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# Exploratory Synthesis in Molten Salts: Role of Flux Basicity in the Stabilization of the Complex Thiogermanates $Cs_4Pb_4Ge_5S_{16}$, $K_2PbGe_2S_6$, and $K_4Sn_3Ge_3S_{14}$

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The influence of the Lewis basicity of alkali polysulfide fluxes ($A_2S_x$) (A = alkali) as a function of *x* on the respective reactivities of Pb and Sn with Ge was studied and found to be strong. $Cs_4Pb_4Ge_5S_{16}$, $K_2PbGe_2S_6$, and $K_4Sn_3Ge_3S_{14}$ could be prepared only under low basicity with $S/A_2S$ ratios of ≥11. These compounds display complex frameworks and are semiconductors. $Cs_4Pb_4Ge_5S_{16}$ is luminescent with red emission.

The broad compositional and structural variability of metal chalcometalates of group 14 (i.e., complex ions of the type $[M_xQ_y]^{z-}$, where M = Si, Ge, Sn; Q = S, Se, Te) is responsible for the existence of a growing and interesting class of compounds.[1] Many exhibit properties that make them promising for investigations in nonlinear optics,[2] ferroelectrics,[3] optical data storage,[4] ion-exchange,[5] and chemical absorption.[6,7] Of particular interest to us has been the development and application of the reactive alkali polychalcogenide flux method in discovering such materials.[8] Using this and conventional methods, a slew of interesting chalcogermanates has been obtained, including $Na_8M_2(Ge_2S_6)_2$ (M = Sn, Pb),[9] $Li_2MGeS_4$ (M = Eu, Pb),[10] $A_2Hg_3M_2S_8$ (A = K, Rb, Cs; M = Ge, Sn),[11,12] $Li_4GeS_4$,[13] $K_2EuMSe_5$ and $KEuMS_4$ (M = Si, Ge),[14] $AREMQ_4$ (A=K, Rb, Cs; RE = rare earth element; M = Si, Ge; Q = S, Se),[15–17] $CsSmGeS_4$,[18] $AgLa_3GeS_7$,[19] $LaCa_2GeS_4Cl_3$,[20] and $A_{0.5}Pb_{1.75}GeS_4$ (A= Li, Na).[21] Additional investigations aimed at studying and expanding this class of materials are therefore justified.

One of the great synthetic advantages of the polychalcogenide flux method of synthesis is the rational manner in which its basicity (and hence reactivity) can be changed by simply altering the $S/A_2S$ (A = alkali metal) ratio.[22] This influences the melting point, the viscosity, the size of the polysulfide chains, and the overall Lewis basicity of the flux. It is important to enhance our understanding of the effects of altering the character of the fluxes on the reactivity patterns and corresponding outcomes. This could facilitate the development of useful synthetic methodologies for complex chalcogenides.

Careful review of the conditions of previously reported compounds reveals that the majority has been prepared in relatively basic fluxes (e.g., $1.5 < S/A_2S < 6$). Polysulfide melts with much lower basicity ($S/A_2S > 6$) remain somewhat unexplored for the synthesis of new compounds.[8,22,23] In this context, we studied the reactivity of thiogermanate anions in combination with linking metals

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**Table 1.** Molar Ratios and Isothermal Temperatures of the Reactions for the Syntheses of $Cs_4Pb_4Ge_5S_{16}$, $K_2PbGe_2S_6$, and $K_4Ge_3Sn_3S_{14}$

| compd | Ge | Pb or Sn | $A_2S$ | S | temp (°C) |
|---|---|---|---|---|---|
| $Cs_4Pb_4Ge_5S_{16}$ | 1.3 | 1 | 1 | 12 | 400 |
| $K_2PbGe_2S_6$ | 1.3 | 1 | 1 | 12 | 500 |
| $K_4Sn_3Ge_3S_{14}$ | 1 | 1 | 1 | 12 | 500 |

such as Sn and Pb in low-basicity fluxes. We find that these fluxes are uniquely capable of stabilizing new phases.

In this Communication, we present the compounds $Cs_4Pb_4Ge_5S_{16}$, $K_2PbGe_2S_6$, and $K_4Sn_3Ge_3S_{14}$ that were prepared in fluxes of relatively low Lewis basicity ($S/A_2S = 12$). These compounds could not form in more basic fluxes, suggesting that low basicity is important for the stabilization of all three. The compounds are intermediate-gap semiconductors, and $Cs_4Pb_4Ge_5S_{16}$ showed strong luminescence.

Outcomes of more basic reaction conditions were also studied. $Cs_4Pb_4Ge_5S_{16}$ could still be prepared at $S/Cs_2S = 11$, but at $S/Cs_2S \leq 9$, the main products were PbS, $GeS_2$, S, and a variety of $Cs_2S_y$ phases. Attempts to synthesize $Cs_4Pb_4Ge_5S_{16}$ from a stoichiometric ratio of $Cs_2S$/Pb/Ge/S were also unsuccessful. Reaction conditions for the successful synthesis of the compounds are summarized in the Table 1.[24−26]

The synthetic conditions for $K_2PbGe_2S_6$ are even narrower than those for $Cs_4Pb_4Ge_5S_{16}$. In reactions with flux ratios of $S/K_2S \leq 11$, this compound was absent in the products, which instead contained PbS, $GeS_2$, and S. Very similar results were observed for $K_4Ge_3Sn_3S_{14}$. At ratios of $S/K_2S \leq 11$, the main products were ternary phases such as $K_2Sn_2S_5$ and $KSnS_2$. $K_2PbGe_2S_6$ and $K_4Ge_3Sn_3S_{14}$ could be prepared by direct stoichiometric reaction at 500 °C, but only as minor products.

The crystal structure of $Cs_4Pb_4Ge_5S_{16}$ features a three-dimensional centrosymmetric $[Pb_4Ge_5S_{16}]^{4-}$ network with charge-balancing $Cs^+$ ions embedded in it (Figure 1).[27] Two different thiogermanate anions are stabilized in this compound, and a more descriptive formula for it is $Cs_4Pb_4(Ge_2S_6)_2(GeS_4)$. There are four types of Pb atoms. Pb1 is located inside a distorted rectangular pyramid, which forms by S atoms from two $[Ge_2S_6]^{4-}$ and two $[GeS_4]^{4-}$ anions. The atoms Pb2, Pb3, and Pb4 exhibit highly distorted octahedral coordination: Pb2 is coordinated by four $[Ge_2S_6]^{4-}$ anions, and Pb3 and Pb4 are surrounded by two $[Ge_2S_6]^{4-}$ and two $[GeS_4]^{4-}$ anions. All Pb−S distances vary from 2.742(2) to 3.355(2) Å. The Ge−S distances are in the range 2.156(2)−2.284(2) Å, which is in agreement with Ge−S distances found in other compounds.[28] The cesium atoms, Cs1 and Cs2, are surrounded by six S atoms in highly distorted coordination environments (Figure 1b,c).

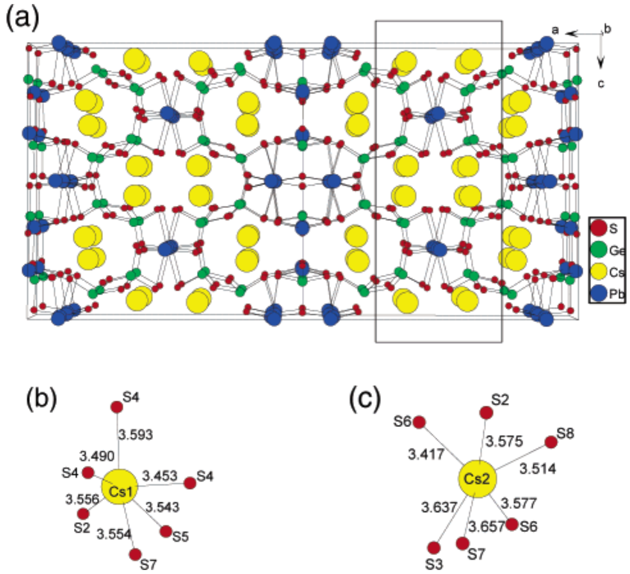

**Figure 1.** (a) $Cs_4Pb_4Ge_5S_{16}$ structure viewed along the [010] direction. (b,c) Six S atoms form distorted octahedra and prisms around the Cs1 and Cs2 atoms, respectively. The Cs1 ion has two additional sulfur atoms at the 3.75 Å, which are not shown for clarity. Cs−S distances are in angstroms.

The structure of $K_2PbGe_2S_6$ has a three-dimensional $[PbGe_2S_6]^{2-}$ anionic network with tunnels running parallel to the [001] direction (Figure 2a). The framework has features in common with $[Pb_4Ge_5S_{16}]^{4-}$, as indicated by the brackected sections in Figures 1a and 2a. The charge-balancing $K^+$ ions are accommodated in these tunnels (Figure 2a). $K^+$ is inside a distorted square pyramid of five sulfur atoms with K−S distances of 3.249(4)−3.356(5) Å. The anionic framework is build from $[Ge_2S_6]^{4-}$ dimers that are linked by Pb atoms. Each Pb atom is surrounded by six S atoms that define a distorted antiprism (Figure 2b,c). The Pb−S distances range from 2.844(1) to 3.150(2) Å. Ge−S bond distances in the $[Ge_2S_6]^{4-}$ dimmers are in the range of 2.155(2)−2.268(3) Å.

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(24) **Preparation of $Cs_4Pb_4Ge_5S_{16}$.** A mixture of Ge (0.66 mmol), Pb (0.5 mmol), $Cs_2S$ (0.5 mmol),and S (6.0 mmol) was sealed under vacuum ($<10^{-3}$ Torr) in a silica tube and heated at 400 °C for 96 h. This was followed by cooling to room temperature at 5 °C/h. The excess flux ($Cs_2S_x$) was removed with MeOH to reveal yellowish-white air-stable crystals (~80% yield based on Ge). Energy dispersive analysis (EDS) with a scanning electron microscope (SEM) gave an average (five crystals were analyzed) composition of "$Cs_{3.5}Pb_{4.2}Ge_5S_{16.7}$", which is close to the chemical formula determined by single-crystal X-ray diffraction analysis.

(25) **Preparation of $K_2PbGe_2S_6$.** A mixture of Ge (1.0 mmol), Pb (0.75 mmol), $K_2S$ (0.75 mmol), and S (9.0 mmol) was sealed under vacuum ($<10^{-3}$ Torr) in a silica tube and heated at 500 °C for 96 h. The tube was then cooled to room temperature at 5 °C/h. The excess flux ($K_2S_x$) was removed with MeOH to reveal air-stable yellowish-white crystals (~20% yield based on Ge, additional phases were binary PbS and $GeS_2$). EDS analysis gave an average (five crystals) composition of "$K_{2.4}Pb_{1.1}Ge_2S_{5.5}$".

(26) **Preparation of $K_4Sn_3Ge_3S_{14}$.** A mixture of Sn (0.8 mmol), Ge (0.8 mmol), $K_2S$ (0.8 mmol), and S (9.6 mmol) was sealed in a silica tube and processed as described in ref 25. The excess flux ($K_2S_x$) was removed with MeOH to reveal air-stable yellowish-white crystals (~80% yield based on Ge). These crystals are air stable. EDS analysis gave an average (five crystals were analyzed) composition of "$K_{4.1}Ge_3Sn_{2.8}S_{13.4}$".

(27) A Siemens SMART Platform CCD diffractometer operating at room temperature (rt) and using graphite-monochromatized Mo Kα radiation was used for data collection. Absorption corrections were performed with the program SADABS. Crystal data: (a) $Cs_4Pb_4Ge_5S_{16}$, orthorhombic, space group *Cmca* (No. 64), $a = 38.3020(19)$ Å, $b = 9.0770(5)$ Å, $c = 19.442(1)$ Å, $V = 6759.4(6)$ Å$^3$, Z = 8, R1($F$) = 0.0249, wR2($F^2$) = 0.0636. (b) $K_2PbGe_2S_6$, monoclinic, space group $C2/c$ (No. 15), $a = 9.268(2)$ Å, $b = 14.338(3)$ Å, $c = 8.919(2)$ Å, $\beta = 90.56(0)°$, $V = 1185.1(5)$ Å$^3$, $Z = 4$, R1($F$) = 0.0181, wR2($F^2$) = 0.0405. (c) $K_4Sn_3Ge_3S_{14}$, monoclinic, space group $P2_1/n$ (No. 14), $a = 6.9442(16)$ Å, $b = 15.118(4)$ Å, $c = 12.071(3)$ Å, $\beta = 100.51(0)°$, $V = 1246.0(5)$ Å$^3$, $Z = 2$, R1($F$) = 0.0247, wR2($F^2$) = 0.0594.

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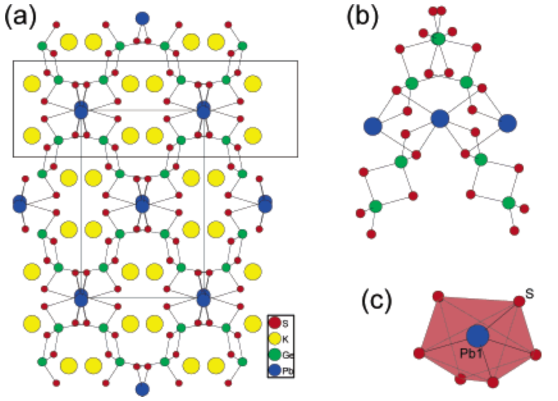

**Figure 2.** (a) [001] view of the $K_2PbGe_2S_6$ unit cell. (b) Local coordination of the Pb atoms. (c) Polyhedral representation of the local coordination of the Pb1 atom.

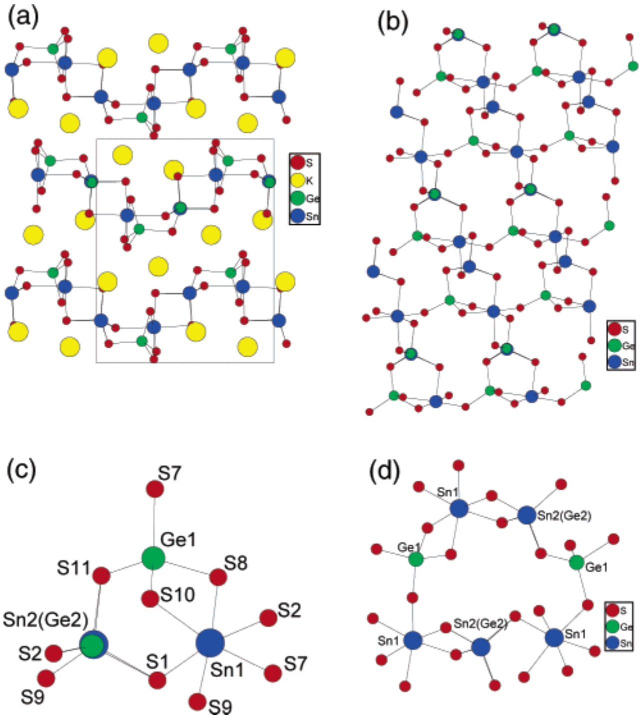

**Figure 3.** (a) [001] view of the $K_4Sn_3Ge_3S_{14}$ unit cell. (b) [010] view of a $[Sn_3Ge_3S_{14}]^{4-}$ layer (potassium atoms are omitted for clarity). (c) Cyclic $[GeSnMS_{10}]$ (M is mixed occupied position by Sn and Ge atoms) trimer with labeling scheme. (d) $[Ge_2Sn_3M_2S_{24}]$ macrocycles.

$K_4Sn_3Ge_3S_{14}$ has corrugated $[Sn_3Ge_3S_{14}]^{4-}$ layers extending in the *ac* plane with $K^+$ cations located between (Figure 3a,b). The basic building units are $[GeS_4]^{4-}$ tetrahedra [Ge−S bond lengths are 2.197(3)−2.237(3) Å], one $SnS_6$ distorted octahedron [Sn−S bond lengths are 2.540(2)−2.622(1) Å], and one $MS_4$ tetrahedron in which Ge and Sn atoms are disordered. These three building units form cyclic $[GeSnMS_{10}]$ trimers through corner and edge sharing (Figure 3c). Subsequently, several of these trimers are condensed into $[Sn_3Ge_2M_2S_{24}]$ macrocycles (Figure 3d). The formal oxidation state of all Sn atoms is 4+. The K1 and K2 atoms adopt eight- and seven-coordination environments, respectively.

Single-crystal optical absorption measurements[29] in the visible region of the spectrum show that $Cs_4Pb_4Ge_5S_{16}$ has a relatively steep absorption edge that corresponds to an energy band gap of 2.6 eV (477 nm; Figure 4). This value is consistent with its pale yellow color. Cathodoluminescence measurements[30] revealed that this compound has a strong red-colored room-temperature luminescence with a broad maximum at 1.95 eV (636.4 nm; Figure 4).

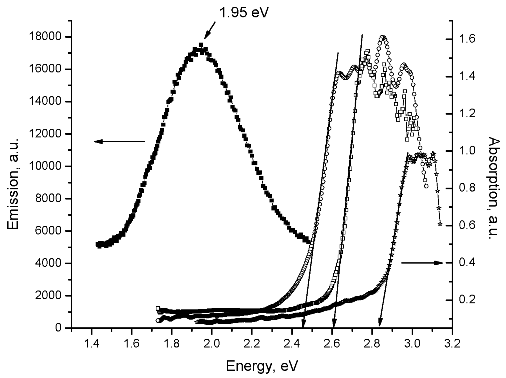

**Figure 4.** Single-crystal optical absorption and cathodoluminescence spectra: ■, cathodoluminescence spectrum of $Cs_4Pb_4Ge_5S_{16}$; □, single-crystal VIS optical absorption of $Cs_4Pb_4Ge_5S_{16}$ with band gap at 2.61 eV; ★, optical absorption of $K_2PbGe_2S_6$ with band gap of 2.83 eV; ○, absorption spectrum of $K_4Sn_3Ge_3S_{14}$ with band gap at 2.46 eV.

$K_2PbGe_2S_6$ is a semiconductor with a band gap of 2.85 eV (435.5 nm), which is in agreement with its pale yellow color (Figure 4). $K_4Sn_3Ge_3S_{14}$ features a slightly smaller gap of 2.46 eV. The electronic transitions associated with the band-gap absorptions are probably charge transfer from primarily S-based valence bands to Pb- and Sn-based conduction bands.

To conclude, reactive alkali polychalcogenide fluxes offer the ability to influence the reactivity patterns of certain metals and thus provide more control in exploratory solid-state chemistry. As a result, the semiconductor compounds $Cs_4Pb_4Ge_5S_{16}$, $K_2PbGe_2S_6$, and $K_4Sn_3Ge_3S_{14}$ were successfully prepared in alkali polychalcogenide flux of low Lewis basicity. These conditions appear to be necessary for stabilization of these phases, as increasing the flux basicity results in the breakdown of the structures and the formation of simpler species. $Cs_4Pb_4Ge_5S_{16}$ has a suitable lattice that is capable of sustaining intense luminescence with red emission at 1.95 eV (636 nm).

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**Supporting Information Available:** X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Single-crystal visible spectroscopy: Optical transmission measurements were made at room temperature on single crystals with a Hitachi U-6000 spectrophotometer equipped with an Olympus BH-2 microscope. The crystals were placed on the glass slide and covered with mineral oil. Measurements were done for at least four crystals from each batch.

(30) Cathodoluminescence spectroscopy: The spectra were collected at room temperature with a JEOL JSM-6300F field emission scanning electron microscope equipped with Gatan MonoCL SP high-performance cathodoluminescence system. The accelerating voltage was 10 kV, and the spectrum was acquired in the 200−800 nm range. The analysis was conducted on single crystals (4−5 crystals). Only $Cs_4Pb_4Ge_5S_{16}$ showed luminescence.