Reviews

Molten Alkali-Metal Polychalcogenides as Reagents and Solvents for the Synthesis of New Chalcogenide Materials

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An old molten salt technique is highlighted for its enormous potential for the synthesis of new materials. Transition- and main-group-metal chalcogenides with unusual structures can be synthesized and crystallized at relatively low temperatures (200–450 °C) from alkali-metal polychalcogenide molten salts (fluxes). Often long polychalcogenide chains are stabilized. The materials that are stable in this temperature regime are unstable at higher temperatures. The abundance of the different structure types obtained underscores the structural and bonding diversities of chalcogenide and polychalcogenide ligands in the solid state. A survey of reactions in alkali-metal polychalcogenide molten salts, known to yield new materials (with Ti, Cu, Au, Hg, and Sn), is given.

1. Introduction

The great majority of solid-state chalcogenide compounds known to date have been synthesized at temperatures higher than 500 °C.[1,2] The reason for the high-temperature conditions is primarily the fact that the starting materials are often solids (e.g., the elements of simple binary chalcogenides) and a significant diffusion of reactants is necessary for the reaction to take place and for a homogeneous product to be obtained. In some cases, frequent regrindings are necessary, which requires stopping the reaction and opening the container. This is the so-called ceramic method of synthesis. Even if a homogeneous product is obtained, the growth of single crystals, a necessary prerequisite for the proper characterization of new materials, is not readily achieved. To facilitate crystal growth, important techniques such as chemical vapor transport[3] (CVT) and molten salt[4] (or flux growth) often come to the rescue. CVT works well with binary chalcogenides but often fails with ternary systems and when alkali metals are involved. Flux growth is a promising technique and has proven to be successful in a number of binary and ternary chalcogenide systems.[5] Although there is no doubt a considerable number of new compounds remains to be discovered by high-temperature procedures,

most compounds formed at these temperatures are generally in the most thermodynamically stable modification. The synthesis of new materials becomes difficult at high temperatures because the thermodynamically stable known phases often cannot be avoided. If unusual chemical and physical properties are to be found, new kinetically stable or metastable materials must become available. Therefore, different types of syntheses must be explored.

Contrary to the extensive solid-state chemistry of compounds containing Q^{2-} ions (Q = S, Se, Te), the corresponding chemistry of Q_x^{2-} ligands is largely unknown and extends only to Q_2^{2-} compounds. For example, prior to our work, only four solid-state compounds with higher Q_x^{2-} fragments ($x \geq 3$) existed. These are NH_4CuS_4,[6] ($NH_4)_2PdS_{11}$,[7] Nb_2Se_9,[8,9] and $P_2Nb_4S_{21}$.[10] Except for the pyritic MQ_2 structure type, which is a dense three-dimensional ensemble of M^{2+} and Q^{2-} ions, the great majority of Q_2^{2-}-containing solids possess low-dimensional structures (e.g., $NbSe_3$-type compounds). If one considers the structural possibilities that exist for solids with Q_x^{2-} fragments (in which $x > 2$), it becomes apparent that low-dimensional and microporous structures will be favored because of the decreased charge/length ratio. The internal Q atoms of the Q_x^{2-} ligands have near zero formal charge and will be less likely (than external Q atoms) to participate in ternary bonding interactions with other metals. This leaves the negatively charged external Q atoms available for bonding to metal ions. For example, a Q^{2-} ion can be found to be bonded covalently with up to six metal atoms (e.g., NiS) while a Q atom in a Q_2^{2-} ligand can bind with up to three (e.g., FeS_2). For a Q_3^{2-} ion, the very few known cases (e.g., low-dimensional

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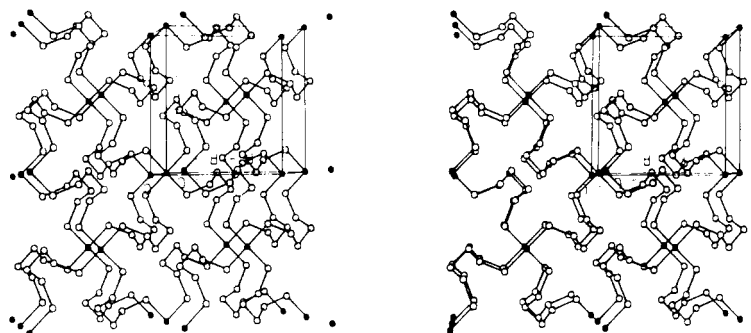
Figure 1. Perspective view of the layered $[PdS_{11}]^{2-}$ network. The NH_4^+ ions have been omitted for clarity. The S_6^{2-} ligands are disordered in the structure. Only one orientation of the S_6^{2-} ligands is shown.

$P_2Nb_4S_{21}$[10]) show that only the terminal Q atoms are involved in bonding. Chalcogen compounds of transition and main-group metals, be they molecular[11] or solid state,[12] are remarkable for their extraordinary variable bonding characteristics and structural diversity. This stems not only from the great propensity of chalcogens to bind to multiple metal centers simultaneously but also from their ability to catenate.

Low-dimensional structures are of great interest due to the variety of anisotropic electrical, optical, and magnetic properties they may possess. Polychalcogenide compounds in general are useful materials. By "polychalcogenide" I mean a compound that contains chalcogen–chalcogen bonds. For example, polysulfide ligands have been implicated as reactive species in the hydrodesulfurization (HDS) of oil and are thought to be present at the surfaces of metal sulfide catalysts.[13] Crystals of solid-state polysulfides with low-dimensional structures are likely to exhibit suitable cleavage planes with well-defined surfaces containing polysulfide ligands of known geometry and thus may serve as models for HDS surfaces. Polychalcogenide glasses are important materials for nonlinear optical, infrared wave guide, photoconductive, optical switching, and optical information storage applications.[14] The structural features of the Q_x^{2-} fragments present in these amorphous materials are not well-known. Crystalline versions of such systems will provide significant structural insight into chalcogenide glasses and help us understand their charge transport and mechanical properties. Solid-state compounds containing Q–Q bonds are capable of redox chemistry as shown in eq 1 and have been tested for uses as

$$Q-Q + 2Li \rightleftharpoons 2Q^-Li^+ \qquad (1)$$
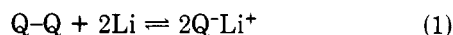
rechargeable cathode materials for high-energy density battery applications.[15] Furthermore, work concerning the reaction products of metals in alkali polysulfides is relevant to and will provide useful insight into the significant corrosion problems associated with the highly researched high-energy density Na/S battery,[16] by identifying the corrosion products and the conditions under which they form.

Polychalcogenide solids cannot be prepared by high-temperature techniques even in the excess of sulfur, because of the thermal instability of the Q_x^{2-} fragments. This instability increases with increasing x, resulting in smaller fragments as follows:

$$Q_x^{2-} \rightarrow Q_{x-n}^{2-} + nQ \qquad (2)$$
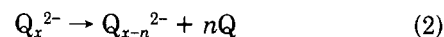
A classical example of such instability is the transformation of $TiS(S_2)$ to TiS_2 and S above 500 °C.[17] Polychalcogenide ligands are more likely to be incorporated into solid-state lattices, at lower synthesis temperatures. Although room-temperature conditions using nonaqueous solvents can yield low-dimensional polychalcogenide solids, they are not particularly conducive to single-crystal growth (although there are exceptions, vide infra). It becomes clear that low to intermediate temperatures ($T < 500$ °C) must be used for such systems. New phases stabilized at these temperatures will likely be metastable with respect to phases prepared at higher temperatures and thus may have unique properties. Surprisingly, and particularly for chalcogenides, this temperature regime has not been researched extensively for the synthesis of solid-state compounds. This intermediate temperature range is probably considered to be too hot for chemists interested in the synthesis of molecular species (lack of suitable organic solvents) and too cold for most solid-state chemists (low mobility of solid reactants) and thus tends to be avoided. Solution conditions and intermediate temperatures are more likely to favor crystal growth due to the higher mobility of dissolved species. Molten salts can provide such conditions.

Molten salts in general are well studied, can be prepared to span a wide temperature range, and thus are attractive for use as solvents for the synthesis of new chalcogenide (or other) compounds.[18] They have been used as solvents

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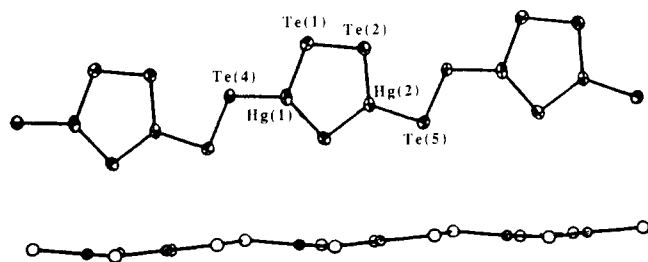(17) Heraldsen, H.; Kjekshus, A.; Rost, E.; Steffensen, A. *Acta Chem. Scand.* **1963**, *17*, 1283–1292.

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Figure 2. Two views of the one-dimensional structure of the $[Hg_2Te_5]^{2-}$ chain.

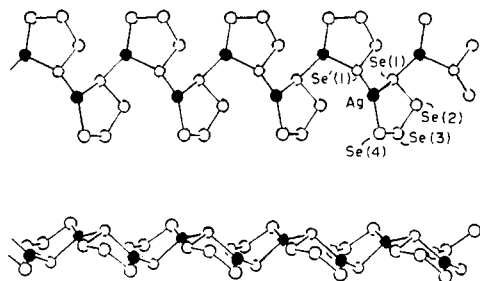**Figure 3.** Two views of the one-dimensional structure of [Ag-(Se)₄]$_n^{n-}$ chain.[22]

for more than a hundred years, primarily as high-temperature crystallization media but not as solvents for the synthesis of new materials. Three types of molten salt fluxes have been used to obtain known chalcogenide compounds: (a) metal halides, (b) metal chalcogenides, and alkali-metal polysulfides.[4a,19]

The search for materials with new structure types in several laboratories focuses on exploring the synthetic utility of molten salts as solvents/reagents at temperatures less than 450 °C. In this article, I will illustrate the potential of the technique as a synthetic tool and detail recent progress in this field.

2. Room-Temperature Synthesis of Crystalline Polychalcogenide Solids Directly from M^{n+} and Q_x^{2-}

Few metal polychalcogenide polymers have been crystallized directly out of the reaction mixture at room temperature. There are six notable structurally characterized examples thus far: $[(NH_4)Cu(S_4)]_n$,[6,20] $[(Ph_4P)_2Hg_2Te_5]_n$,[21] $[(Ph_4P)Ag(Se_4)]_n$,[22] and $[(Me_4N)Ag(Q_5)]_n$ (Q = S[23], Se[24]) and $(NH_4)_2PdS_{11}$.[7] $[(Ph_4P)_2Hg_2Te_5]_n$ has a polymeric one-dimensional structure assembled from Hg^{2+}, Te_2^{2-}, and Te^{2-} ions. $[Hg_2Te_5]^{2n-}$ is approximately flat. $(NH_4)_2PdS_{11}$ possesses a remarkable two-dimensional (2-D) structure assembled from Pd^{2+} ions and S_5^{2-} and S_6^{2-} ligands. The NH_4^+ ions fill voids in the 2-D PdS_x network. The structures of $[PdS_{11}]_n^{2n-}$ and $[Hg_2Te_5]_n^{2n-}$ are shown in Figures 1 and 2. $[(NH_4)Cu(S_4)]_n$ was obtained from aqueous ammoniacal S_x^{2-} solutions of Cu^+. $[(Ph_4P)_2Hg_2(Te_2)_2Te]_n$ was obtained from dimethylformamide solu-

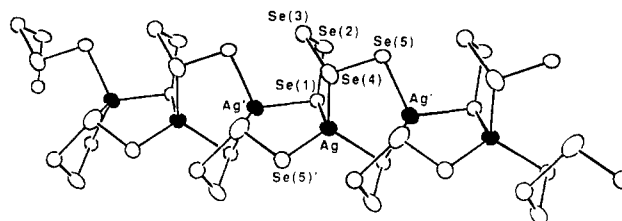**Figure 4.** One-dimensional structure of $[Ag(Se_5)]_n^{n-}$ chain.

tions extracted from K/Hg/Te alloys by the addition of Ph_4P^+. A common characteristic of these compounds is that they are salts containing anionic M/Q components and nonbonding counterions. The silver polyselenide compounds were obtained from DMF solutions at ambient temperature according to eq 3 (E = N, P).

$$Ag^+ + Na_2Se_x + R_4E^+ \rightarrow [(R_4E)Ag(Se_x)]_n \quad (3)$$
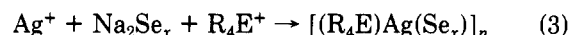
The structure of $[(Ph_4P)Ag(Se_4)]_n$ is shown in Figure 3 and contains polymerized $AgSe_4$ five-membered rings. The Ag^+ coordination sphere is trigonal planar. The Ph_4P^+ cations act as noninteracting spacers between the [Ag-(Se₄)]$_n^{n-}$ corrugated chains. The bridging mode of the Se_4^{2-} ligand in this compound is encountered in the molecular clusters $[Ag(Se_4)]_4^{4-}$ [24] and $[Cu(S_4)]_3^{3-}$.[25] The Ag---Ag distance is very long at 4.52 Å with the corresponding Ag–Se(1)–Ag angle being relatively large at 119.7°. This keeps any orbital overlap along the chain localized, thus precluding broad-band formation along the chain axis. The large Ph_4P^+ ions hold the [Ag(Se₄)]$_n^{n-}$ chains approximately 12.5 Å apart, making any possibility of interchain communication unlikely, which is consistent with the insulating properties of this material.

The structure of $[(Me_4N)Ag(Q_5)]_n$, shown in Figure 4, is composed of noninteracting Me_4N^+ cations and one-dimensional, noncentrosymmetric [Ag(Se₅)]$_n^{n-}$ macroanions. The Ag atom in [Ag(Q₅)]$_n^{n-}$ assumes tetrahedral geometry. The Q_5^{2-} ligands exhibit the unprecedented configuration shown here:
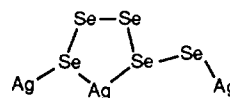
The entire [Ag(Se₅)]$_n^{n-}$ chain is made of fused five-membered $AgSe_4$ and Ag_2Se_3 rings. The shortest Ag---Ag distance is 3.786 Å. The Me_4N^+ cation keeps the [Ag-(Se₅)]$_n^{n-}$ chains approximately 9 Å apart. A better perspective on the lattice architecture of $[(Ph_4P)Ag(Se_4)]_n$ and $[(Me_4N)Ag(Se_5)]_n$ can be obtained by inspection of the packing diagrams shown in Figures 5 and 6.

It should be noted that the synthesis of these few polymeric crystalline polychalcogenides from room-temperature solutions has been serendipitous and currently there is no controlled way by which to make new ones. For example, when the counterion is changed to Pr_4N^+ and Et_4N^+, molecular, instead of polymeric, structures are isolated. If alkali-metal ions are used instead of the large organic counterions in nonaqueous organic solvents, isolation of single-crystals and homogeneous products becomes difficult if not impossible at ambient temperature. Although research in soluble molecular chalcogenides will reveal the subtle but important factors that determine cluster versus polymer formation in these systems and thus

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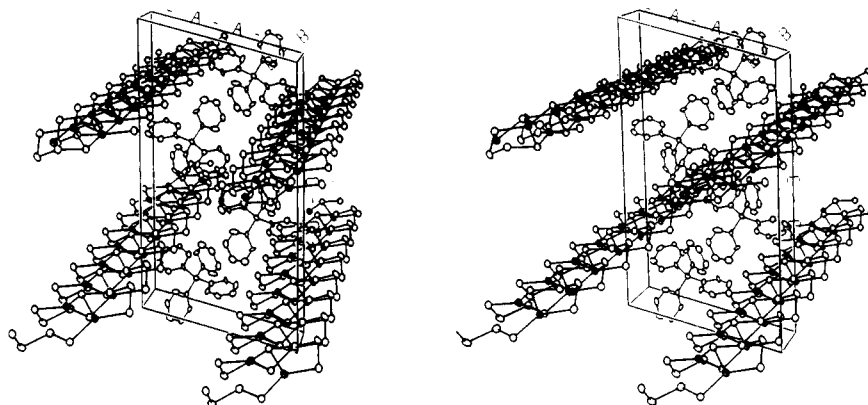
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Figure 5. Three-dimensional arrangement of the $[Ag(Se)_4]_n{}^{n-}$ chains and the Ph_4P^+ counterions. Black circles represent silver atoms.[22]
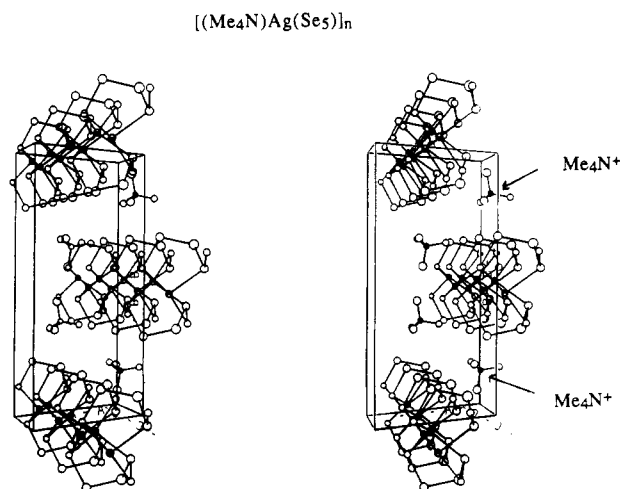
$[(Me_4N)Ag(Se_5)]_n$

Figure 6. Three-dimensional arrangement of the $[Ag(Se)_5]_n{}^{n-}$ chains and the Me_4N^+ counterions. Black circles represent silver atoms. The Me_4N^+ ions are indicated.

Figure 7. Phase diagram of the K_2S/S system. Adapted from ref 28.

allow for controlled polymer syntheses, a more reliable way for such syntheses is needed.

To date, a reliable synthetic technique for making solid-state structures with polychalcogenide fragments is not available. Work, however, on polychalcogenide melts first by Ibers et al.[26] and then by us suggests that these solvent systems are the best media, if used at <400 °C (but still not reliable) for polychalcogenide synthesis with significant probability of avoiding thermodynamic traps.

3. Alkali-Metal Polychalcogenide Melts as Solvents

The easiest way to form an alkali-metal polychalcogenide is to fuse an alkali-metal chalcogenide with a chalcogen usually above 450 °C, eq 4.

$$A_2Q + (x - 1)Q \rightarrow A_2Q_x \qquad (4)$$

The phase diagrams of alkali-metal polysulfides are the most studied compared to those of the heavier congeners. The melting points of A_2S_x lie between that of A_2S and S_8. A great deal of information is known about the A_2S/S systems (particularly Na) due to the systematic investigations prompted by the promising behavior of the sodium/β-alumina/sulfur rechargeable battery.[27] A typical
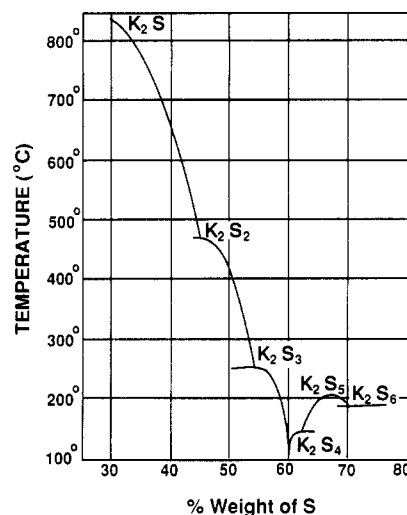
phase diagram of the K_2S/S system is shown in Figure 7.[28] The local minima in the melting point curve correspond to eutectic compositions. It is clear that for stoichiometric compositions of K_2S_x where $x \geq 3$ the melting point is well below 400 °C and reaches 160 °C for $x = 4$. Therefore, the lowest possible temperature for synthetic chemistry in this system is ca. 60 °C, which lies at the upper limit at which most organic solvents boil off or decompose, yet it is low enough to form kinetically stable products. Similar considerations apply for the other A_2Q_x systems.[29] A desirable feature of polychalcogenide melts is that upon cooling they solidify to a glassy solid. This glassy matrix can be removed by dissolution in water or nonaqueous solvent and does not interfere with the isolation of the crystalline products. In the corresponding alkali-metal polyselenides, the minimum operating temperature is somewhat higher at ~250 °C. Phase diagram information on the heavier alkali metals and chalcogen is scant, and the minimum melting points are not known. Therefore, one must proceed in an empirical fashion. The available phase diagrams of some A_2Te_x suggest melting points of ~300 °C.[29] Table I contains melting point information on most alkali-metal polychalcogenides. One important property of the polychalcogenide melts is the wide temperature range (ca.

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Table I. Melting Points (°C) of Some Known Alkali-Metal Polychalcogenides[27-29]

Li$_2$S	Li$_2$S$_2$				
900–975	369.5				
Na$_2$S	Na$_2$S$_2$	Na$_2$S$_3$	Na$_2$S$_4$	Na$_2$S$_5$	
1180	490	229	275	252	
Na$_2$Se	Na$_2$Se$_2$	Na$_2$Se$_3$	Na$_2$Se$_4$		Na$_2$Se$_6$
>875	490	490	490		258
Na$_2$Te	Na$_2$Te$_2$				Na$_2$Te$_6$
953	348				436
K$_2$S	K$_2$S$_2$	K$_2$S$_3$	K$_2$S$_4$	K$_2$S$_5$	K$_2$S$_6$
840	470	252	145	206	189
K$_2$Se	K$_2$Se$_2$	K$_2$Se$_3$	K$_2$Se$_4$	K$_2$Se$_5$	K$_2$Se$_6$
	460	380	205	190	
K$_2$Te	K$_2$Te$_2$	K$_2$Te$_3$			
Rb$_2$S	Rb$_2$S$_2$	Rb$_2$S$_3$	Rb$_2$S$_4$	Rb$_2$S$_5$	Rb$_2$S$_6$
530	420	213	160	225	201
Cs$_2$S	Cs$_2$S$_2$	Cs$_2$S$_3$	Cs$_2$S$_4$	Cs$_2$S$_5$	Cs$_2$S$_6$
	460	217	160	210	186
Cs$_2$Se					
Cs$_2$Te					

Figure 8. One-dimensional structures of (A) $[Ti_3(S_2)_6(S)_2]_n^{4n-}$ and (B) $[Ti_2(Se_2)_3(Se)_2]_n^{2n-}$. Black circles are Ti; open circles are chalcogen.[26,35]

200–800 °C) in which they remain liquid without significant evaporative chalcogen loss. This allows for great flexibility in the choice of reaction temperatures. It is significant to point out that variations in the A_2Q/Q ratio result in chemically different polychalcogenide melts and thus present a new reaction parameter that often affects the composition of the final product.

In a typical reaction, elemental metal, a metal sulfide, or halide is added to a A_2Q/Q mixture. The latter is ground to homogeneity, inserted in a silica or Pyrex tube, and sealed under vacuum. The temperature is then raised to a specified level. At that temperature, the A_2Q/Q fuses to a A_2Q_x mixture where x can vary from 3 to 6. The cooling procedure that we typically use is 2 °C/h. The products are isolated by removing the excess A_2Q_x with water or other polar solvents. The products are usually insoluble in all common organic solvents and in most cases are stable with regard to hydrolysis and air oxidation. It is obvious that this method is not useful if the products are soluble in the solvents used to remove the excess A_2Q_x. Single-crystal X-ray diffraction studies are essential to establish the nature of the new materials. It is possible that a number of reported syntheses of binary and ternary chalcogenides in which a A_2CO_3/S mixture was used are in fact syntheses in polychalcogenide molten salts.[30,31] Generation of polychalcogenides during syntheses could be envisioned as follows:

$$3K_2CO_3 + 2(x + 1)S \rightarrow 2K_2S_x + K_2S_2O_3 + 3CO_2 \quad (5)$$

Sodium polysulfide melts were used to recrystallize binary and ternary metal sulfides from high temperatures (>700 °C) by Scheel[32] and others.[33] Materials such as ZnS, CdS, MnS, PbS, NaCrS$_2$, KCrS$_2$, NaInS$_2$, KFeS$_2$, FeS$_2$, NiS$_2$, CoS$_2$, MoS$_2$, NbS$_2$, LaS$_{2-x}$, Cu$_3$VS$_4$, and HgS were grown successfully from such melts. The use of other alkali-metal polychalcogenides was suggested but not pursued. Although Scheel was aware of the potential of the polychalcogenide melts for synthesis, he was more interested in using these systems for crystal growth of known binary and ternary sulfides. This is the reason he
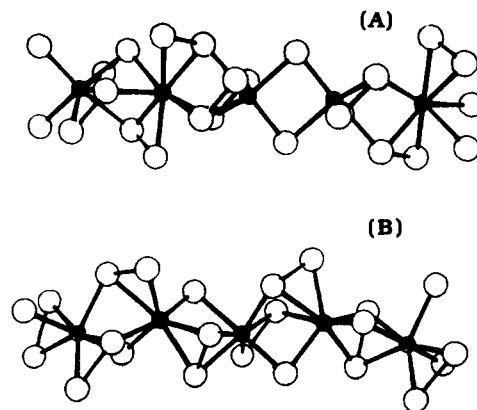
used high temperatures and sodium polysulfides as flux. In his only published paper in this area in 1974, he wrote "The polysulfides of larger alkali ions have not been investigated in detail; they are also potential solvents although the tendency of compound formation increases with ionic radius."[32]

An important point to consider about the polychalcogenide melts is that they are not only solvents but are also reagents that provide the chalcogen. The polychalcogenide environment is a highly oxidizing (corrosive) medium as well as a basic (nucleophilic) one. This property allows one to use the elemental form of the metal in a redox reaction. The basicity of the medium provides the appropriate ligand to the oxidized, positively charged metal. The recrystallization of a solid-state sulfide from such melts suggests that at some point partial or complete dissolution of the solid-state sulfide occurs through attack by the S_x^{2-} present in solution to form soluble species (see eq 6). As with hydrothermal synthesis, a dissolution–reprecipitation mechanism ("mineralizer effect") is very important and promotes crystal growth.

$$MS_n + mS_x^{2-} \rightarrow [MS_n(S_x)_m]^{z-} \quad (6)$$

Given the appropriate conditions of temperature and concentration, certain solids, known or new, could crystallize out of solution. The possibilities for synthesis of new materials using these melts are indeed enormous.

4. New Materials from Molten Polychalcogenide Salts at Intermediate Temperatures

In 1987, Ibers and co-workers published the first examples of the use of alkali-metal polychalcogenides to synthesize new solid-state chalcogenide compounds, and they pointed out the great potential for synthesis of these melts. The compounds K$_4$Ti$_3$S$_{14}$,[26,34] and Na$_2$Ti$_2$Se$_8$[35] crystallize from such melts in the temperature range 345–470 °C. These compounds contain infinite semiconducting chains of $[Ti_3(S_2)_6(S)_2]_n^{4n-}$ and $[Ti_2(Se_2)_3(Se)_2]_n^{2n-}$ respectively composed of Ti^{4+} centers bonded to Q$_2^{2-}$ and Q^{2-} ligands. The structures of these chains are shown schematically in Figure 8. These structures can be thought of as deriving from the one-dimensional structure of patronite V(S$_2$)$_2$[36] either by addition of K$_2$S (as in $[Ti_3(S_2)_6(S)_2]_n^{4n-}$) or by

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Table II. Crystal Data for Metal Polychalcogenide Phases Prepared by the Polychalcogenide Molten Salt Method in the Author's Laboratory

compd	cell parameters	space group	color	$A_2Q/M/Q$ ratio	max temp, °C
α-KCuS$_4$	a = 5.245 (1) Å, b = 8.338 (3) Å, c = 12.539 (3) Å, V = 548.4 Å^3	$P2_12_12_1$	orange red	(2–3):1:8	215
β-KCuS$_4$	a = 5.260 (2) Å, b = 16.771 (6) Å, c = 6.928 (5) Å, β = 113.52°, V = 560 (1) Å^3	$P2_1/c$	orange red	3/1/8	250
α-KCuSe$_4$	a = 5.509 (2) Å, b = 8.660 (3) Å, c = 12.826 (4) Å, V = 612 Å^3	$P2_12_12_1$	dark red	(1–4):1:8	340
α-CsCuSe$_4$	a = 5.572 (4) Å, b = 8.96 (2) Å, c = 12.88 (2) Å, V = 693 Å^3	$P2_12_12_1$	black	(1–4):1:8	310
Na$_3$AuSe$_8$	a = 16.948 (8) Å, b = 8.610 (3) Å, c = 13.931 (5) Å, β = 143.32° (2), V = 1214 Å^3	$C2/c$	golden brown	2:1:8	290
NaAuSe$_2$	a = 6.724 (8) Å, b = 8.374 (9) Å, c = 6.991 (8) Å, β = 105.23°, V = 380 Å^3	$P2_1$	black	3:1:8	290
KAuS$_5$	a = 8.310 (2) Å, b = 10.758 (3) Å, c = 15.468 (4) Å, V = 1383 Å^3	$Ibam$	golden yellow	1.8:1:8	250
KAuSe$_5$	a = 8.625 (6) Å, b = 11.293 (9) Å, c = 16.425 (11) Å, V = 1600 Å^3	$Ibam$	redish black	2:1:8	250
K$_3$AuSe$_{13}$	a = 14.949 (6) Å, b = 4.858 (2) Å, c = 13.723 (5) Å, β = 93.86° (3), V = 994 Å^3	$P2/c$	black	1.8:1:8	250
KAuSe$_2$	a = 7.699 (3) Å, b = 3.665 (1) Å, V = 217 Å^3	$P4/mbm$	metallic bluish black	1.8:2:8	250
K$_2$Hg$_3$S$_4$	a = 10.561 (5) Å, b = 6.534 (3) Å, c = 13.706 (2) Å, V = 946 Å^3	$Pbcn$	yellow	3:1:8	220
K$_2$Hg$_3$Se$_4$	a = 10.820 (2) Å, b = 6.783 (1) Å, c = 14.042 (2) Å, V = 1031 Å^3	$Pbcn$	red	3:1:8	250
Cs$_2$Hg$_3$Se$_4$	a = 12.047 (4) Å, b = 6.465 (2) Å, c = 14.771 (6) Å, V = 1150 Å^3	$Pbcn$	orange yellow	2:1:8	250
K$_2$Hg$_6$S$_7$	a = 13.805 (8) Å, c = 4.080 (3) Å, V = 778 Å^3	$P42_1m$	black	4:1:8	220
Cs$_2$Hg$_6$Se$_7$	a = 14.505 (7) Å, c = 4.308 (2) Å, V = 906 Å^3	$P4_2nm$	black		
K$_2$Sn$_2$S$_8$	a = 9.580 (8) Å, b = 10.004 (5) Å, c = 14.131 (7) Å, β = 107.82° (6), V = 1289 (3) Å^3	$P2_1/n$	orange	2:1:8	275

Figure 9. Structure of α-[CuQ$_4$] (Q = S, Se).[39]
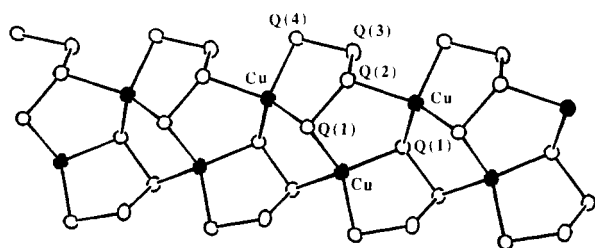
Figure 10. Structure of β-[CuS$_4$].[39]

reduction with Na (as in [Ti$_2$(Se$_2$)$_3$(Se)$_2$]$_n^{2n-}$). Both structures contain two independent Ti atoms. Those in [Ti$_3$(S$_2$)$_6$(S)$_2$]$_n^{4n-}$ are eight coordinate while those in [Ti$_2$(Se$_2$)$_3$(Se)$_2$]$_n^{2n-}$ are seven coordinate. Even molecular species can be synthesized in polychalcogenide melts. For example, K$_3$Nb$_2$Se$_{11}$ was prepared from K$_2$Se$_x$ at 375 °C and contains discrete [Nb$_4$Se$_{22}$]$^{6-}$ ions.[37]

We have used lower temperatures (200 < T < 340 °C) and attempted to obtain materials containing even higher Q$_x^{2-}$ ligands. Table II shows new compounds discovered by using the polychalcogenide molten salt synthetic method (vide infra).

4.1. The A/Cu/Q (A = K, Cs; Q = S, Se) Systems. Our initial synthetic attempts concentrated on Cu because Cu/S compounds in general exhibit interesting electrical properties and Cu potentially can form mixed-valence compounds. The reaction of Cu in molten K$_2$S$_x$ (1:3 ratio) affords several different products depending on the temperature used. In this redox reaction, Cu metal is oxidized and some K$_2$S$_4$ is reduced. At temperatures higher than 350 °C, CuS is isolated while from the 300–350 °C region KCu$_4$S$_3$ is the predominant product.[38] However, at or below 250 °C, novel polychalcogenide phases are produced.[39] α-KCuS$_4$ ($T \sim$ 210 °C) and β-KCuS$_4$ ($T \sim$ 250
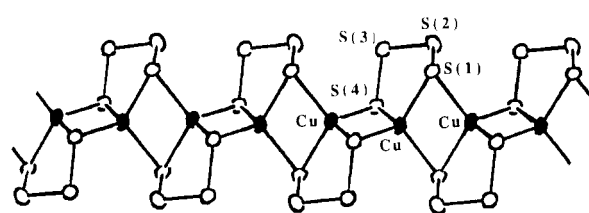
°C) form in quantitative yield as orange-red needles by slow cooling of the molten reaction mixture.

The structure of α-KCuS$_4$, shown in Figure 9, is isostructural with (NH$_4$)CuS$_4$.[6] It contains tetrasulfide ligands chelated tetrahedrally to Cu atoms and consists of noncentrosymmetric infinite chains parallel to the a axis. The chains are made of fused CuS$_4$ five-membered rings related to each other by a crystallographic 2-fold screw axis. The S$_4^{2-}$ ligand features an asymmetric bridging mode bound to three Cu$^+$ centers; the Cu–Cu distance is 3.592 (2) Å. The shortest K–S distance is 3.223 (4) Å. The Cs salt of this compound has a similar structure.

The structure of β-KCuS$_4$ is shown in Figure 10, and it is composed of centrosymmetric infinite one-dimensional chains (running parallel to the a axis) in which an almost linear array (Cu–Cu–Cu angle is 173.5°) of tetrahedral Cu atoms is bridged by S$_4^{2-}$ ligands. This bridging occurs via the terminal sulfur atoms of the chelating tetrasulfide unit and is distinct from that in the α-polymorph, resulting in an entirely new structural type. It is the only example of a single tetrasulfide ligand bonding to three almost collinear metal centers. There are two very short Cu–Cu distances at 2.607 (1) and 2.661 (1) Å. The presence of sulfide bridging ligands does not allow characterization of these short distances as bonding, although they may be viewed as d^{10}–d^{10} "attractive interactions".[45] To gain further insight into this question, theoretical band struc-

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(43) These compounds contain both linear Au$^+$ and square-planar Au^{3+} centers. The average Au$^+$–Se and Au^{3+}–Se distances are 2.42 and 2.48 Å, respectively. Rabenau, A.; Schulz, H. *J. Less-Common Met.* **1976**, *48*, 89–101.

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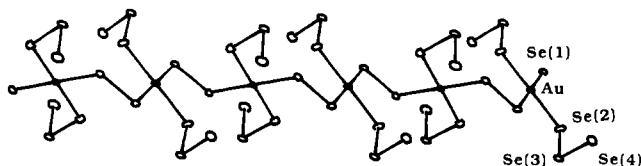
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Figure 11. Structure of the $[AuSe_8]_n^{3n-}$ chain.

Figure 12. Layered structure of $[AuSe_2]_n^{n-}$, looking perpendicular to the layers.

Figure 13. Stereoview of the packing diagram of the Na^+ salt of $[AuSe_2]_n^{n-}$, looking parallel to the layers.

ture calculations are now in progress. The β-$[Cu(S_4)]_n^{n-}$ chain can be viewed as fused five-membered CuS_4 and four-membered Cu_2S_2 rings. The center of symmetry in the β-$[Cu(S_4)]_n^{n-}$ chain lies at the center of the Cu_2S_2 rhombus. The average Cu–S distance is 2.369 (6) Å. The shortest K–S distance is 3.237 (4) Å. α-$[Cu(S_4)]_n^{n-}$ is structurally related to $[Ag(Se_4)]_n^{n-}$.[22] In the latter ion, Ag^+ exhibits trigonal planar geometry and the bridging mode of the Se_4^{2-} ligands differs from those of S_4^{2-} ligands in α-$[Cu(S_4)]_n^{n-}$.

β-$[Cu(S_4)]_n^{n-}$, or perhaps its unknown solution precursor, is probably thermodynamically more stable than the corresponding species associated with the α-polymorph. The β-form is obtained from a slightly higher temperature (250 °C) melt than that required (215 °C) for the α-polymorph. The α- to β-transformation is not reversible and only happens when in molten K_2S_x (x = 4, 5). Upon cooling from 250 °C to room temperature, no β- to α-transition is observed. This implies different solution precursors of the two phases. Similarly, once formed at higher temperatures (300 and 350 °C, respectively), CuS and KCu_4S_3 do not transform to the $KCuS_4$ polysulfide phases upon slow cooling to room temperature. Attempts to effect an α- to β-conversion by heating crystals of α-$KCuS_4$ at 250 °C in the absence of K_2S_4 solvent resulted in decomposition to CuS and K_2S_x. Quenching experiments from the maximum reaction temperature to room temperature did not result in the formation of either α-$KCuS_4$ or β-$KCuS_4$.

The alkali-metal polyselenide system requires a slightly higher temperature. Despite extensive attempts, thus far only the α-phase has been isolated. α-$ACuSe_4$ (A = K, Cs) phases can be isolated from A_2Q melts if the temperature remains in the range 250–340 °C. The needle-shaped dark-red crystals in the polyselenide systems tend to grow larger than those of polysulfides. They are semiconducting from ambient to liquid nitrogen temperature. An activation barrier of 0.88 eV was calculated from single-crystal charge transport data. Further electrical charge transport studies are in progress.[40]

4.2. The A/Au/Q System.
The Au system yields an intriguing set of new compounds with novel structural architectures and underscores the significance of the polychalcogenide molten salt method for new materials synthesis. Generally it appears that polyselenide melts favor Au^{3+} compounds while polysulfide ones favor Au^+ compounds.

In the Na/Au/Se system, we discovered two novel solid-state low-dimensional compounds. When the ratio of 2:1:8 is used and the reaction is carried out at 290 °C, golden-brown needles of Na_3AuSe_8 are formed. The structure of Na_3AuSe_8 is a remarkable one-dimensional ensemble, composed of Au^{3+} atoms bound to Se_2^{2-} and Se_3^{2-} ligands. The square-planar Au^{3+} centers are bridged by μ_2-type Se_2^{2-} ligands to form an infinite $AuSe_2$ chain. The remaining Se_3^{2-} ligands complete the square-planar coordination by binding in a trans fashion to the metal. The structure of Na_3AuSe_8 is shown in Figure 11. Adjacent $AuSe_4$ square planes within the same chain form an angle of $\sim 80°$ with one another. What is unprecedented

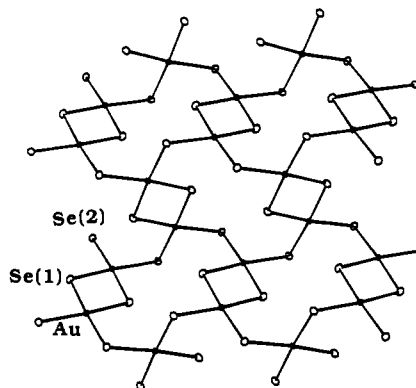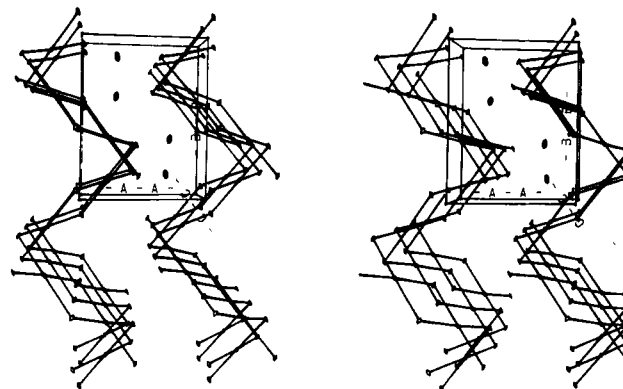in this structure is the monodentate binding mode of the Se_3^{2-} ligands, forming only one covalent bond with Au. The $[Au(Se_2)(Se_3)_2]_n^{3n-}$ chains can be viewed as the oxidative addition product of a Se_6^{2-} chain to the Au^+ atoms of a hypothetical $[AuSe_3]_n^{n-}$ chain. The average Au–Se distance is 2.49 Å while the average Se–Se distance is 2.35 Å. The other Se terminal atom is only ionically bonded to the charge balancing Na^+ atom. The minimum Na–Se distance is 2.937 Å.

When the Na/Au/Se ratio is increased to 3:1:8, another new phase, which does not possess polyselenide ligands, $NaAuSe_2$, forms. The stucture is shown in Figure 12. It is composed of a covalently bonded $[AuSe_2]_n^{n-}$ anionic layered network, counterbalanced by Na^+ ions. It represents a new structure type for an MX_2 stoichiometry. The average Au–Se distance in $NaAuSe_2$ is 2.48 Å. The layers are made of polymerized $[Au_2Se_2]Se_2$ dimeric units with a central rhombic $[Au_2Se_2]^{2+}$ core. The Au^{3+} center is strictly square planar. The dimensions of the $[Au_2Se_2]^{2+}$ core in $NaAuSe_2$ are similar to those in molecular $[Au_2Se_{10}]^{2-}$.[41] The mean intracore Au–Au distance in the $[AuSe_2]_n^{n-}$ sheets is 3.73 Å; between Au_2Se_2 units, the Au–Au distance is 3.91 Å. The $[AuSe_2]_n^{n-}$ layers are not flat and form corrugated sheets that stack in phase in the c direction, as shown in Figure 13. The minimum Na–Se distance is 2.916 Å. It is evident that chalcogen-rich melts favor Na_3AuSe_8 while increased amounts of Au favor $NaAuSe_2$.

Substitution of K^+ for Na^+ results in different structure types.[42] The structure of K_3AuSe_{13} shown in Figure 14 is even more intriguing. This is a Au^{3+} compound, composed of centrosymmetric one-dimensional $[Au(Se_3)(Se_5)_2]_n^{3n-}$ chains running parallel to the c axis. The chains can be described as a one-dimensional assembly of square-planar
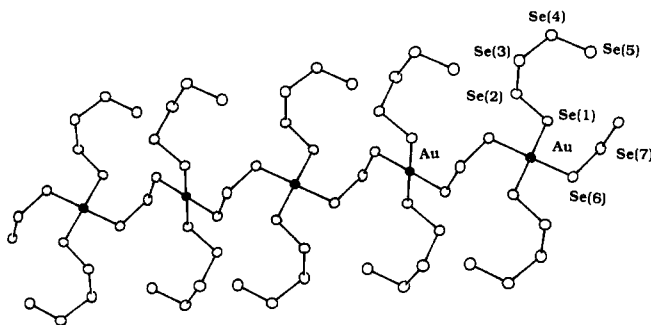
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Figure 14. Structure of the $[AuSe_{13}]_n^{3n-}$ chain.

(A)   (B)
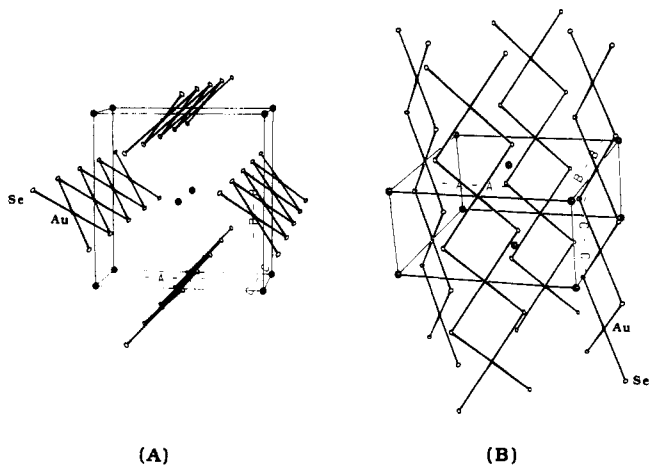
Figure 15. One-dimensional structure of the K^+ salt of $[AuSe_2]_n^{n-}$. Two views.

Figure 16. One-dimensional structure of $[AuSe_5]_n^{n-}$ showing the mode of dimerization.

Au^{3+} centers (situated on a center of symmetry) that have two arm-like trans Se_5^{2-} ligands and are bridged by Se_3^{2-} ligands. The Au---Se distances compare well with the corresponding distances in $AuSe^{43}$ (2.48 Å) and in molecular $[Au_2Se_{10}]^{2-41}$ (2.45 Å). The average Au–Se and Se–Se distances are 2.47 and 2.35 Å, respectively. The K^+ ions reside in cavities created by the Se atoms in the polyselenide chains. K_3AuSe_{13} is the first solid-state compound to contain both Se_3^{2-} and Se_5^{2-} ligands and to our knowledge it is the most Se-rich Au compound to date. The $[Au(Se_3)(Se_5)_2]_n^{3n-}$ chains can be viewed as the oxidative addition product of a Se_{10}^{2-} chain to the Au^+ atoms of a hypothetical $[AuSe_3]_n^{n-}$ chain. Like homologous $[Au(Se_2)(Se_3)_2]_n^{3n-}$, $[Au(Se_3)(Se_5)_2]_n^{3n-}$ represents another remarkable example of a monodentate long polyselenide (Se_5^{2-}), where one negative end is coordinated to a transition metal while the other is loose, ionically interacting with an alkali ion.

If more Au is added in the melt, $KAuSe_2$ is formed. This is a one-dimensional compound with a $PdCl_2$-structure-type[44] $[AuSe_2]$ unit. Figure 15 shows the flat ribbons made of edge-sharing $AuSe_4$ square planes. They are similar to the structure of $[PdS_2]_n^{2n-}$.[12a] The Au–Au distance is 3.66 Å. The Au–Se distance is 2.475 Å, and the Au–Se–Au angle is 95.5°. Crystals of $KAuSe_2$ cleave easily, yielding long thin fibers with metallic shine. It is interesting to compare and contrast the structure of the $[AuSe_2]_n^{n-}$ framework in the Na^+ and K^+ salts. The layered versus one-dimensional structure is a clear manifestation of a counterion size effect. Substitution of Na^+ for K^+ in the $KAuSe_2$ structure would result in a significant decrease in the cation partial volume, which would bring the $[AuSe_2]_n^{n-}$ chains close enough that considerable Coulombic interchain repulsions might develop, thus destabilizing the structure. These repulsions could be overcome by com-
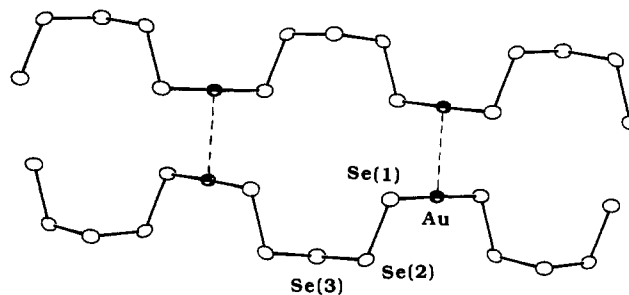
bining the chains into layers through interchain Au–Se bonding.

The redox chemistry associated with the $Au^{1+/3+}$ ions in conventional solutions is also expressed in the polychalcogenide melts. An Au^+ compound, $KAuSe_5$, forms when the $K_2Se/Au/Se$ ratio is 2:1:8.[42] The structure of $KAuSe_5$ is shown in Figure 16. It is comprised of covalent one-dimensional $[AuSe_5]_n^{n-}$ anionic chains and charge compensating K^+ ions. The $[AuSe_5]_n^{n-}$ chains are composed of Se_5^{2-} ligands bridging two Au atoms via terminal Se atoms. The structure of $[AuSe_5]_n^{n-}$ chains can be derived from the structure of polymeric selenium by substitution of a Au^+ atom for every sixth Se atom. The Au^+ centers are linear with a Se–Au–Se bond angle of 179.0° (2). The $[AuSe_5]_n^{n-}$ chains are noncentrosymmetric and possess a mirror plane passing through the Se(3) atom and bisecting the pentaselenide fragment. The bridging mode of the Se_5^{2-} ligands in $[Au(Se_5)]_n^{n-}$ is similar to that of the Se_3^{2-} ligands in $[Au(Se_3)(Se_5)_2]_n^{3n-}$. These chains interact with each other to form dimers through close Au---Au d^{10}-d^{10} contacts,[45] 2.950 (3) Å, as depicted in Figure 18. The Au–Au contacts are considerably shorter than those observed in $KAuSe^{46}$ and α- and β-$AuSe^{43}$ and comparable to those in Ag_3AuSe_2.[47] The observed Au–Se bond distances (2.410 (4) Å) are similar to those found in $KAuSe^{46}$ at 2.414 (1) Å. The average Se–Se bond distances in $KAuSe_5$ are normal (2.353 (6) Å) and in the range found for other Se–Se bond distances in polyselenide complexes.[22] The shortest K---Se distances in $KAuSe_5$ are K(1)–Se(1) 3.339 (4) Å and K(2)–Se(1) 3.384 (4) Å. Similar synthetic investigations showed that the redox chemistry in the corresponding potassium polysulfide systems, is not as pervasive as in the polyselenides, and Au^+ compounds are more common. Thus far, only isostructural $KAuS_5$ has been characterized.[48] It has close 2.963 (3) Å Au–Au contacts.

The slight but significant variation in the polyselenide melt (solvent) composition and the isolation of both Au^+ and Au^{3+} polyselenide compounds highlight the complexity of these reaction mixtures and the delicate coordination and redox equilibria present among various Au^{m+} ($m = 1$, 3) and Se_x^{2-} species.

4.3. The A/Hg/Q System. Hg and HgQ react with A_2Q_x melts and give rise to new structure types, $K_2Hg_6S_7$ and $K_2Hg_3S_4$.[49] The structure of $K_2Hg_6S_7$ is unusual. Although the Hg^{2+} and S^{2-} atoms form a 3-D network, the structure clearly possesses 1-D character. There are clearly visible 1-D tunnels running through the lattice parallel to the crystallographic c axis, as shown in Figure 17. Two different sets of parallel tunnels exist. A set of empty,

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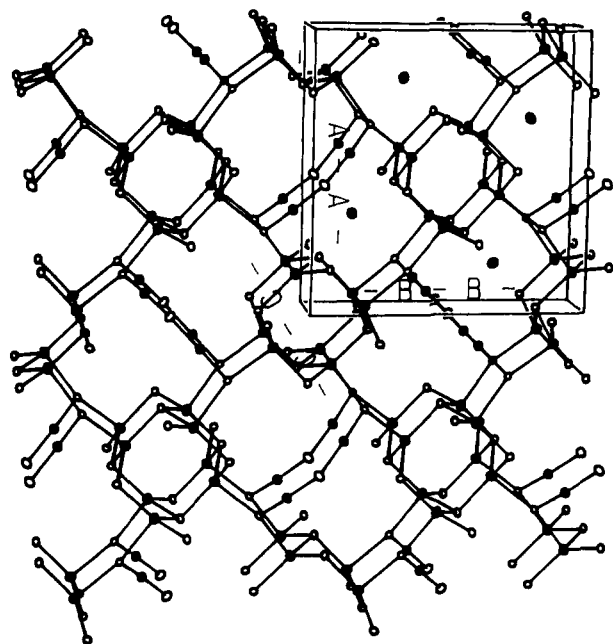(49) Kanatzidis, M. G.; Park, Y. *Chem. Mater.* **1990**, *2*, 99–101.

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Figure 17. Three-dimensional framework structure of $K_2Hg_6S_7$.[49]

(A)

(B)

Figure 18. One-dimensional structure (two views) of the $[Hg_3Q_4]_n^{2n-}$ chain.[49]

Figure 19. Stereoview of the layered structure of the $[Sn_2S_8]^{2-}$ network looking down the (010) axis.

narrow tunnels of ca. 4.77-Å diameter with an octagonal cross section is composed of tetrahedral (distorted) Hg^{2+} and trigonal pyramidal S^{2-} ions. A second set of wider tunnels have a 12-membered ring cross section composed of both tetrahedral and linear Hg^{2+} ions, "glued" together by triply and doubly bridging S^{2-} ions. One triply bridging S^{2-} ion assumes an unusual T-type coordination as shown here:

$$Hg(1)\!\!-\!\!\!\!\!\underset{\displaystyle |\atop\displaystyle Hg(2)}{S(3)}\!\!\!\!\!-\!\!Hg(1)$$
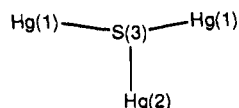
The $Hg(1)-S(3)-Hg(1)$ and $Hg(1)-S(3)-Hg(2)$ angles are 158.1° and 100.9°, respectively. The coordination of the $Hg(1)$ atoms is tetrahedral while that of the $Hg(2)$ atoms is linear. The $Hg(1)-S(3)$ bonds are unusually long at 2.718 (4) Å while the $Hg(2)-S(3)$ bonds are normal (for two coordinate Hg^{2+} ion) at 2.345 (8) Å. There are two kinds of Hg–S bonds in $K_2Hg_6S_7$. A set of long bonds (range 2.467 (5)–2.718 (5) Å) is associated with the tetrahedral Hg^{2+} centers and a set of short ones (range 2.345 (8)–2.366 (9) Å) with the linear Hg^{2+} centers.

The K^+ ions are found inserted in the center of the large tunnels, interacting with the chalcogenide lone pairs, which are directed toward the tunnel center. The K---S distances are found in the range 3.299–3.618 Å. The K^+ ions fit snugly in these channels. Substitution of S by Se cannot stabilize the isostructural compound. The enlarged Hg–Se channels, however, can accommodate the larger Cs^+ ions and results in a stable nearly isostructural compound, $Cs_2Hg_6Se_7$.[48]

$K_2Hg_3Q_4$ forms when the K_2Q/Q ratio is increased. The structure of $K_2Hg_3Q_4$ is composed of centrosymmetric one-dimensional $[Hg_3Q_4]_n^{2n-}$ chains parallel to the *b* axis, as shown in Figure 18. The chains can be regarded as a one-dimensional assembly of distorted tetrahedral $[HgQ_4]^{6-}$ building blocks connected by two-coordinate Hg^{2+} ions. Alternatively, it can be viewed as a one-dimensional spiro polymer of eight-membered Hg_4Q_4 rings. As in $K_2Hg_6S_7$, there are two sets of long and short Hg–Q bonds in this structure type, associated with tetrahedral and quasi-linear Hg^{2+} centers, respectively. The average Hg–Q distances are (a) for tetrahedral centers Hg–S 2.57 Å and Hg–Se 2.66
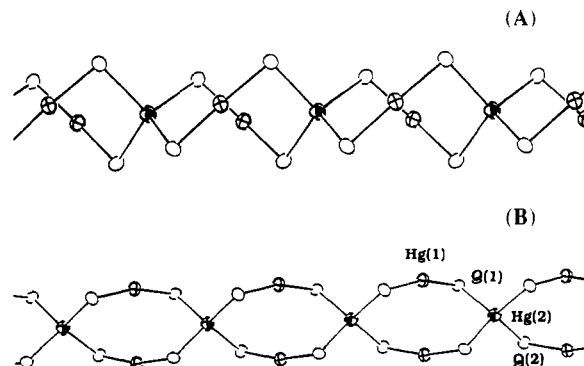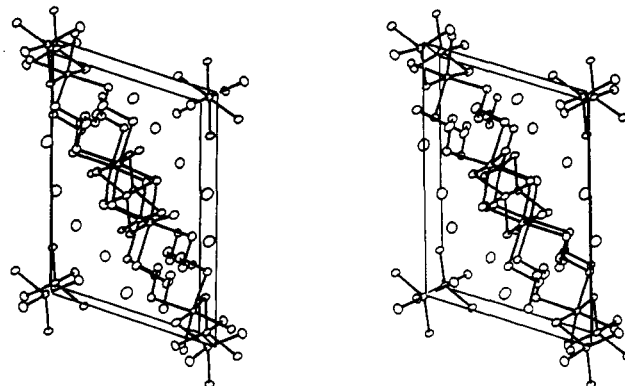
Å and (b) for linear centers Hg–S 2.37 Å and Hg–Se 2.48 Å. Isostructural $Cs_2Hg_3Se_4$ can be prepared from the corresponding cesium melt.

$A_2Hg_3Q_4$ (A = K, Cs; Q = S, Se) and $K_2Hg_6S_7$ belong to a new general family with the chemical formula $(A_2Q)_n\!\cdot\!(HgQ)_m$ (A = alkali metal). It should be noted that alkali-metal polychalcogenide melts are not essential to form some members of the $(A_2Q)_n(HgQ)_m$ family. For example, $Cs_2Hg_6Se_7$ was obtained by direct solid-state reaction of Cs_2Se and HgSe at a higher temperature (i.e., 370 °C).

The structures of $(A_2Q)_n(HgQ)_m$ derive from the successive dismantling of the three-dimensional adamantine structure of HgS,[50] as it attempts to accommodate the varying amounts of A_2Q. Thus, the μ_4-coordination of the Q^{2-} ions in the HgQ structure is reduced to μ_3- and μ_2-coordination in $[Hg_6Q_7]_n^{2n-}$ and to only μ_2-coordination in $[Hg_3Q_4]_n^{2n-}$. K_6HgQ_4[51] also belongs to this homologous family (where $n = 3$, $m = 1$) but it contains tetrahedral $[HgQ_4]^{6-}$ units (the HgQ lattice has been broken up to individual $[HgQ_4]^{6-}$ units). This is very similar to the successive breakup of the structures of the main-group elements (e.g., Si, P) that ensues upon reduction with very electropositive metals to form the familiar Zintl phases.[52] It is likely that the A_2Q/HgQ system constitutes an infinitely adaptive pair similar to the $(BaS)_n(FeS)_m$[53] and $(ZnS)_n(In_2S_3)_m$[54] systems.

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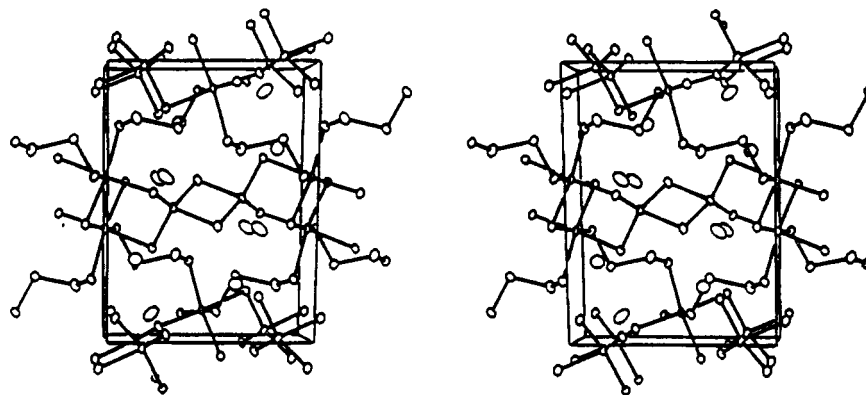
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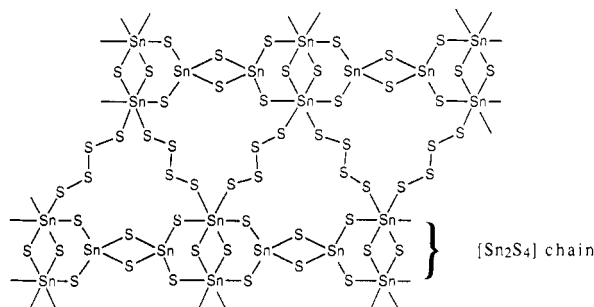**Figure 20.** Stereoview of the layered structure of $[Sn_2S_8]^{2-}$ network looking down the (100) axis.

Figure 21. Schematic representation of the $[Sn_2S_8]^{2-}$ layers.

4.4. Reactions with Sn. Main-group elements are expected to form Zintl-like compounds with metal–chalcogen covalent networks. The existence of $K_4Ti_3S_{14}$ and $Na_2Ti_2Se_8$ kindled our interest to investigate Sn, another potentially tetravalent metal on the opposite side of the periodic table, which can form compounds isostructural with Ti. The orange $K_2Sn_2S_8$ can be isolated in high yield as small chunky crystals.[55] This water-stable compound has an unprecedented layered structure, shown in Figures 19 and 20. $K_2Sn_2S_8$ is not isostructural to $Na_2Ti_2Se_8$. Two structurally distinct tetrahedral and octahedral Sn atoms occur in the structure. Interestingly, these metal centers are bound together by sulfide and tetrasulfide ligands. Thus the accurate formulation of the material would be $K_2Sn_2S_4(S_4)$. The tetrahedral Sn ions are bound only by S^{2-} ligands while the octahedral ones are bonded to both S^{2-} and S_4^{2-} ligands. The average Sn–S distances in the SnS_4 tetrahedra and SnS_6 octahedra are 2.42 and 2.57 Å, respectively. The $[Sn_2S_8]_n^{2n-}$ layers are parallel to the (101) crystallographic plane. This structure is assembled by cross-linking one-dimensional $[Sn_2S_4]$ parallel chains with S_4^{2-} ligands, as shown schematically in Figure 21. The $[Sn_2S_4]$ chains are composed of edge-sharing SnS_4 tetrahedral that then corner share with two edge-sharing SnS_6 octahedra; see Figure 22. The only other anionic layered Sn/S network is found in the hydrothermally synthesized $[Sn_5S_{12}]_n^{4n-}$,[56] which also features two different Sn environments, trigonal-bipyramidal and octahedral.

5. Concluding Remarks

A new class of chalcogenide materials is accessible at intermediate temperatures using low-melting alkali-metal polychalcogenides as solvents. The latter are now proven to be a significant synthetic tool in the field of chalcogenide chemistry. The low-dimensional compounds presented
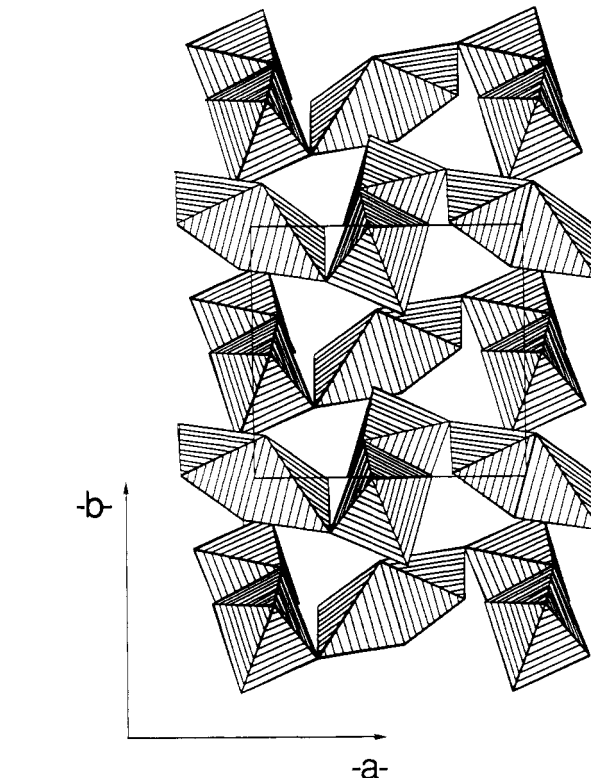
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Figure 22. Polyhedral representation of the coordination SnS_4 tetrahedra and SnS_6 octahedra in the $[Sn_2S_8]^{2-}$ network. The K^+ ions and S_4^{2-} ligands are not shown. View down the (001) axis.

here are beautiful examples of the structural diversity and bonding flexibility expressed by the chalcogenide ligand family in the solid state and rival that found in soluble molecular species. The incorporation of structural units normally encountered in molecular chalcogenide complexes into polymeric structures should stimulate the interest of both molecular and solid-state chemists. This, essentially, solution, synthetic technique may eventually allow reaction control, currently available (only to some extent) in molecular chalcogenide chemistry. It could serve as an interface area between high- and low-temperature synthesis and should help bridge the ever narrowing chasm between molecular and solid-state chemistry. The remarkable ability of Q_x^{2-} ligands to bridge different substructures in two and three dimensions and the very large number of compounds accessible by this synthetic route advocate the considerable potential for discovering new low-dimensional and even three-dimensional microporous solids containing polychalcogenide fragments as building blocks. What the properties of the new materials will be still remains to be seen. As a bonus, these new compounds may in fact be

the corrosion products found at the electrode interfaces of alkali metal/sulfur cells. Corrosion impedes the development of these cells, and thus any new insight into this problem will be useful in designing suitable electrode materials.

It is evident that this is an exciting new synthetic area and thus far only the surface has been scratched. The bulk of this work and even more interesting chalcogenides are yet to come.

Articles

Amorphous Metallic Powders Prepared by Chemical Reduction of Metal Ions with Potassium Borohydride in Aqueous Solution

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Amorphous metal–metalloid powders have been prepared by chemical reduction of Fe^{2+}, Co^{2+}, and Ni^{2+} ions with potassium borohydride in aqueous solution. The chemical composition of the samples, TM–B–O, varies with the metal and with the preparation steps. The as-prepared Co–B–O and Ni–B–O samples are definitely amorphous, while the Fe–B–O sample mainly consists of bcc α-Fe. Crystallization of the samples through thermal treatment has been investigated by X-ray diffraction. The Co–B–O sample evolves toward fcc metallic cobalt accompanied first by metastable o-Co_3B and, at high temperature, by t-Co_2B. The Ni–B–O sample gives rise to fcc metallic Ni and o-Ni_3B, which decomposes at higher temperatures. Iron borides are not detected in the thermal treatment of the Fe–B–O sample. No evidence of metal oxides is present in all the samples, thus suggesting the prevalent bonding of oxygen to boron.

Introduction

The science and technology of amorphous alloys is increasing rapidly in view of some excellent physical and mechanical properties of these materials.[1]

Conventional preparation methods by rapid quenching lead to ribbons[1] and thin foils,[2] which to be compacted in a three-dimensional object need to be comminuted. To avoid grinding, which is difficult and expensive because of the high ductility of these materials, methods for preparing amorphous alloy powders are being developed: among these, several atomization techniques,[3] vapor deposition,[4] and mechanical alloying[5] have been reported. All of these methods suffer certain drawbacks that make them impractical for the preparation of significant quantities of homogeneous alloys. Wet chemical synthetic methods offer an alternative to these problems as well as the opportunity to control certain factors in order to meet the needs of the end user.

Reduction of metal salts has been widely reported for the preparation of highly dispersed and reactive metal powders with particular attention to their application in catalytic and stoichiometric chemical synthesis.[6–9] Recently the amorphous structure of metal powders obtained by reduction of metal salts with alkaline borohydrides has been outlined;[10–14] the prepared powders are very complex materials, which have properties strongly dependent upon the metals and some of the preparation steps.

Further investigations carried out on amorphous powder obtained by reduction of Ni^{2+}, Co^{2+}, and Fe^{2+} cations with KBH_4 are reported in this paper.

Experimental Section

Metallic powders containing either Co, Ni, or Fe were prepared according to Schlesinger et al.[15] and Brown and Brown.[6] In a typical preparation 0.2 mol of solid KBH_4 was slowly added, in

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