Cooling of Melts: Kinetic Stabilization and Polymorphic Transitions in the KInSnSe$_4$ System

Seong-Ju Hwang,* Ratnasabapathy G. Iyer, Pantelis N. Trikalitis, Andrew G. Ogden, and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Received October 5, 2003

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. 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 $>$600 °C/min. Under such conditions, the crystallization of a melt could lead to novel kinetically stable phases. β-KBi-(Sb)P$_2$Se$_6$, a metastable phase, was discovered by this method. This approach now has been successfully extended to chalcogenides of groups 13 and 14. We describe here the synthesis of three forms of KInSnSe$_4$, two kinetically stable phases: β-KBi-(Sb)P$_2$Se$_6$, a metastable phase, was discovered by this method. This approach now has been successfully extended to chalcogenides of groups 13 and 14. We describe here the synthesis of three forms of KInSnSe$_4$, two kinetically stable forms (i) a slow cooled α-form with infinite chains of [InSnSe$_4$]$^{2-}$- and (ii) a quenched β-form possessing slabs of [InSnSe$_4$]$^{2-}$, and (iii) a γ-form with a framework 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. 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. 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$_4$]$^{2-}$ running along the [001] direction separated by charge balancing potassium ions. The crystal structure of I is related to that of TlSe and has infinite chains of [InSnSe$_4$]$^{2-}$ running along the [001] direction separated by charge balancing potassium ions. An empirical absorption correction was done using SADABS, and the full anisotropic structure refinement was carried out using the SHELXTL programs.
The ionic radius of Sn is larger than that of In, and the average bond distance for M(4) (2.552(3) Å) coincides well with the trend in metal occupancy, since the M(4) atoms are disordered over all tetrahedral sites. The variation of average bond distance and M(2), which is shorter than that for the sites M(3) and M(4) contains more In.

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. 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) bond lengths in the (Sn,In)₂Se₆ units containing 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: 3.54(9) Å for K(1) and 3.51(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-KlnSnSe₄ (III). In the γ-form the covalent In/Sn/Se framework has now become denser and three-dimensional with corner-sharing MSe₄ tetrahedra, and architecture similar to that of BaGa₂S₄. Figure 3. K⁺ ions fill the voids.

That β-KlnSnSe₄ (II) is a kinetically stable form comes from the observation that it is a quenched form and it converts to α-KlnSnSe₄ (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

---

5. For β-KlnSnSe₄, crystal data at room temperature follow: diffractometer and radiation as in ref 4. P2₁/c, a = 7.772(3) Å, b = 12.457(4) Å, c = 18.658(6) Å, β = 98.149(6)°. V = 1788.11(1) Å³, Z = 8, Dcalcd = 4.371 g cm⁻³, reddish-orange plate, 0.276 × 0.129 × 0.024 mm³, μ = 22.14 mm⁻¹, θmax = 28°, 17307 total reflections. 4198 unique reflections with R(int) = 0.0854, refinement on F². GOF = 0.936. RI = 4.46%, wR2 = 13.76% for I > 2σ(I). Sn and In sites are not distinguishable with X-ray diffraction, but they can be inferred from the observed bond lengths and bond valence sum calculations.

6. Crystal data for γ-KlnSnSe₄ at 293 K follow: Diffractometer and radiation as in ref 4. Cubic Pna2₁, a = 13.7849(11) Å, V = 2619.5(4) Å³, Z = 12, Dcalcd = 4.476 g/cm³. μ = 22.443 mm⁻¹, crystal dimensions 0.08 × 0.08 × 0.06 mm³, θmax = 28°, empirical absorption correction with SADABS, refinement on F². R(int) = 0.0817, GOF = 1.296, RI = 6.4%, wR2 = 10.56 for I > 2σ(I). In/Sn atoms occupy the same crystallographic sites.

strong peaks are discernible for peaks at 184 and 201 cm$^{-1}$ for $\text{[InSnSe}_4\text{]}^\text{-}$. 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 $\alpha$-form upon slow cooling.\(^9\)

UV$-$vis spectroscopy indicates a room temperature band gap of \(2.40 \text{ eV}\) for $\alpha\text{-KInSnSe}_4$, \(1.80 \text{ eV}\) for $\beta\text{-KInSnSe}_4$, and \(1.49 \text{ eV}\) for $\gamma\text{-KInSnSe}_4$. The decreasing trend in band gaps from $\alpha$ to $\gamma$ 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 $\beta$-form could be quenched and not the $\alpha$-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 $\alpha$- and $\beta$-$\text{KInSnSe}_4$ phases can be understood from the viewpoint of structural order. Taking into account that $\beta\text{-KInSnSe}_4$ has lower crystal symmetry and consists of mixed edge- and corner-shared tetrahedra, we could expect it to be of higher entropy than $\alpha\text{-KInSnSe}_4$. Since an increase of temperature enhances the contribution of entropy to the total free energy, the $\beta$-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 $\beta$-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 $\alpha$-form, which is fastest to nucleate. The $\gamma$-form was never observed upon cooling, but only upon heating either the $\alpha$- or $\beta$-form in the solid state. This suggests that the $\gamma$-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.

Acknowledgment. Financial support from the National Science Foundation (Grant DMR-0127644) is gratefully acknowledged. A.G.O. was a summer NSF-REU student.

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.

ICO351545

(9) It is interesting that quenching melts with stoichiometric ratios substantially away from the ideal $\text{KInSnSe}_4$ composition, e.g., $\text{K}_{x}\text{In}_{1-x}\text{SnSe}_4$ (0.4 < $x$ < 1.6), led consistently to the $\alpha$-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.