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Cooling of Melts: Kinetic Stabilization and Polymorphic Transitions in the $KInSnSe_4$ System

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Through a flame-melting/rapid-cooling process, metastable forms of solid state compounds can be discovered. We describe here an example where both slow and rapid crystallizations of a stoichiometric “$KInSnSe_4$” melt give rise to kinetic forms of $KInSnSe_4$. These forms (α- and β-) convert to the thermodynamically stable γ-form upon heating below the melting point.

The application of alkali-metal chalcogenide fluxes allows the convenient exploration of new ternary or quaternary metal chalcogenides by providing a solution environment for reactions and making possible the utilization of lower temperatures.[1] Depending on reaction time and flux composition, both thermodynamically and kinetically stable phases can be accessed. An alternative to the flux route to kinetic phases would be a quenching process in which a melt is rapidly cooled to room temperature. We have developed a flame-melting/rapid-cooling method in which the reactants are melted by a torch flame and then rapidly quenched into room temperature or liquid N_2 temperature with cooling rates of >600 °C/min. Under such conditions, the crystallization of a melt could lead to novel kinetically stable phases. β-$KBi(Sb)P_2Se_6$, a metastable phase, was discovered by this method.[2] This approach now has been successfully extended to chalcogenides of groups 13 and 14. We describe here the synthesis of three forms of $KInSnSe_4$, two kinetically stable forms (i) a slow cooled α-form with infinite chains of ${}^{1}_{\infty}[InSnSe_4]^{1-}$and (ii) a quenched β-form possessing slabs of ${}^{2}_{\infty}[InSnSe_4]^{1-}$, and (iii) a γ-form with a framework ${}^{3}_{\infty}[InSnSe_4]^{1-}$ structure accessible only by a solid state thermally induced relaxation of the α- and β-forms. The γ-form is believed to be the thermodynamically stable version.

α-$KInSnSe_4$ (**I**) can be obtained as yellow needle crystals from a conventional stoichiometric reaction at 850 °C followed by slow cooling.[3a] β-$KInSnSe_4$ (**II**) could be prepared as reddish-orange plate crystals through a flame melting−rapid cooling method at a cooling rate of ~600 °C/min.[3b] Although both forms usually coexist in a batch, their ratio is found to depend on the cooling rate. That is, an increase of the cooling rate from the melt gives rise to an increased proportion of β-phase.

The crystal structure of **I** is related to that of TlSe and has infinite chains of $[InSnSe_4]^{1-}$ running along the [001] direction separated by charge balancing potassium ions, Figure 1.[4] These chains are formed by edge-sharing of $(Sn,In)Se_4$ tetrahedra in which Sn and In atoms are disordered in tetrahedral sites. The K atoms sit on a 4a Wycoff position (422 site symmetry) with exactly half occupancy. It is coordinated by eight Se atoms at the same distance of 3.477(1) Å. The neighboring eight Se atoms form two square planes above and below the K plane, which lie in parallel with (001) plane, see Figure 1.

The tetrahedral geometry of the $(Sn,In)Se_4$ units is slightly distorted with the Se−(Sn,In)−Se bond angles of 98.65(3)° and 115.14(2)°, and only one (Sn,In)Se bond distance (2.565(1) Å). The smaller angle is directed to adjacent metal

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(3) (a) α-$KInSnSe_4$ was prepared from a stoichiometric mixture of K_2Se, In, Sn, and Se that was sealed under vacuum (~2×10^{-4} mbar) in a fused silica tube. Well-formed yellow needle-shaped crystals of α-$KInSnSe_4$ suitable for single-crystal X-ray investigation were obtained by forming a melt at 850 °C and cooling at −10 °C/min to room temperature. (b) β-$KInSnSe_4$ was synthesized by the stoichiometric reaction of K_2Se, In, Sn, and Se. The starting materials were vacuum-sealed in a fused silica tube, thoroughly melted in a torch flame, and allowed to rapidly cool in air. The cooling rate from the melt temperature to ~200 °C is estimated approximately at ~ −600 °C/min. At room temperature (rt), transparent reddish plate crystals could be isolated. (c) EDS microprobe analysis, performed with a JEOL JS6400V scanning electron microscope equipped with a Vantage Spectrum detector, gave an average composition of “$K_{1.0}In_{1.0}Sn_{1.0}Se_{3.8}$”. The EDS results are good to ±3−4%.

(4) (a) For α-$KInSnSe_4$, crystal data at room temperature follow: Siemens Platform SMART CCD diffractometer, Mo Kα radiation ($\lambda = 0.71073$ Å). *I*4/*mcm*, $a = 8.193(2)$ Å, $c = 6.688(2)$ Å, $V = 448.9(2)$ Å^3, $Z = 2$, $D_{calcd} = 4.353$ g cm^{-3}, orange plate, $0.058 \times 0.105 \times 0.014$ mm^3, $\mu = 21.93$ mm^{-1}, $\theta_{max} = 28°$, 1300 total reflections, 163 unique reflections with $R(\text{int}) = 0.0265$, refinement on F^2, GOF = 1.185. R1 = 1.72%, wR2 = 4.36% for $I > 2\sigma(I)$. An empirical absorption correction was done using SADABS, (b) and the full anisotropic structure refinement was carried out using the SHELXTL programs.

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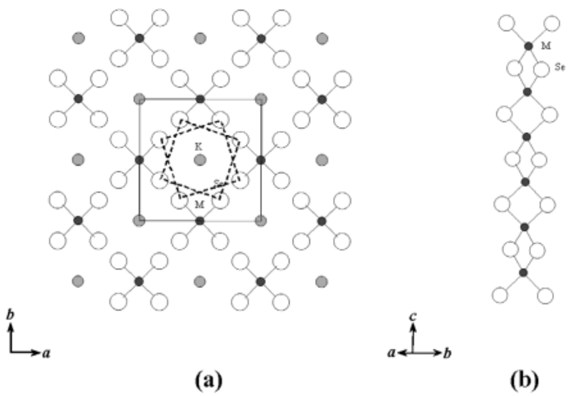

Figure 1. (a) Projection of the structure of α-KInSnSe$_4$ along the *c*-axis and (b) the ${}^{1}_{\infty}[\mathrm{InSnSe_4}]^{1-}$ chain. Large open circles are Se atoms, black circles are Sn (In) atoms, and medium gray circles are K atoms. The dashed rectangles represent two square planes formed by eight Se atoms coordinating to K atom (square antiprism). M represents disordered cation sites for Sn and In.

cations, which helps to decrease the electrostatic repulsion between adjacent Sn^{4+} and In^{3+} cations in the edge-shared tetrahedra.

Well-formed crystals of **II** can be prepared by rapid quenching of the melt, as mentioned above. This compound has layers of ${}^{2}_{\infty}[\mathrm{InSnSe_4}]^{1-}$ oriented parallel to (010) plane, see Figure 2.[5] As in **I**, the Sn and In atoms are disordered over all tetrahedral sites. The indium selenostannate layer is formed by the side-by-side linking of one-dimensional chains along the [001] direction created by the alternating edge-shared (Sn,In)$_2$Se$_6$ dimer unit and (Sn,In)Se$_4$ tetrahedra. Alternatively, one can identify another type of chain formed by corner-sharing of tetrameric (Sn,In)$_4$Se$_9$ units running along the [100] direction. The potassium ions in (**II**) are located in high coordination sites between the layers.

All metal sites contain both In and Sn atoms but with definite atomic preferences for each site. M(1) and M(2) have a majority of Sn, whereas M(3) and M(4) contain more In. The average (Sn,In)−Se bond distance is 2.539 Å for M(1) and M(2), which is shorter than that for the sites M(3) and M(4) (2.552(3) Å). The variation of average bond distance coincides well with the trend in metal occupancy, since the relative Sn/In occupancy ratio is larger for the former sites than for the latter and the ionic radius of Sn^{4+} is smaller than that of In^{3+}. There are also marked differences in the (Sn,In)−Se bond lengths in the (Sn,In)$_2$Se$_6$ units containing the M(1) and M(2) sites. In M(1) and M(2), half of Se atoms take part in edge-sharing with neighboring tetrahedra while the rest are shared by adjacent tetrahedra through corner-sharing, Figure 2b. In contrast, all Se atoms bonded to the M(3) and M(4) atoms participate in corner-sharing with neighboring tetrahedra.

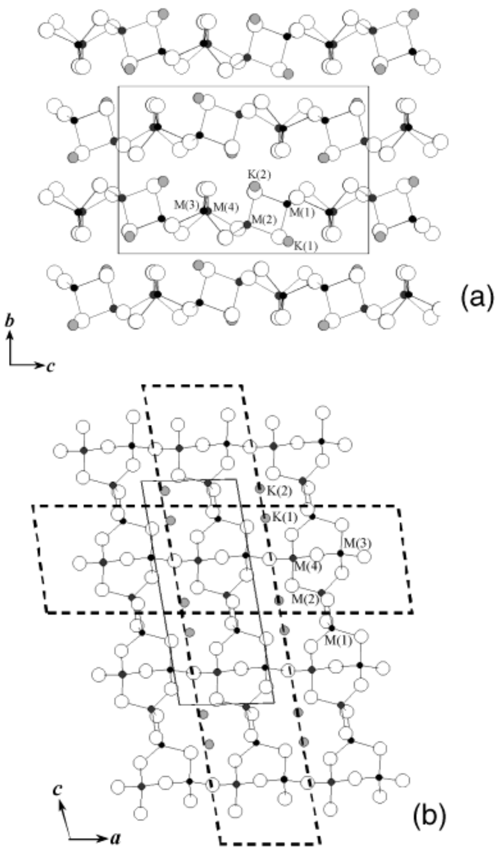

Figure 2. Projection of the structure of β-KInSnSe$_4$ along (a) the *a*-axis and (b) the *b*-axis showing the stacking of the layers and the in-plane structure of the ${}^{2}_{\infty}[\mathrm{InSnSe_4}]^{1-}$ layer. Large open circles are Se atoms, black circles are Sn (In) atoms, and medium gray circles are K atoms. The dashed rectangles highlight one-dimensional chains as a component unit of two-dimensional indium selenostannate network. M represents disordered cation sites for Sn and In.

The two nonequivalent K atoms are coordinated by seven Se atoms and have irregular polyhedral geometry. Among the seven KSe bonds, one KSe bond has a longer distance of 4.011(9) Å for K(1) and 4.007(9) Å for K(2), which is much longer than the average of the other bonds: 3.541(9) Å for K(1) and 3.512(9) Å for K(2).

When we heated the α-(or β-)forms in the solid state at 650 °C and quenched in air, we were surprised to discover the cubic crystals of γ-KInSnSe$_4$ (**III**).[6] In the γ-form the covalent In/Sn/Se framework has now become denser and three-dimensional with corner-sharing MSe$_4$ tetrahedra, and architecture similar to that of BaGa$_2$S$_4$,[7] Figure 3. K$^+$ ions fill the voids.

That β-KInSnSe$_4$ (**II**) is a kinetically stable form comes from the observation that it is a quenched form and it converts to α-KInSnSe$_4$ (**I**) upon heating (12−24 h) below the melting point. The α-form is obtained only upon cooling the melt at <10 °C/min, and thus, it nucleates faster than any of the forms. Interestingly, the α-form converts to the

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(5) For β-KInSnSe$_4$, crystal data at room temperature follow: diffractometer and radiation as in ref 4. $P2_1/c$, $a = 7.772(3)$ Å, $b = 12.457(4)$ Å, $c = 18.658(6)$ Å, $\beta = 98.149(6)°$, $V = 1788.11(1)$ Å^3, $Z = 8$, $D_{\mathrm{calcd}} = 4.371$ g cm^{-3}, reddish-orange plate, 0.276 × 0.129 × 0.024 mm^3, $\mu = 22.14$ mm^{-1}, $\theta_{\max} = 28°$, 17307 total reflections, 4198 unique reflections with $R(\mathrm{int}) = 0.0854$, refinement on F^2, GOF = 0.936. R1 = 4.46%, wR2 = 13.76% for $I > 2\sigma(I)$. Sn and In sites are not distinguishable with X-ray diffraction, but they can be inferred by the observed bond lengths and bond valence sum calculations.

(6) Crystal data for γ-KInSnSe$_4$ at 293 K follow: Diffractometer and radiation as in ref 4. Cubic $Pa\bar{3}$, $a = 13.7849(11)$ Å, $V = 2619.5(4)$ Å^3, $Z = 12$, $D_{\mathrm{calcd}} = 4.476$ g/cm^3, $\mu = 22.443$ mm^{-1}, crystal dimensions 0.08 × 0.08 × 0.06 mm^3, $\theta_{\max} = 28$, empirical absorption correction with SADABS, refinement on F^2, $R(\mathrm{int}) = 0.0817$, GOF = 1.296, R1 = 6.4%, wR2 = 10.56 for $I > 2\sigma(I)$. In/Sn atoms occupy the same crystallographic sites.

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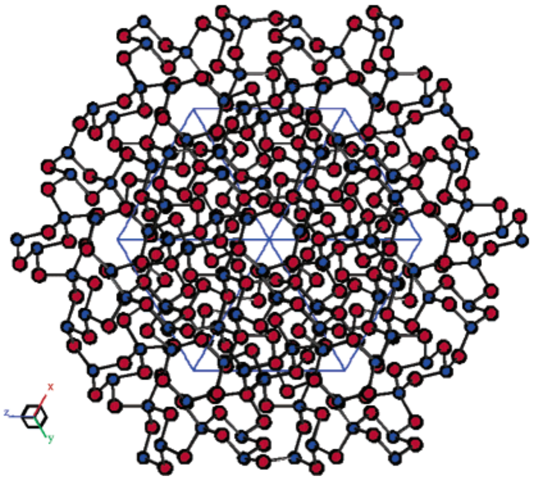

Figure 3. Structure of γ-KInSnSe$_4$ viewed down the [111] direction, showing a complex three-dimensional framework. Red circles are Se atoms, and blue circles are Sn (In) atoms. K atoms were omitted for clarity.

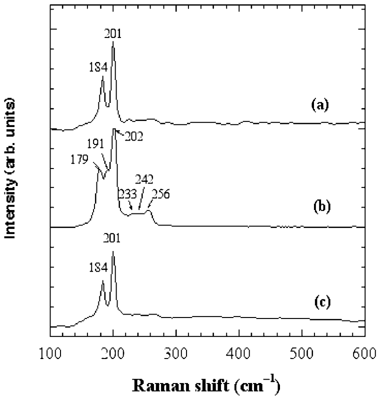

Figure 4. Fourier transform Raman spectra for (a) α-KInSnSe$_4$, (b) β-KInSnSe$_4$, and (c) spectrum of material after melting β followed by slow cooling. The spectrum is nearly the same as that of α-KInSnSe$_4$. Spectra were recorded with a BIO-RAD FT spectrometer with a Spectra-Physics Topaz T1õ106c laser.

γ-form[8] suggesting that it too is a kinetic product, and the thermodynamically stable form is γ. This is also consistent with the fact that the differential thermal analysis diagrams of either α or β possibly indicate a weak and broad exothermic event in the range 600−630 °C. The melting point of **I**, **II** and **III** occurs between 700 and 710 °C. Interestingly, the density increases as follows: α-KInSnSe$_4$ < β-KInSnSe$_4$ < γ-KInSnSe$_4$.[4−6]

The progressively higher density is achieved by fusing the [InSnSe$_4$]$^{1-}$ chains into layers and to a framework. Therefore we expect the transformation (i.e., from $\alpha \rightarrow \beta \rightarrow \gamma$) to be achievable by the application of pressure.

The change in structure to α upon melting β and slow cooling the melt can be detected in the Raman spectra of the two forms of KInSnSe$_4$, Figure 4. The pattern of **I** is surely different from that of **II**, and it shows two intense peaks at 184 and 201 cm^{-1} for **I**. In contrast, a number of strong peaks are discernible for **II** at 179 (s), 191 (m), and 202 (s) cm^{-1} (s = strong, m = medium, w = weak). This compound also shows several weaker and broader features at 233 (w), 242 (w), and 256 (m) cm^{-1}. The simpler spectrum of **I** originates from the fact that it contains only edge-shared tetrahedra whereas **II** possesses both corner- and edge-shared tetrahedra. The spectrum of **II** is significantly changed upon melting and recrystallization and acquires nearly the same spectral features as **I**, confirming the transition to the α-form upon slow cooling.[9]

UV−vis spectroscopy indicates a room temperature band gap of 2.40 eV for α-KInSnSe$_4$, 1.80 eV for β-KInSnSe$_4$, and 1.49 eV for γ-KInSnSe$_4$. The decreasing trend in band gaps from α to γ is consistent with the increasing dimensionality of the structure.

The flame-melting/rapid-cooling method used here is effective in trapping kinetically accessible compounds. It is surprising that the denser β-form could be quenched and not the α-form. Intuitively, one might expect the enhanced vibrational motion present in high temperature liquids to lead to phases of lower density upon quenching. In light of this, the relative stability of α- and β-KInSnSe$_4$ phases can be understood from the viewpoint of structural order. Taking into account that β-KInSnSe$_4$ has lower crystal symmetry and consists of mixed edge- and corner-shared tetrahedra, we could expect it to be of higher entropy than α-KInSnSe$_4$. Since an increase of temperature enhances the contribution of entropy to the total free energy, the β-phase evidently is trapped from the high temperature melt by the rapid quenching process. It is also possible that the melt contains large fragments of the slabs found in the β-form which are then well poised to crystallize quickly. It is remarkable that single crystals large enough for crystallographic examination can be obtained from such rapid crystallization rates. Cooling more slowly, however, provides for the atoms ample time to find the more ordered, highly symmetric α-form, which is fastest to nucleate. The γ-form was never observed upon cooling, but only upon heating either the α- or β-form in the solid state. This suggests that the γ-form is probably the thermodynamically stable form which appears to be too slow to nucleate upon cooling of the melt. The difficulty in nucleating could arise from its rather elaborate three-dimensional covalent structure. A detailed study of the electronic structures of both phases is required to attempt a better understanding of these polymorphic phase transitions.

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, bond length and angles, and anisotropic thermal parameters for all compounds (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Transformation occurs in the solid state at ~650 °C for 24 h and is confirmed with powder X-ray diffraction.

(9) It is interesting that quenching melts with stoichiometric ratios substantially away from the ideal "KInSnSe$_4$" composition, e.g., K$_{2-x}$In$_{2-x}$Sn$_x$Se$_4$ ($0.4 < x < 1.6$), led consistently to the α-form. This suggests the layered form cannot tolerate a large number of vacancies. It also betrays an exceptional ability of the tetragonal TlSe structure type to accommodate an extensive number of vacancies on the crystallographic sites occupied by the alkali metals and also nucleate rapidly.