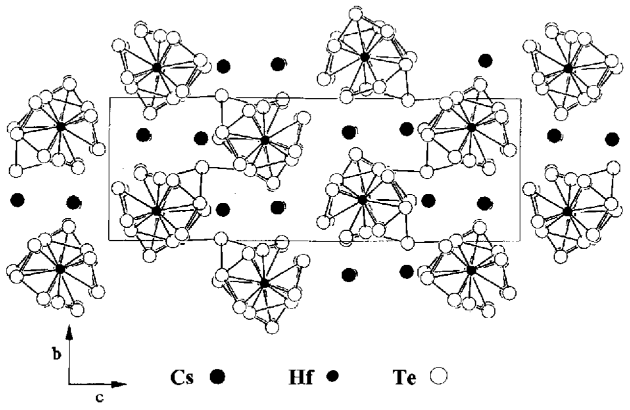
Figure 5. (a) Unit cell of KCu_2NbSe_4 viewed along [100]. (b) Unit cell of $CsCu_2NbTe_4$ viewed along [010]



Ternary A/M/Q (M = Group IV) Systems

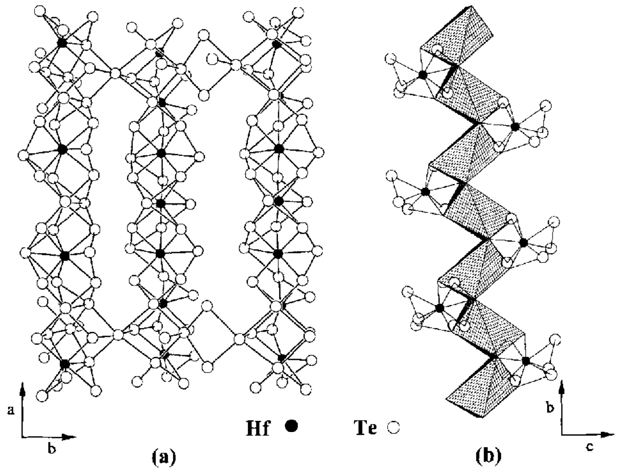
We have investigated several ternary alkali-metal/group-IV metal/chalcogen systems since the initial studies of $K_4Ti_3S_{14}$[15], $Na_2Ti_2Se_8$[16] and $K_4M_3Te_{17}$ (M = Zr, Hf)[17]. Probing of the Cs/M/Te system has led us to the compounds $Cs_3Ti_3Te_{11}$[39,40], $Cs_4Zr_3Te_{16}$[41,42] and $Cs_5Hf_5Te_{26}$[40]. Again a change in composition is seen with change in group IV metal or A^+ cation [compare $Cs_4Zr_3Te_{16}$ with $K_4M_3Te_{17}$ (M = Zr, Hf)[17]]. The $^{1}_{\infty}[Ti_3Te_{11}^{3-}]$, $^{1}_{\infty}[Zr_3Te_{16}^{4}]$, and $^{1}_{\infty}[Zr_3Te_{17}^{4-}]$ anions are unequivocally one-dimensional whereas the description of the $[Hf_5Te_{26}]^{5-}$ anion as two-dimensional rather than one-dimensional arises from the somewhat arbitrary assignment of a bond to a Te···Te interaction of 3.25 Å (Figure 6). Triangular face-sharing chains of bicapped trigonal-prismatic Hf cations are woven together by Te anions to form $^{2}_{\infty}[Hf_5Te_{26}^{5-}]$ layers (Figure 7a). These layers are separated by 11- and 12-coordinate Cs^+ cations.

Figure 6. Unit cell of $Cs_5Hf_5Te_{26}$. Te−Te bonds are drawn for interactions less than 3.3 Å



One particular feature of the structure of the $^{2}_{\infty}[Hf_5Te_{26}^{5-}]$ layer is worth noting. A chain-like structure is built of bicapped trigonal-prismatic Hf centers that share triangular faces. The chains are linked by $TeTe_6$ octahedra every fifth unit, with Te···Te interactions ranging from 2.935(9) to 3.470(9) Å, to form zigzag layers (Figure 7b). A similar octahedral geometry about Te is seen in the helical chain structure of elemental Te, where each Te atom has two intrachain neighbors at 2.834 Å and four interchain neighbors at 3.491 Å[43]. Clearly these complex metal systems can stabilize unique coordination environments: unique structures can translate into unique physical properties. The $Cs_5Hf_5Te_{26}$ structure contains a host of Te−Te interactions: 15 less than 3 Å, 8 between 3 and 3.3 Å, and 7 between 3.3 and 3.6 Å. It is difficult to assign Te−Te bond orders to these Te···Te interactions that are intermediate to a Te−Te single bond distance and the van der Waals $Te^{2-}\cdots Te^{2-}$ distance of about 4.2 Å. A ramification of this is the difficulty

Figure 7. (a) View of $^{2}_{\infty}[\mathrm{Hf_5Te_{26}^{5-}}]$ layer. Te−Te bonds are drawn for interactions less than 3.5 Å to show octahedral geometry about bridging Te atom. (b) $\mathrm{TeTe_6}$ octahedra share edges to form a backbone onto which chains are anchored



of assigning oxidation states in metal tellurides such as $\mathrm{Cs_5Hf_5Te_{26}}$. In simple structures band structure calculations can provide insight as to whether intermediate interactions truly have bonding character[5,6]. The complexity of the present anions coupled with the presence of the heavy $\mathrm{Cs^+}$ cations restricts the value of such calculations.

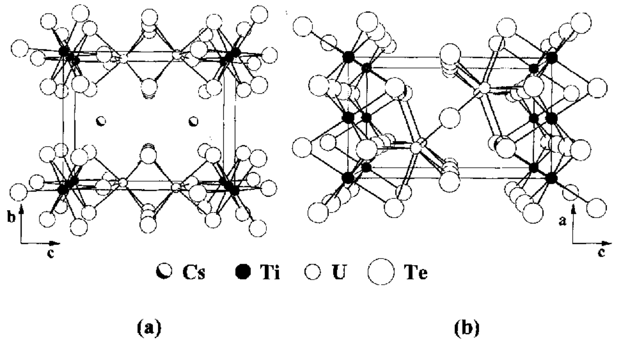
Uranium and Thorium Systems

Where oxidation states could be ascertained in the above compounds Zr and Hf were in the +4 state. These ions with coordination number 8 have radii of about 0.83 Å. In considering what other ions might have similar coordination preferences but considerably different radii we were led to $\mathrm{U^{4+}}$ with a radius of 1.00 Å and $\mathrm{Th^{4+}}$ with a radius of 1.06 Å. Of course, other oxidation states of U and Th are potentially accessible. The large uranium atom can adopt many coordination environments, including $\mathrm{UTe_6}$ octahedra in UTe[44], regular and distorted $\mathrm{USe_8}$ quadratic antiprisms in α-$\mathrm{USe_2}$[45], and $\mathrm{UTe_9}$ tricapped trigonal prisms in β-$\mathrm{UTe_3}$[46]. The binary telluride phases[46,47] are structurally interesting because they exhibit many intermediate Te−Te distances. Whereas there are many known ternary uranium sulfides and selenides[48], the chemistry of ternary uranium chalcogenides containing alkali metals or copper was essentially unexplored until recently. The only reported alkali-metal phases were $\mathrm{KUS_2}$[49] and $\mathrm{KUS_3}$[50]. The only reported copper-containing ternary uranium chalcogenide compounds, $\mathrm{Cu_2U_6Q_{13}}$[51,52] and $\mathrm{Cu_2U_3Q_7}$ (Q = S, Se)[53], have trigonal-planar Cu atoms and distorted $\mathrm{UQ_8}$ bicapped trigonal prisms.

We have investigated a variety of Cs/U/Q systems and have synthesized and characterized $\mathrm{CsUTe_6}$, $\mathrm{Cs_8Hf_5UTe_{30.5}}$, $\mathrm{CsTiUTe_5}$, and $\mathrm{CsCuUTe_3}$[39,42,54]. The first two compounds have one-dimensional structures and will not be described here.

$\mathrm{CsTiUTe_5}$ contains $^{2}_{\infty}[\mathrm{TiUTe_5^-}]$ layers separated by pentagonal-prismatic $\mathrm{Cs^+}$ cations (Figure 8)[54]. The layers are constructed from edge-sharing $\mathrm{UTe_8}$ bicapped trigonal prisms connecting chains of face-sharing $\mathrm{TiTe_6}$ octahedra. This is one of very few examples of face-sharing octahedra in tellurides. From magnetic susceptibility measurements the value of μ_{eff} at 300 K is 2.23(1) μ_B, intermediate between that expected for $\mathrm{U^{4+}}$ and $\mathrm{U^{5+}}$. Despite the presence of an infinite linear Te−Te chain within the layers [Te−Te = 3.065(1) Å], the material is a semiconductor.

Figure 8. Unit cell of $\mathrm{CsTiUTe_5}$ viewed along (a) [100], (b) [010]



$\mathrm{CsCuUTe_3}$[54], $\mathrm{KCuUSe_3}$[55], and $\mathrm{CsCuCeS_3}$[55] are isostructural with $\mathrm{KCuZrQ_3}$ and show that in the absence of a transition metal the lanthanides and actinides can have the relatively low coordination number of six.

The number of known uranium chalcogenide compounds greatly exceeds the number of known thorium chalcogenides. As there appeared to be no known chemistry of ternary thorium chalcogenides containing alkali metals we have extended the above studies of uranium systems to thorium. Often, analogous structures occur in compounds of uranium and thorium[56,57]. It is far more interesting, however, when the composition or structure or both change in going from uranium to thorium. This occurs in our extension to thorium where we have synthesized and characterized the new isostructural compounds $\mathrm{KTh_2Te_6}$[58] and $\mathrm{CsTh_2Te_6}$[59] (compare $\mathrm{CsUTe_6}$).

The structures of $\mathrm{KTh_2Te_6}$ and $\mathrm{CsTh_2Te_6}$ feature double layers of $\mathrm{ThTe_8}$ bicapped trigonal prisms separated by $\mathrm{A^+}$ cations that are coordinated by eight Te anions in a rectangular parallelepiped (Figure 9a). The smallest rectangular face of each trigonal prism is constructed from two $\mathrm{Te_2}$ pairs with Te−Te separations of 3.055(4) Å. The distance between $\mathrm{Te_2}$ pairs of adjacent trigonal prisms is 3.085(4) Å. Thus infinite one-dimensional Te−Te chains are present in the layers. The electrical conductivity of $\mathrm{CsTh_2Te_6}$ is less than $10^{-5}\ \Omega^{-1}\ \mathrm{cm^{-1}}$ at room temperature.

Quaternary A/Ln/M/Q (Ln = Rare Earth) Systems

The known A/Ln/M/Q structures were summarized recently[60]. Most are not layered structures. However, there are $^{2}_{\infty}[\mathrm{LnGeQ_4^-}]$ layers in $\mathrm{KLnGeQ_4}$ (Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se) that comprise $\mathrm{MQ_4}$ and $\mathrm{LnQ_7}$ monocapped trigonal prisms (Figure 10)[61]. The $\mathrm{LnQ_7}$ monocapped trigonal prisms share two of the three edges of their rectangular faces to form chains along the [010]

Figure 9. Comparison of crystal structures of (a) $CsTh_2Te_6$ and (b) $CsCuCe_2S_6$. Cu^+ sites in (b) are 1/2 occupied

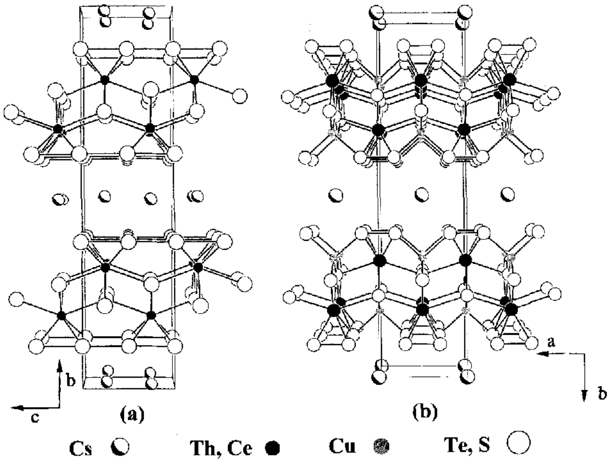


Figure 10. Unit cell of $KLaGeS_4$ viewed along [010]

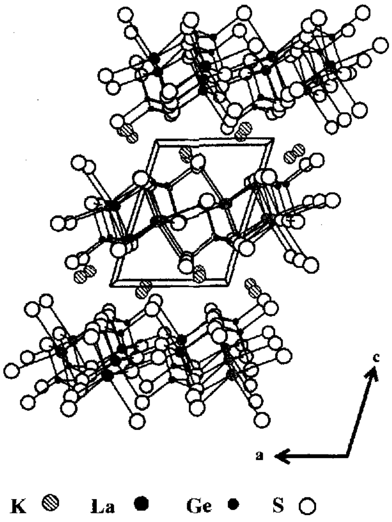
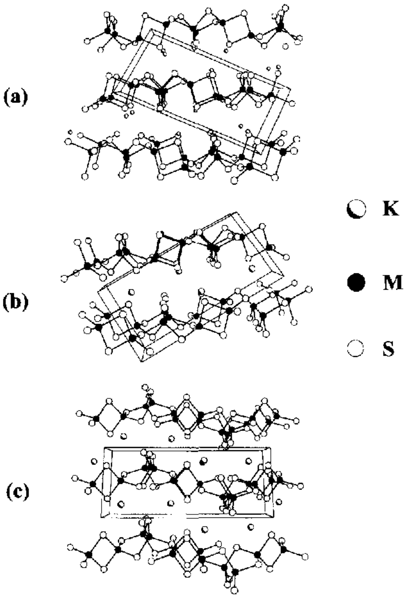


Figure 11. Views along [100] of the structures of (a) $KGaSnS_4$, (b) $KInGeS_4$, and (c) $KGaGeS_4$



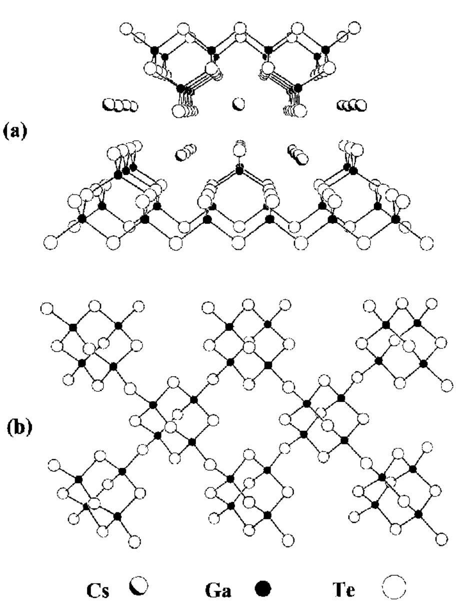
direction; the third edge is shared with an MQ_4 tetrahedron. In turn, each MQ_4 tetrahedron shares its two remaining vertices with two trigonal prisms in an adjacent chain. Additionally, the chains are cross-linked by the Q^{2-}-anions capping the rectangular face of each prism. All of the capping Q^{2-} anions point in the same direction along [010]. Thus, the structure is noncentrosymmetric. The magnetic moments, 3.6(1) μ_B for $KNdGeS_4$ and 7.8(1) μ_B for $KGdGeS_4$, are consistent with those expected for Nd^{3+} and Gd^{3+}, respectively.

Several quaternary A/Cu/Ce/Q compounds are known. $K_2Cu_2CeS_4$[62] is isostructural with $Na_2Cu_2ZrS_4$ (Figure 3). The structures of $CsCuCe_2S_6$[55], $KCuCe_2Se_6$[55], and $KCuCe_2S_6$[62] are very closely related to those of KTh_2Te_6 and $CsTh_2Te_6$ (Figure 9b). One can arrive at the former structures from the latter ones by filling in 1/2 of the intralayer tetrahedral vacancies with Cu^+ cations. Whereas the ATh_2Te_6 structures contain infinite Te–Te chains, the only Q–Q bonding within the layers of the related copper-containing compounds is in the form of isolated Q–Q pairs. This is most likely a manifestation of the Cu^+ cations prying apart the adjacent trigonal prisms. Evidence for the existence of $KCuTh_2Te_6$ and $CsCuTh_2Te_6$ as well as ATh_2S_6 and ATh_2Se_6 would be welcome. The absence or presence of infinite Q–Q bonding in these hypothetical phases would further elucidate this system.

Ternary and Quaternary A/M/Q Systems (M = Main Group Metal)

The layers in $KInGeS_4$, $KGaSnS_4$, and $KGaGeS_4$ comprise substitutionally disordered main-group metal atoms

Figure 12. (a) Unit cell of $CsGaTe_2$ viewed along [$\bar{1}$10]. (b) View along [001] showing interconnection of Ga_4Te_{10} adamantane-type units in the $^2_\infty[GaTe_2^-]$ layer



with tetrahedral coordination[63]. Although these compounds have different structures, they are closely related (Figure 11). The $^{2}_{\infty}[MM'Q_4^-]$ layers comprise chains of corner-sharing tetrahedra linked together by pairs of edge-sharing tetrahedra. The diversity of these materials is testament to the variety of structures that can be constructed not only from simple tetrahedral building blocks but also from similar *assemblies* of tetrahedral units. The coordination numbers of the K^+ cations are 8 for $KGaGeS_4$ and 8 and 9 for $KInGeS_4$ and $KGaSnS_4$. Similar layers to those in the triclinic $KGaSnS_4$ structure have been observed in the orthorhombic $TlInSiS_4$ structure[64]. $KInGeS_4$, $KGaSnS_4$, and $KGaGeS_4$ have conductivities less than 10^{-5} Ω^{-1} cm^{-1}.

The structure of $CsGaTe_2$[65] contains a net of adamantane-type Ga_4Te_{10} units, each of which bridges four additional units through corner-sharing of tetrahedra (Figure 12). The Cs^+ cations residing between the layers exhibit bicapped trigonal-prismatic coordination. Many closely related compounds have been previously reported, including the $TlGaSe_2$[66], $KGaS_2$[67], $NaAlSe_2$[68], and $KInS_2$[69]. Compounds with isolated $M_4Q_{10}^{4-}$ adamantane-type units are also known[70–79].

This brief review demonstrates the rich chemistry of layered ternary and quaternary metal chalcogenides as well as the utility of the reactive-flux method for the preparation of such compounds. These systems clearly exhibit a strong dependence of composition on structure and physical properties, a daunting prospect in that a great deal of exploratory synthesis remains to be done before general trends in structure and physical properties may be discerned. Yet, the versatility of these systems is also encouraging; once structure-property relationships are better understood and the ability to tailor crystal structures is improved, the fabrication of practical advanced materials may be possible.

Most of the work described in this review was done in our laboratory. Involved in this work were Drs. *Michael F. Mansuetto, Jason A. Cody, Ping Wu, Patricia M. Keane*, and *Ying-Jie Lu* along with *Eric Wu, Samson Chien, Todd M. Fuelberth*, and *Chi M. Cheung*. This research was supported by the *U. S. National Science Foundation* under Grant Numbers DMR88-13623 and DMR91-14934.

☆ Dedicated to Prof. Dr. *Hans Georg von Schnering* on the occasion of his 65th birthday.

[1] J. Rouxel, Ed., *Crystal Chemistry and Properties of Materials with Quasi-one-dimensional Structures* D. Reidel Publishing Company, Dordrecht, Netherlands, **1986**.
[2] F. J. Di Salvo, *Science.* **1990**, *247*, 649–655.
[3] F. J. Di Salvo in *Advancing Materials Research* (Eds.: P. A. Psaras, H. D. Langford), National Academy Press, Washington, D. C., **1987**.
[4] F. Hulliger, *Structural Chemistry of Layer-Type Phases* (Ed.: F. Lévy), D. Reidel Publishing Company, Dordrecht-Holland, **1976**.
[5] A. Mar, S. Jobic, J. A. Ibers, *J. Am. Chem. Soc.* **1992**, *114*, 8963–8971.
[6] E. Canadell, S. Jobic, R. Brec, J. Rouxel, M.-H. Whangbo, *J. Solid State Chem.* **1992**, *99*, 189–199.
[7] W. Rüdorff, *Chimia.* **1965**, *19*, 489–499.
[8] C. Delmas, C. Fouassier, P. Hagenmuller, *Mater. Sci. Eng.* **1977**, *31*, 297–301.
[9] W. Bronger in *Crystallography and Crystal Chemistry of Materials with Layered Structures* (Ed.: F. Lévy), D. Reidel Publishing Company, Dordrecht-Holland, **1976**.
[10] S. A. Sunshine, D. A. Keszler, J. A. Ibers, *Acc. Chem. Res.* **1987**, *20*, 395–400.
[11] J. K. Burdett in *Structure and Bonding in Crystals* (Eds.: M. O'Keeffe, A. Navrotsky), Academic Press, New York, **1981**.
[12] R. Hoffmann, *Solids and Surfaces: A Chemist's View of Bonding in Extended Structures* VCH Publishers, New York, **1988**.
[13] H. J. Scheel, *J. Cryst. Growth.* **1974**, *24/25*, 669–673.
[14] R. W. Garner, W. B. White, *J. Cryst. Growth.* **1970**, *7*, 343–347.
[15] S. A. Sunshine, D. Kang, J. A. Ibers, *J. Am. Chem. Soc.* **1987**, *109*, 6202–6204.
[16] D. Kang, J. A. Ibers, *Inorg. Chem.* **1988**, *27*, 549–551.
[17] P. M. Keane, J. A. Ibers, *Inorg. Chem.* **1991**, *30*, 1327–1329.
[18] M. G. Kanatzidis, Y. Park, *J. Am. Chem. Soc.* **1989**, *111*, 3767–3769.
[19] M. G. Kanatzidis, Y. Park, *Chem. Mater.* **1990**, *2*, 99–101.
[20] Y. Park, M. G. Kanatzidis, *Chem. Mater.* **1991**, *3*, 781–783.
[21] Y. Park, D. C. Degroot, J. Schindler, C. R. Kannewurf, M. G. Kanatzidis, *Angew. Chem.* **1991**, *103*, 1404–1407; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1325–1328.
[22] J. Li, H.-Y. Guo, R. A. Yglesias, T. J. Emge, *Chem. Mater.* **1995**, *7*, 599–601.
[23] N. S. Hartig, P. K. Dorhout, S. M. Miller, *J. Solid State Chem.* **1994**, *113*, 88–93.
[24] C. C. Raymond, P. K. Dorhout, S. M. Miller, *Inorg. Chem.* **1994**, *33*, 2703–2704.
[25] M. G. Kanatzidis, *Chem. Mater.* **1990**, *2*, 353–363.
[26] M. G. Kantzidis, A. C. Sutorik, *Prog. Inorg. Chem.* **1995**, *43*, 151–265.
[27] M. F. Mansuetto, P. M. Keane, J. A. Ibers, *J. Solid State Chem.* **1993**, *105*, 580–587.
[28] M. F. Mansuetto, P. M. Keane, J. A. Ibers, *J. Solid State Chem.* **1992**, *101*, 257–264.
[29] M. A. Pell, J. A. Ibers, *J. Alloys Compd. 1996*, *240*, 37–41.
[30] M. F. Mansuetto, J. A. Ibers, *J. Solid State Chem.* **1995**, *117*, 30–33.
[31] M. A. Pell, J. A. Ibers, *J. Am. Chem. Soc.* **1995**, *117*, 6284–6286.
[32] T.-M. Chen, J. D. Corbett, *Z. Anorg. Allg. Chem.* **1987**, *553*, 50–56.
[33] Y.-J. Lu, J. A. Ibers, *J. Solid State Chem.* **1993**, *107*, 58–62, *ibid.* **1994**, *III*, 447–448.
[34] Y.-J. Lu, J. A. Ibers, *J. Solid State Chem.* **1991**, *94*, 381–385.
[35] Y.-J. Lu, J. A. Ibers, *Inorg. Chem.* **1991**, *30*, 3317–3320.
[36] M. Latroche, J. A. Ibers, *Inorg. Chem.* **1990**, *29*, 1503–1505.
[37] Y.-J. Lu, J. A. Ibers, *Comments Inorg. Chem.* **1993**, *14*, 229–243.
[38] J. A. Cody, E. J. Wu, C. M. Cheung, J. A. Ibers, *J. Solid State Chem.* **1996**, *121*, 225–229.
[39] J. A. Cody, M. F. Mansuetto, M. A. Pell, S. Chien, J. A. Ibers, *J. Alloys Compd.* **1995**, *219*, 59–62.
[40] M. A. Pell, J. A. Ibers, *Chem. Mater.* **1996**, *8*, 1386–1390.
[41] J. A. Cody, J. A. Ibers, *Inorg. Chem.* **1994**, *33*, 2713–2715.
[42] J. A. Cody, M. F. Mansuetto, S. Chien, J. A. Ibers, *Mater. Sci. Forum.* **1994**, *152–153*, 35–42.
[43] C. Adenis, V. Langer, O. Lindqvist, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1985**, *45*, 941–942.
[44] G. Busch, O. Vogt, A. Delapalme, G. H. Lander, *J. Phys. C: Solid State Phys.* **1979**, *12*, 1391–1401.
[45] H. P. Beck, W. Dausch, *J. Solid State Chem.* **1989**, *80*, 32–39.
[46] H. Noël, J. C. Levet, *J. Solid State Chem.* **1989**, *79*, 28–33.
[47] A. J. K. Haneveld, F. Jellinek, *J. Less-Common Met.* **1970**, *21*, 45–49.
[48] H. Noël, *J. Solid State Chem.* **1984**, *52*, 203–210.
[49] J. Padiou, J. Lucas, J. Prigent, *C. R. Séances Acad. Sci., Ser. C.* **1966**, *262*, 1869–1871.
[50] J. Padiou, J. Guillevic, *C. R. Séances Acad. Sci., Ser. C.* **1969**, *268*, 822–824.
[51] H. Noël, *J. Less-Common Metals.* **1980**, *72*, 45–49.
[52] N. Noël, M. Potel, *J. Less-Common Metals.* **1985**, *113*, 11–15.
[53] A. Daoudi, M. Lamire, J. C. Levet, H. Noël, *J. Solid State Chem.* **1996**, *123*, 331–336.
[54] J. A. Cody, J. A. Ibers, *Inorg. Chem.* **1995**, *34*, 3165–3172.
[55] A. C. Sutorik, J. Albritton-Thomas, T. Hogan, C. R. Kannewurf, M. G. Kanatzidis, *Chem. Mater.* **1996**, *8*, 751–761.
[56] G. Amoretti, A. Blaise, P. Burlet, J. E. Gordon, R. Troc, *J. Less-Common Met.* **1986**, *121*, 233–248.
[57] F. Hulliger, *J. Less-Common Met.* **1968**, *16*, 113–117.

[58] E. J. Wu, M. A. Pell, J. A. Ibers, unpublished results.

[59] J. A. Cody, J. A. Ibers, *Inorg. Chem.* **1996**, *35*, 3836–3838.

[60] P. Wu, J. A. Ibers, *J. Alloys Compd.* **1995**, *229*, 206–215.

[61] P. Wu, J. A. Ibers, *J. Solid State Chem.* **1993**, *107*, 347–355.

[62] A. C. Sutorik, J. Albritton-Thomas, C. R. Kannewurf, M. G. Kanatzidis, *J. Am. Chem. Soc.* **1994**, *116*, 7706–7713.

[63] P. Wu, Y.-J. Lu, J. A. Ibers, *J. Solid State Chem.* **1992**, *97*, 383–390.

[64] Y. Nakamura, A. Aruga, I. Nakai, K. Nagashima, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1718–1722.

[65] E. J. Wu, T. M. Fuelberth, M. A. Pell, J. A. Ibers, *Z. Kristallogr.*, submitted.

[66] D. Müller, H. Hahn, *Z. Anorg. Allg. Chem.* **1978**, *438*, 258–272.

[67] P. Lemoine, D. Carré, M. Guittard, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *40*, 910–912.

[68] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *197*, 171–172.

[69] B. Eisenmann, A. Hofmann, *Z. Kristallogr.* **1991**, *195*, 318–319.

[70] E. Philippot, M. Ribes, O. Lindqvist, *Rev. Chim. Miner.* **1971**, *8*, 477–489.

[71] A. Cade, M. Ribes, É. Philippot, M. Mairin, *C. R. Acad. Sci. Paris* **1972**, *274*, 1054–1056.

[72] M. Ribes, J. Olivier-Fourcade, E. Philippot, M. Maurin, *J. Solid State Chem.* **1973**, *8*, 195–205.

[73] G. Eulenberger, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32*, 3059–3063.

[74] G. Eulenberger, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36*, 521–523.

[75] B. Eisenmann, H. Schäfer, *Z. Anorg. Allg. Chem.* **1982**, *491*, 67–72.

[76] G. Eulenberger, *J. Solid State Chem.* **1984**, *55*, 306–313.

[77] K. O. Klepp, G. Eulenberger, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 705–712.

[78] B. Eisenmann, J. Hansa, H. Schäfer, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40*, 450–457.

[79] W. S. Sheldrick, B. Schaaf, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1994**, *49*, 655–659.

[80] *Binary Alloy Phase Diagrams* (Ed.: T. B. Massalski), William W. Scott, Jr., Materials Park, Ohio, **1990**.

[96144]