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Phase-Change Materials Exhibiting Tristability: Interconverting Forms of Crystalline α-, β-, and Glassy $K_2ZnSn_3S_8$

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S Supporting Information

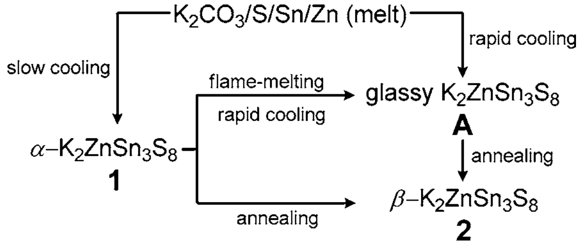
ABSTRACT: We show that $K_2ZnSn_3S_8$ is a phase-change system that exhibits tristability. Kinetic and thermodynamic forms of different compounds in the K/Zn/Sn/S system have been synthesized and thoroughly characterized. We report an example where slow and rapid cooling of a melt of K_2CO_3/S/Sn/Zn leads to different kinetically stable products (crystalline layered α-$K_2ZnSn_3S_8$, **1**, and glassy $K_2ZnSn_3S_8$, **A**, respectively). These forms convert to a thermodynamically stable compound (crystalline cubic β-$K_2ZnSn_3S_8$, **2**) upon annealing below their melting points. The band gaps of compounds **1**, **A**, and **2** are 2.30, 2.15, and 2.55 eV, respectively.

The chemistry of metal chalcogenides is evolving rapidly thanks to the development of new synthetic methods and the remarkably broad compositional and structural diversity of these compounds. The interest in this class of materials is driven by the potential technological applications,[1] such as semiconductivity, photoconductivity,[2] solar energy conversion,[3] thermoelectrics,[4] nonlinear optics,[5] and ion-exchange capability.[6] Among the different synthetic methods, the use of alkali-metal polychalcogenide fluxes is very effective in allowing the discovery of a variety of new compounds.[7] Although the conventional use of alkali-metal polysulfides involves the reaction of A_2S and S, where A_2S is synthesized in liquid ammonia,[8] we here use alkali-metal carbonates and sulfur, which can provide in situ a useful polysulfide flux. While a number of reported binary and ternary chalcogenides have been synthesized using a mixture of A_2CO_3 and S,[9−11] the reaction mechanism between carbonates and sulfur is unclear. In 1990, we proposed a general equation for this reaction in which alkali-metal polysulfides (A_2S_x) are produced along with $A_2S_2O_3$ and CO_2 byproducts (eq 1).[12] This method enables a straightforward route to new syntheses, thereby obviating the use of A_2S itself.

$$3A_2CO_3 + (2x + 2)S \rightarrow 2A_2S_x + A_2S_2O_3 + 3CO_2 \qquad (1)$$

Here we demonstrate the use of this convenient flux-forming reaction to access new phase-change materials, all of which are polymorphs of the same composition α-$K_2ZnSn_3S_8$ (**1**), glassy $K_2ZnSn_3S_8$ (**A**), and β-$K_2ZnSn_3S_8$ (**2**). Crystalline compound **1** is formed through the slow cooling (~1 °C/min) of a melt of K_2CO_3/S/Sn/Zn from 700 °C to room temperature. However, water quenching of the same melt led to amorphous glassy compound **A**, which upon annealing below its melting point crystallizes to metastable single-phase compound **2** [see the Supporting Information (SI) for the preparation details]. Moreover, we find that compound **1** converts to **A** when it is flame-melted and water-quenched and to **2** when annealed below its melting point, indicating that compound **2** is the thermodynamically stable phase (Scheme 1).

Scheme 1. Reaction Scheme of Compounds 1, A, and 2[a]



[a] More details are provided in SI. Rapid cooling was accomplished by quenching in water and slow cooling by a 1°C/min cooling rate.

The crystal structures of **1** and **2** were determined with single-crystal X-ray diffraction (XRD) analysis.[13] Tetrahedral units are the basic building blocks of the Zn/Sn/S networks of both structures, but they vary in the way such tetrahedra are connected and to the site occupation of Zn and Sn atoms.

The crystal structure of compound **1** consists of layers of $^2/_\infty[ZnSn_3S_8{}^{2-}]$ that are parallel to the (011) plane (Figure 1a). Each layer is built up by the side-by-side linking of one-dimensional chains along the [001] plane, which is created by the edge-shared Sn_2S_6 dimer unit and $(Sn,Zn)S_4$ tetrahedra. Alternatively, another type of chain can be viewed as corner-shared $(ZnSn_3)S_9$ tetrameric units running along the [100] direction (Figure 1b). The K^+ ions are located in high coordination sites between the layers.

Although this type of structural motif is related to the previously reported $AM^{III}M^{IV}Q_4$ (A = alkali-metal ions; Q = chalcogens) systems such as β-$KInSnSe_4$,[15] $KGaSnS_4$,[16] $KInGeS_4$,[16] and $KGaGeS_4$,[16] to our knowledge, the $A_2M^{II}M^{IV}{}_3Q_8$ phase with the same structural topology has not been reported so far. In all reported $AM^{III}M^{IV}Q_4$ phases, the tetrahedral metal sites contain both M^{III} and M^{IV}, whereas in compound **1**, the Zn (M^{II}) and Sn (M^{IV}) atoms occupy different crystallographic positions. The M−S bond lengths, which range from 2.347(4) to 2.420(4) Å for Zn−S and from

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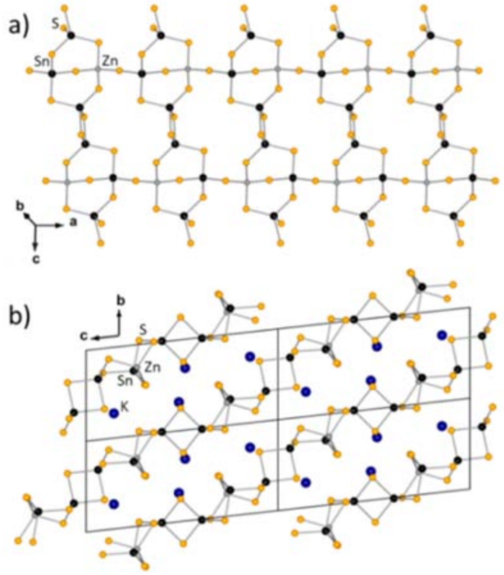

Figure 1. Segment of the crystal packing in compound **1**: (a) projection of the $^{2}/_{\infty}[ZnSn_3S_8{}^{2-}]$ layer along the (011) plane; (b) packing of the layers and intercalated K ions viewed along the *a* axis.

2.361(3) to 2.459(4) Å for Sn−S, are comparable to those found in similar sulfides built from tetrahedra.[4] The two K atoms are eight-coordinate, with K−S distances ranging from 3.205(2) to 4.069(2) Å.

An amorphous glass phase **A** was obtained as a reddish ingot by rapid water quenching of the melt of K_2CO_3/S/Sn/Zn. It could also be prepared through water quenching of the flame-melted compound **1**. The nominal composition of **A** has been determined to be $K_2ZnSn_3S_8$ by microprobe analysis using energy-dispersive spectroscopy (Figure S1 in the SI). Differential thermal analysis (DTA) of **A** shows a glass transition at about 220 °C, followed by a sharp, single-step crystallization at 398 °C and melting at 468 °C (Figure 2a). The well-defined strong exothermic event exhibited by the glass indicates the facile one-step release of energy contained in the glass upon conversion to β-$K_2ZnSn_3S_8$. This is consistent with the fact that there are no compositional changes during interconversion.[17]

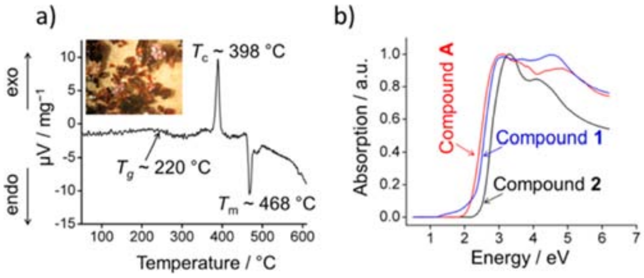

Figure 2. (a) DTA trace of amorphous compound **A** representing the glass transition, crystallization followed by the melting point. The inset represents a picture of compound **A**. (b) Solid-state electronic absorption UV−vis/NIR spectra for **1**, **A**, and **2**.

When the glass phase **A** is heated slightly above the crystallization temperature for 1 h, followed by water quenching, orange blocks of compound **2** crystallize as a single phase. Compound **2** has also been synthesized by heating compound **1** below its melting point (445 °C) for 24 h and then air quenching (cooling rate ~ 200 °C/min). Compound **2** does not convert to other phases upon annealing below its melting point (~468 °C) for 48 h. This suggests that **2** is probably the thermodynamically stable phase in these quaternary K/Zn/Sn/S systems.

The crystal structure of compound **2** is cubic possessing a three-dimensional, tetrahedral anionic framework of $[(ZnSn)S_4]^{2-}$, wherein Zn and Sn are disordered over the same tetrahedral sites (Figure 3). The site occupancies of Zn and Sn were refined as 25% and 75%, respectively. The K^+ ions fill voids in the framework and have 9- and 12-coordination. The asymmetric unit content was found to be $K_{0.5}Zn_{0.25}Sn_{0.75}S_2$ (this composition is equivalent to β-$K_2ZnSn_3S_8$). The M−S bond lengths range from 2.369(3) to 2.381(3) Å. The K−S distances range from 3.218(3) to 4.049(5) Å for 9-coordinate K ions and from 3.608(3) to 3.719(5) Å for 12-coordinate ones. This compound is isostructural with the thermodynamically stable cubic compounds $AGaSnSe_4$ (A = K, Rb)[18] and $KInSnSe_4$.[15] Known isomorphous sulfide analogues include $BaGa_2S_4$[19a] and $AGaSnS_4$ (A = Na, K, Rb, Cs, Tl).[19b]

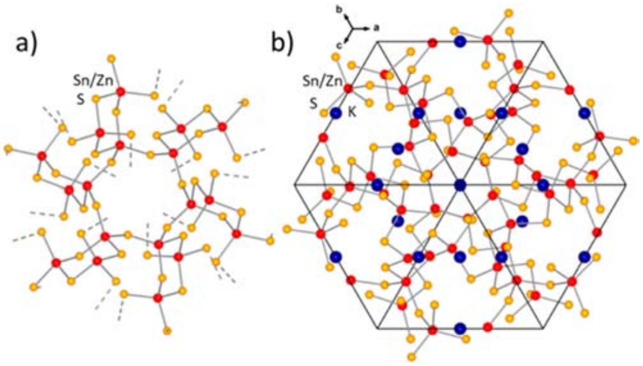

Figure 3. Crystal structure of compound **2**: (a) projection of the corner-sharing MS_4 tetrahedral units; (b) packing of β-$K_2ZnSn_3S_8$ viewed down the [111] direction.

The experimental powder XRD patterns of **1** and **2** compare well with those simulated on the basis of their single-crystal X-ray structures (Figure S2 in the SI). Diffuse-reflectance UV−vis/near-IR (NIR) spectroscopy indicates a room-temperature band gap of 2.30 eV for compound **1**, 2.15 eV for compound **A**, and 2.55 eV for compound **2** (Figure 2b), which are in accordance with their colors.

At the outset of this study, one of our targets was to prepare a zinc analogue of the layered KMS-1 compound $K_{2x}Mn_xSn_{3-x}S_6$ (x = 0.5−0.95), which was previously reported in our group.[6a−c] The latter has been shown to have outstanding ion-exchange properties and to be unique in its ability to selectively remove Sr^{2+} ions and heavy metals from aqueous solutions. The structure of KMS-1 features SnS_2-type $[MnSn_2S_6]^{2-}$ layers with octahedral Mn and Sn atoms. The fact that the isostructural KMS-1 analogue $K_{2x}Zn_xSn_{3-x}S_6$ was not observed is attributed to the far stronger tendency of Zn^{2+} to adopt tetrahedral rather than octahedral geometry. However, preliminary reactions under hydrothermal conditions show different behavior, in that $K_{2x}Zn_xSn_{3-x}S_6$ possessing a KMS-1-type structure can be synthesized. The first results were obtained recently and will be reported soon.

The reactions of potassium carbonate, sulfur, zinc, and tin afforded two different compounds of $K_2ZnSn_3S_8$ (**1** and **A**), depending on the cooling rate used. Both compounds convert to the thermodynamically stable product **2** upon annealing below their melting points. The formation of compound **2** was never observed upon cooling of the melt but only upon heating of either **A** or **1** in the solid state. Considering the general lack of detailed knowledge about mechanisms of solid-state transformations, such materials may provide ideal model systems for future mechanistic studies of phase-change processes and phase-interconversion studies. Additionally, the convenience of using alkali-metal carbonates and chalcogens for making alkali-metal polychalcogenide fluxes may obviate the need for liquid ammonia for the reaction of alkali metals with chalcogens. Because of its simplicity and low cost, it opens facile access to the synthesis of complex chalcogenides. We showed that $K_2ZnSn_3S_8$ is a phase-change system. Generally, phase-change materials exhibit bistability; that is, they adopt two different interconverting phases, and this can lead to useful device and logic applications.[20] The $K_2ZnSn_3S_8$ system exhibits tristability at a given temperature and is a rare case of three interconverting phases. Such a feature may enable unique applications such as multiswitch and ternary memory.[21]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, spectroscopic data, tables of crystallographic details, and CIF files for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(13) Data were collected on a diffractometer equipped with a STOE imaging-plate detector system IPDS2 using graphite-monochromatized Mo Kα radiation with (λ = 0.71073 Å) at 100 K. Structure solution was performed by direct methods, full-matrix least-squares refinement against F^2 using *SHELXS-97* and *SHELXL-97* software.[14] α-$K_2ZnSn_3S_8$ (**1**): triclinic; $P\bar{1}$; a, b, and c = 7.3656(15), 7.9996(16), and 15.319(3) Å, respectively; α, β, and γ = 95.04(3), 91.64(3), and 115.76(3)°, respectively; V = 807.5(3) Å^3; Z = 2; D_{calcd} = 3.11 g/cm^3; R1 = 0.0732 [$I > 2\sigma(I)$]; wR2 = 0.1824 (all data); GOF = 1.05. $K_{0.5}Zn_{0.25}Sn_{0.75}S_2$ (**2**): cubic; $Pa\bar{3}$; a = 13.126(2) Å; V = 2261.5(6) Å^3; Z = 24; D_{calcd} = 3.331 g/cm^3; R1 = 0.0481 [$I > 2\sigma(I)$]; wR2 = 0.1390 (all data); GOF = 1.11. For more details, see the SI.

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