Alignment of the NLO side groups in the layers was achieved by single-point corona poling, with the point source held at +10 kV, at a distance of 1.5 cm from the surface. Poling voltages greater than 10 kV sometimes resulted in damage to the film, manifested as a slight cloudiness. Note, however, that this voltage was still below the saturation point of the signal. The variation of the signal with poling voltages will be discussed more fully in a later publication. Due to the low glass transition temperature of 1 (T_g = 25 °C), the poling was carried out at room temperature while the SHG measurements were being made. Upon removal of the voltage, the second-harmonic signal decayed to zero within a few minutes.

The second-harmonic coefficient of the polymer film, d_{33}, was obtained from a Maker fringe analysis of the data,[10] giving d_{33} = 5.5 pm/V. This value of d_{33} was obtained by using the isotropic model for poled polymers, where d_{33}/d_{31} = 3.[2a] Singer et al.[3d] have found this model to be appropriate for analysis of their side-chain polymers. Recently, however, Eich et al.[3e] have observed deviations from this ratio, possible due to mesogenic interactions among the side groups. The applicability of the isotropic model to poly(organophosphazenes) is currently under investigation.

Given that the degree of alignment was not maximized in this experiment and that we are using a less efficient donor moiety than other studies of functionalized polymers,[2c,3d] this is a very promising value of d_{33}. Work to attach more efficient donors and to increase the glass transition temperature of the polymer is in progress.

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Molten Salt Synthesis of Low-Dimensional Ternary Chalcogenides. Novel Structure Types in the K/Hg/Q System (Q = S, Se)

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Recently we demonstrated that by using alkali-metal polysulfide melts as solvents at intermediate temperatures (i.e., 150–350 °C), novel, low-dimensional solid-state compounds can be isolated in crystalline form.[1] This intermediate temperature regime has not been explored as a synthetically useful area.[2] It has been regarded by molecular coordination chemists as too hot for any normal solvents to be stable and stay in liquid form and by classical solid-state chemists as too cold for most reactions to proceed. This is particularly true in chalcogenide chemistry.[3] We believe that an enormous number of interesting and perhaps metastable compounds occur at these temperatures and could be crystallized, provided suitable solvents are available. Molten salts have been well studied[4] and can be prepared to exhibit a wide range of temperatures at which they remain liquid and thus are appropriate media for synthetic applications. Indeed they have been used as such at high temperatures.[5] Alkali-metal polychalcogenide melts in particular are very interesting because melting points as low as ~150 °C can be achieved[6] and can serve as solvents as well as reagents (i.e., chalcogen and alkali-metal donors). Recrystallizations of binary sulfides have been accomplished in these melts at high (>700 °C) temperatures.[7] The purposeful use of these systems for synthesis of new materials has not been seriously pursued. Low-dimensional chalcogenides are of intense interest due to their useful electronic[8] and catalytic[9]

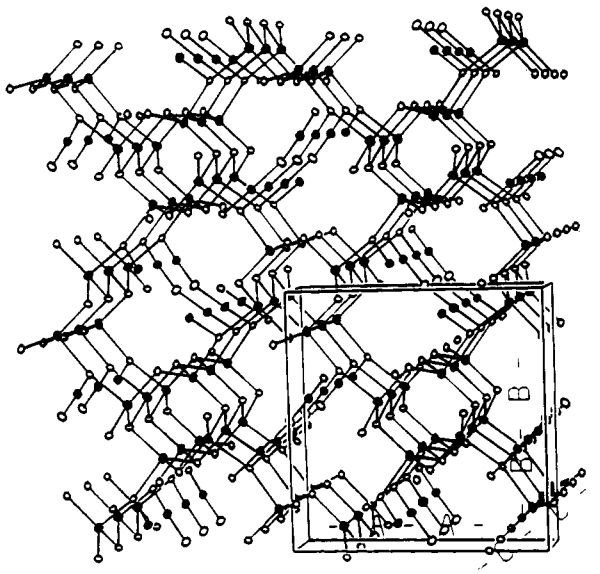

Figure 1. Three-dimensional structure of the $[Hg_6S_7]_n^{2n-}$ network.[17,18] The K atoms have been omitted for clarity. The Hg atoms are represented by black circles and the sulfur atoms by open circles. The S–Hg–S angle about the two-coordinate Hg atom is 172.4 (4)°.

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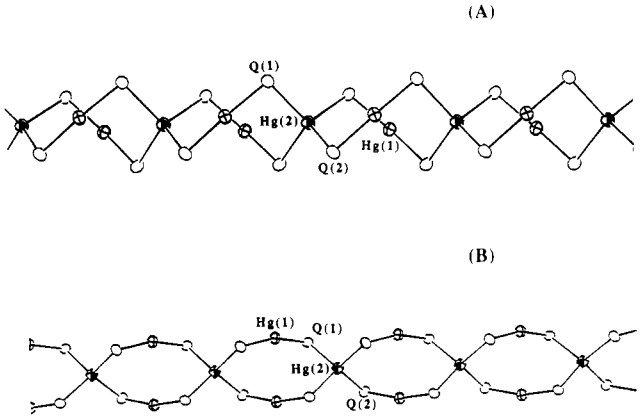
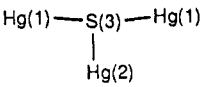


Figure 2. Two views of the one-dimensional structure of $[Hg_3Q_4]_n^{2n-}$ with labeling scheme. Selected distances (Å): $K_2Hg_3S_4$: Hg(1)–S(1), 2.36 (1); Hg(1)–S(2), 2.38 (1); Hg(2)–S(1), 2.58 (1); Hg(2)–S(2), 2.56 (1). Selected angles (deg): S(1)–Hg(1)–S(2), 165.3 (3); S(1)–Hg(2)–S(2), 105.7 (3); S(2)–Hg(2)–S(2), 111.0 (4); S(1)–Hg(2)–S(1), 104.7 (3); S(1)–Hg(2)–S(2), 114.9 (3); Hg(1)–S(1)–Hg(2), 96.5 (3); Hg(1)–S(2)–Hg(2), 95.8 (3). $K_2Hg_3Se_4$: Hg(1)–Se(1), 2.486 (6); Hg(1)–Se(2), 2.474 (6); Hg(2)–Se(1), 2.671 (6); Hg(2)–Se(2), 2.657 (6). Se(1)–Hg(1)–Se(2), 164.2 (2); Se(1)–Hg(2)–Se(2), 104.4 (2); Se(2)–Hg(2)–Se(2), 110.7 (2); Se(1)–Hg(2)–Se(1), 106.2 (2); Se(1)–Hg(2)–Se(2), 115.7 (2); Hg(1)–Se(1)–Hg(2), 95.7 (2); Hg(1)–Se(2)–Hg(2), 95.8 (2).

properties, and therefore new such materials and/or methods of synthesis are highly desirable.[10] Recently the compounds $K_4Ti_3S_{14}$,[11] $Na_2Ti_2Se_8$,[12] and $K_3Nb_2Se_{11}$[13] were reported to form in polychalcogenide melts at 340–375 °C. In this report we show that alkali-metal polychalcogenide melts at 210–250 °C promote the synthesis and crystal growth of the new ternary compounds $K_2Hg_6S_7$ and $K_2Hg_3Q_4$ (Q = S, Se), which feature novel structure types.

The reaction of 0.348 g (2 mmol) of K_2S_3 and 0.100 g (0.50 mmol) of Hg (or HgS) in an evacuated Pyrex tube at 210 °C for 3 days afforded black needle-shaped crystals of $K_2Hg_6S_7$ (I) in quantitative yield. The product was isolated by removing the excess K_2S_3 by water. Alternatively, the reaction of 0.310 g (1.5 mmol) of K_2S_4 and 0.116 g (0.5 mmol) of HgS in an evacuated Pyrex tube at 220 °C for 4 days afforded yellow hexagon-shaped, light- and moisture-sensitive $K_2Hg_3S_4$ (II). This product was isolated under nitrogen atmosphere by dissolving the excess K_2S_4 with dimethylformamide. The isomorphous selenium analogue, $K_2Hg_3Se_4$ (III), was synthesized in an analogous manner at 250 °C.[14] The structures of these materials were established by single-crystal X-ray diffraction studies.[15]

The structure type of $K_2Hg_6S_7$ is unique. Although the Hg^{2+} and S^{2-} atoms are assembled in three dimensions, the structure clearly possesses one-dimensional (1-D) character. There are clearly visible 1-D tunnels running through the lattice parallel to the crystallographic c axis, as shown in Figure 1. Two different sets of parallel tunnels exist. A set of empty, narrow tunnels with an octagonal cross section composed of tetrahedral (distorted) Hg^{2+} and trigonal-pyramidal S^{2-} ions. The diameter of these narrow tunnels is ca. 4.77 Å. A second set of wider tunnels have 12-membered ring cross section in which both tetrahedral and linear Hg^{2+} ions exist and are "glued" together by triply and doubly bridging S^{2-} ions. One triply bridging S^{2-} ion assumes a T-type coordination as shown here: 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.

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. This structure type is reminiscent of a 3-D zeolite-like network.[16] The K···S distances are found in the range 3.299–3.618 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) associated with the linear Hg^{2+} centers.[17,18]

The structure of $K_2Hg_3Q_4$ is shown in Figure 2. It is composed of centrosymmetric one-dimensional $[Hg_3Q_4]_n^{2n-}$ chains running parallel to the b axis. The makeup of 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 spiropolymer 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. Selected bond distances for $K_2Hg_3Se_4$ are given in the caption of Figure 2.

The compounds $K_2Hg_3Se_4$ and $K_2Hg_3S_4$ decompose rapidly in moist air and light to form black HgQ. Both types of compounds, $K_2Hg_3Q_4$ and $K_2Hg_6S_7$, can be regarded as members of a new general family with the chemical formula $(A_2Q)_n(HgQ)_m$ (A = alkali metal). Their

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(15) (a) Crystal data for $K_2Hg_6S_7$: tetragonal $P\bar{4}2_1m$ $Z = 2$, $a = b = 13.805$ (8) Å, $c = 4.080$ (3) Å, $V = 778$ Å^3 at 25 °C. $2\theta_{max}$(Mo Kα) = 50°. Number of data measured, 1614. Number of unique data, 453. Number of data having $F_o^2 > 3\sigma(F_o^2)$, 402, Number of variables, 42. Number of atoms, 6. $\mu = 604$ cm^{-1}. Final $R = 0.031$ and $R_w = 0.036$. (b) Crystal data for $K_2Hg_3S_4$: orthorhombic *Pbcn*, $Z = 4$, $a = 10.561$ (5) Å, $b = 6.534$ (3) Å, $c = 13.706$ (2) Å, $V = 946$ Å^3 at 25° C. $2\theta_{max}$(Mo Kα) = 50°. Number of data measured, 2953. Number of unique data, 831. Number of data having $F_o^2 > 3\sigma(F_o^2)$, 326, Number of variables, 33. Number of atoms, 5. $\mu = 502$ cm^{-1}. Final $R = 0.057$ and $R_w = 0.063$. (c) Crystal data for $K_2Hg_3Se_4$: orthorhombic *Pbcn*, $Z = 4$, $a = 10.820$ (2) Å, $b = 6.783$ (1) Å, $c = 14.042$ (2) Å, $V = 1030.6$ Å^3 at −120 °C. $2\theta_{max}$(Mo Kα) = 50°. Number of data measured, 1088. Number of unique data, 903. Number of data having $F_o^2 > 3\sigma(F_o^2)$, 567, Number of variables, 43. Number of atoms, 5. $\mu = 593$ cm^{-1}. Final $R = 0.077$ and $R_w = 0.084$. An empirical absorption correction based on ψ-scans for several reflections was applied to all data sets.

(16) *Atlas of Zeolite Structure Types*: Meier, W. M., Olson, D. H., Eds.; Butterworths: London, 1988.

(17) A full account of this complex structure will be given elsewhere.

(18) Bonds and angles along with atomic labeling for this structure are given in the supplementary material.

structure types can be viewed as deriving from the successive dismantling of the three-dimensional adamantine structure of HgS[19] as it attempts to accommodate the varying amounts of added A_2Q. For example 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 $[Hg_3Q_4]_n^{2n-}$. Another phase that also belongs to this homologous family is K_6HgQ_4[20] ($n = 3$, $m = 1$), which features discrete tetrahedral $[HgQ_4]^{6-}$ units (the HgQ lattice has been reduced 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.[21]

The results reported here show that the three-dimensional structure of HgQ is tractable and can accommodate various amounts of alkali-metal monosulfides. It is likely that the A_2Q/HgQ system constitutes an infinitely adaptive pair similar to the $(ZnS)_n(In_2S_3)_m$[22] and $(BaS)_n(FeS)_m$[23] systems. Work to identify other members of this family is continuing. In conclusion, using alkali-metal polychalcogenides as solvents and reagents is a viable synthetic and crystal growth route to novel chalcogenide solid-state materials.

Acknowledgment. Financial support from the Center for Fundamental Materials Research (CFMR) Michigan State University and the National Science Foundation for a Presidential Young Investigator Award, CHE-8958451, is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates of all atoms and anisotropic and isotropic thermal parameters of all non-hydrogen atoms, bond distances and angles, and a figure with the atomic labeling of $K_2Hg_6S_7$ (7 pages); a listing of calculated and observed ($10F_o/10F_c$) structure factors (14 pages). Ordering information is given on any current masthead page.

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Articles

Reactivity of Metal Oxides Cu_2O, MnO, CoO, NiO, CuO, and ZnO with Indialite

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Reactivities of Cu_2O, MnO, CoO, NiO, CuO, and ZnO with indialite ($Mg_2Al_4Si_5O_{18}$) are studied under air, argon, or vacuum and for temperatures between 800 and 1150 °C, by using X-ray diffraction, magnetic measurements, and ESR spectroscopy. While Cu_2O is inert toward indialite, MO oxides always react: small quantities of cupric oxide disappear in indialite phase at about 950–1000 °C under air and appear again partly above 1030 °C. Magnetic measurements and ESR spectroscopy prove that the oxidation degree of dissolved copper is 2+ and that this dissolved copper does not behave as copper in cupric oxide. For greater concentrations of CuO, a spinel phase appears. The other MO oxides always destroy the indialite framework, giving M_2SiO_4 and a spinel phase for manganese, cobalt, and nickel oxides, α-SiO_2, $MgSiO_3$, and $ZnAl_2O_4$ in the zinc case.

Introduction

Until now, cordierite ($Mg_2Al_4Si_5O_{18}$) has given rise to a rich literature because of its unusual physical properties. Its relatively low polycrystalline linear thermal expansion α_p (1×10^{-6}–4×10^{-6}/°C), low dielectric constant (4–6), and high volume resistivity (>10^4 Ω cm) make it attractive for catalyst carriers and application in electronic packaging.

Mg cordierite exists under three polymorphic forms: a hexagonal high-temperature form, named indialite or α-cordierite, isostructural with beryl (space group $P6/mmc$), an orthorhombic low-temperature form designed β-cordierite (space group $Cccm$) which is the most encountered structure for natural cordierite, and a metastable form, μ-cordierite.[1-3] The hexagonal and orthorhombic structures are characterized by their six-membered rings of tetrahedrally coordinated cations (T_2) perpendicular to the c axis. Alternate layers of the hexagonal ring structure are connected through Mg octahedra and T_1 tetrahedra (Figure 1). Silicon occupies mostly T_2 tetrahedra, and aluminum T_1 tetrahedra. Differences between high- and

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