β-KMP_2Se_6 (M = Sb, Bi): Kinetically Accessible Phases Obtained from Rapid Crystallization of Amorphous Precursors

Jean D. Breshears and Mercouri G. Kanatzidis*

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

Received April 11, 2000

It is rare to find an amorphous material that crystallizes to a metastable single-phase compound, which then transforms to another more thermodynamically stable compound. Such materials are of a fundamental importance and provide an opportunity to characterize kinetics and elucidate mechanistic pathways in well-defined solid-state systems. This is especially important considering the general lack of detailed knowledge concerning mechanisms of solid-state transformations. Some examples include amorphous ball-milled Bi_3NbTiO_9,[1] which undergoes crystallization to a metastable fluorite phase at 270 °C and subsequent conversion to an Aurivillius-type perovskite at the higher temperature of 560 °C. In the $PbTiO_3$ family, a similar temperature-dependent sequence of events gives rise to an amorphous-to-pyrochlore-to-perovskite crystallization process.[2] Another oxide system, that of the $Pb_5Ge_3O_{11}$ family,[3] also exhibits a metastable hexagonal phase on the crystallization path to the thermodynamically stable structure.

In non-oxide systems the only report, to our knowledge, of a well-defined single-phase kinetic crystallization product from amorphous precursors are in films of $MoSi_2$.[4] In this system, amorphous modulating layers of Mo and Si crystallize to metastable β-$MoSi_2$ at 400 °C, which subsequently transforms to α-$MoSi_2$ at 800 °C. Although there are many examples of other metastable intermetallic phases that can be crystallized from amorphous precursors, e.g. Fe_5Si_3,[5] the skutterudites $RE_{1-x}Fe_4Sb_{12}$ (RE = La, Hf, Y),[6] and many quaisicrystal compositions, these all decompose to elemental and binary components rather than transform to another, more thermodynamically stable, single-phase compound.

We here report on our surprising findings of two thermodynamically metastable acentric compounds, viz. β-KMP_2Se_6 (M = Sb, Bi). These compounds are found to crystallize in the polar chiral space group $P2_1$, even though they are built up from the centrosymmetric, "ethane-like" $(P_2Se_6)^{4-}$ group. The β-phases are kinetic crystallization products that transform to the more thermodynamically stable α-KMP_2Se_6 (M = Sb, Bi)[7] structure upon extended exposure to elevated temperature.

β-$KSbP_2Se_6$ crystallizes as a single phase by heating an amorphous precursor of the same nominal composition to slightly above the glass transition temperature, $T_g \sim 195$ °C (Figure 1), or by fast cooling of the melt (>10 °C·min^{-1}). Decreasing the cooling rate from the melt results in increasing transformation to the α-phase until a single α-phase product is obtained (at cooling rates ~1 °C·min^{-1}), in accordance with Ostwald's rule of successive phase transformations.[8] At temperatures above 250 °C, β-$KSbP_2Se_6$ transforms slowly to α-$KSbP_2Se_6$. β-$KSbP_2Se_6$ is a pseudo-one-dimensional compound containing Sb^{3+} tricoordinated by one $(P_2Se_6)^{4-}$ unit at Sb−Se distances ranging from 2.665(2) to 3.003(1) Å, and forming undulating chains by coordination to a second $(P_2Se_6)^{4-}$ group through a single Sb−Se bond at 2.790(1) Å.[9] The chains are loosely packed side-by-side into layers by capping this "butterfly" coordination of Sb^{3+} with an adjoining $(P_2Se_6)^{4-}$ group through a Sb−Se contact at 3.300(2) Å (Figure 2).[10] The monolayers of $[Sb(P_2Se_6)]_n^{n-}$ pseudo-chains stack in an AA... fashion and are separated by the K^+ cations.

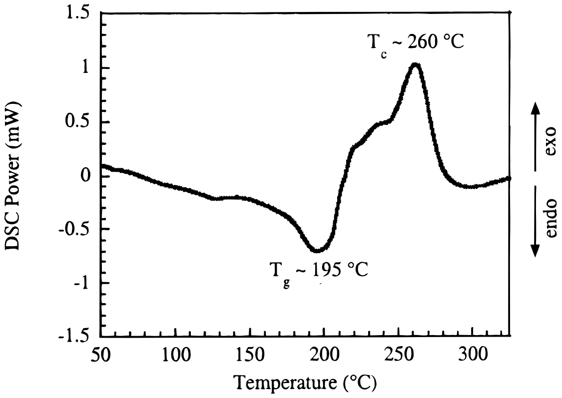

Figure 1. DSC trace of amorphous $KSbP_2Se_6$ showing the glass transition followed by rapid crystallization to β-$KSbP_2Se_6$.

Similarly, β-$KBiP_2Se_6$ is also formed by heating an amorphous precursor or by allowing an evacuated silica tube containing the melt to air cool to room temperature (cooling rate ~200 °C·min^{-1}). Both β-$KBiP_2Se_6$ and β-$KSbP_2Se_6$ are isotypic, though the M−Se bonds are longer in β-$KBiP_2Se_6$ and the larger radius of Bi^{3+} results in an increased coordination number. Each Bi^{3+} is tricoordinated by one $(P_2Se_6)^{4-}$ at Bi−Se distances of 2.812(3) to 2.957(3) Å, bicoordinated by another $(P_2Se_6)^{4-}$ group at distances of 3.335(3) and 3.339(3) Å, and monocoordinated by two $(P_2Se_6)^{4-}$ groups at Bi−Se distances of 2.997(3) and 3.246(3) Å (not shown).[11] The heptacoordinated metal center may be viewed as a monocapped distorted octahedron.[12]

Diffuse reflectance UV−vis/NIR spectroscopy indicates a room-temperature band gap of 2.0 eV for β-$KSbP_2Se_6$, which is identical to that reported for the α-phase. β-$KBiP_2Se_6$ shows a band gap of 1.3 eV (vs 1.6 eV for α-$KBiP_2Se_6$).

---

(1) Castro, A.; Pardo, P. M.; Jiménez *J. Mater. Chem.* **1999**, *9*, 1313−1317.

(2) (a) Lee, J. H.; Chiang, Y. M. *J. Mater. Chem.* **1999**, *9*, 3107−3111. (b) Bersani, D.; Lottici, P. P.; Monterero, A.; Pigoni, S.; Gnappi, G. *J. Non-Cryst. Solids* **1995**, *192*−*193*, 490−493.

(3) (a) Hatano, J.; Mukaigawa, T.; Uehara, H.; Gruverman, A.; Takahashi, K.; Yukino, K. *Jpn. J. Appl. Phys.* **1994**, *33*, 5521−5524. (b) Lan, G.-X.; Sun, H.-Y.; Yin, Z.-Y.; Wang, J.-Y.; Wang, H.-F. *Phys. Stat. Sol. B* **1991**, *164*, 39−44.

(4) Johnson, C. D.; Anderson, K.; Gromko, A. D.; Johnson, D. C. *J. Am. Chem. Soc.* **1998**, *120*, 5226−5232.

(5) Novet, T.; Johnson, D. C. *J. Am. Chem. Soc.* **1991**, *113*, 3398−3403.

(6) Hornbostel, M. D.; Thiel, E. J. H.; Johnson, D. C. *J. Am. Chem. Soc.* **1997**, *119*, 2665−2668.

(7) McCarthy, T. J.; Kanatzidis, M. G. *J. Chem. Soc., Chem. Commun.* **1994**, 1089−1090.

(8) Newsam, J. M. In *Solid State Chemistry: Compounds*; Cheetham, A. K., Day, P., Eds.; Clarendon Press: Oxford, 1992; pp 252−254.

(9) (a) A dark red crystal of β-$KSbP_2Se_6$ was obtained from a stoichiometric ratio of K_2Se, Sb, P_2Se_5, and Se melted in an evacuated silica tube that was allowed to cool at ~10 °C·min^{-1}. Fast cooling from the melt gave larger crystals that were more suitable for single-crystal X-ray investigation than the microcrystalline material found after heating the amorphous precursor (prepared by quenching melts into ice/H_2O). Data were collected on a Bruker SMART CCD platform at 24 °C. Crystallographic details are $a = 6.8925(7)$ Å, $b = 7.8573(8)$ Å, $c = 10.1656(10)$ Å, $\beta = 91.487(2)°$, $V = 550.35(10)$ Å^3, $Z = 2$, $D_c = 4.203$ g·cm^{-3}, space group $P2_1$ (No. 4), μ(Mo Kα) = 229.5 cm^{-1}, $2\theta_{max} = 56.6°$. Total data collected, 2758; unique data, 2015. An empirical absorption correction was applied and the full anisotropic structure refinement using the SHELXTL software package (b) resulted in a final $R_1/wR_2 = 0.0377/0.0949$ with a Flack parameter of 0.46(2). EDS microprobe analysis, performed with a JEOL JS6400V scanning electron microscope equipped with a Vantage Spectrum detector, gave an average composition of $K_{1.0}Sb_{1.0}P_{1.8}Se_{6.2}$. DSC experiments were performed on a Shidmadzu DSC 50, with a heating rate of 10 °C·min^{-1} using a 12.8 mg sample of amorphous $KSbP_2Se_6$. (b) *SHELXTL: Version 5.1*, Sheldrick G. M.; Bruker AXS Inc.: Madison WI.

(10) Far-IR spectra of β-$KSbP_2Se_6$ show absorptions at 520 (s), 477 (s), 450 (s), 434 (w), 419 (s), 296 (s), 257 (w, sh), 218 (w), 200 (m), 185 (m), 174 (w), 162 (w), 145 (m), 133 (w), 119 (m), 105 cm^{-1} (m).

10.1021/ja001270k CCC: $19.00

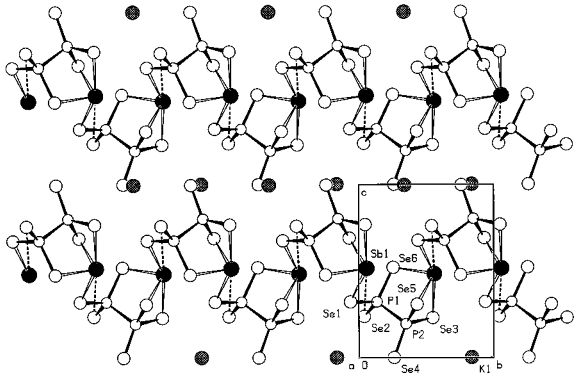

Figure 2. View of β-$KSbP_2Se_6$ perpendicular to the screw axis. The weak interchain bond is emphasized with a dashed line.

The β-KMP_2Se_6 compounds show an interesting relationship to α-KMP_2Se_6 (Figure 3). Comparison to the metastable structures reveals that the bilayers of the α-structure appear to be the result of rotational motions of $[M(P_2Se_6)]^-$ fragments along the pseudo-chains present in the β-KMP_2Se_6 compounds. It should be possible to investigate this transformation mechanism by isothermal kinetics studies within the Avrami−Johnson−Mehl formalism.[13]

The β-KMP_2Se_6 (M = Sb, Bi) are related to the $K(RE)P_2Se_6$ (RE = Y, Gd) compounds previously reported by Chen et al.[14] The main difference lies in the stacking of the $[M(P_2Se_6)]_n^{n-}$ layers, which alternate in the rare-earth phases to give an ABAB... packing, resulting in the nonpolar space group $P2_12_12_1$. This may be attributed to the general contraction of the layers due to the shorter RE−Se bonds (2.945 to 3.068 Å in KYP_2Se_6), which decreases the available space for the K^+ ions in an AA... stacking arrangement. The alkali metal space requirements then force the layer packing into a less dense, alternating arrangement in the rare-earth phases. Such subtle control of structure by alkali ions in chalcogenide compounds has been previously discussed in the literature.[15] Other quaternary main group hexaselenodiphosphate compounds also display alkali-based structural control.[16]

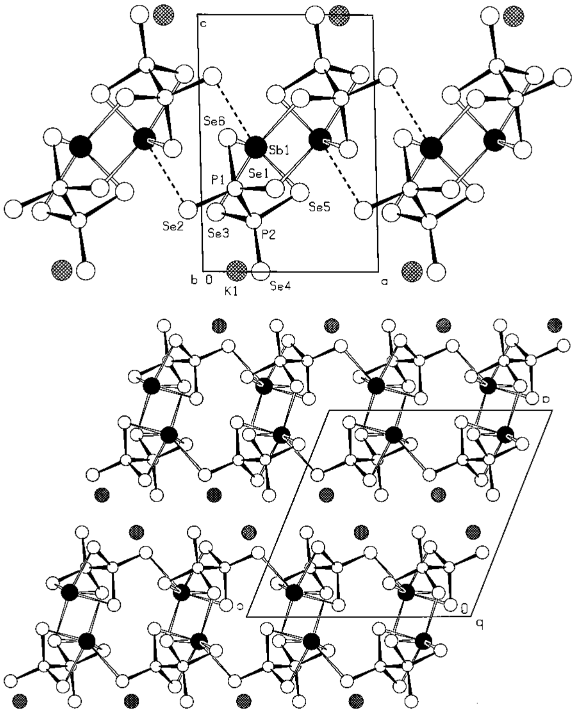

Figure 3. View of β-$KSbP_2Se_6$ down the screw axis (top). The weak interchain bond is emphasized with a dashed line. Comparison (bottom) with the structure of α-KMP_2Se_6 (M = Sb, Bi).

The structural similarity of β-KMP_2Se_6 (M = Sb, Bi) to the rare-earth analogues suggests that the main group compounds could be substitutionally doped with luminescent lanthanide ions and still preserve the polar and chiral structure. Also, the congruently melting $KSbP_2Se_6$ stoichiometry could be useful for phase-change optical data storage, due to the fast crystallization of metastable β-$KSbP_2Se_6$ from the amorphous phase. It might also be possible to utilize the unique transformation properties of the $KSbP_2Se_6$ system in a three-state logic gate. Further work is in progress to quantitate the transformation kinetics in this system and elucidate the mechanistic details of both the amorphous-to-β and the β-to-α transitions.

Acknowledgment. Support from the National Science Foundation (DMR-9817287) is gratefully acknowledged. This work made use of the SEM facilities at the Center for Electron Optics at Michigan State University. We thank Prof. Helmut Eckert for suggesting the possibility of glass formation in these systems. J.D.B. also thanks Jennifer Aitken for helpful discussions and technical assistance.

Supporting Information Available: Tables of crystallographic information (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA001270K

---

(11) A black crystal of β-$KBiP_2Se_6$ was isolated from a stoichiometric ratio of K_2Se, Bi, P_2Se_5, and Se melted with a flame in an evacuated silica tube and allowed to air cool at ~200 °C·min^{-1}. Data were collected on a Siemens SMART CCD platform at −100 °C due to the poor crystal quality. Crystallographic details are $a = 6.9183(13)$ Å, $b = 7.6633(15)$ Å, $c = 10.239(2)$ Å, $\beta = 91.508(3)°$, $V = 542.65(18)$ Å^3, $Z = 2$, $D_c = 4.797$ g·cm^{-3}, space group $P2_1$ (No. 4), μ(Mo Kα) = 369.78 cm^{-1}, $2\theta_{max} = 56.6°$. Total data collected, 3330; unique data, 2382. An empirical absorption correction was applied and the full anisotropic structure refinement using the SHELXTL software package (ref 9b) resulted in a final $R_1/wR_2 = 0.0531/0.1119$ with a Flack parameter of 0.415(19). EDS microprobe analysis gave an average composition of $K_{1.1}Bi_{1.1}P_{1.8}Se_{6.0}$.

(12) β-$KBiP_2Se_6$ far-IR spectra show absorptions at 520 (w), 512 (s), 472 (m), 449 (m), 419 (s), 340 (w), 322 (w), 293 (m), 217 (w), 180 (m), 171 (w, sh), 153 (w, sh), 142 (m), 105 cm^{-1} (m).

(13) (a) Brown, W. E.; Dollimore, D.; Galwey, A. K. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier: Amsterdam, 1980; Vol. 22. (b) Christian, J. W. *The Theory of Transformations in Metals and Alloys: Part 1*, 2nd ed.; Pergamon: Oxford, 1975; pp 528−542. (c) Avrami, M. *J. Chem. Phys.* **1940**, *8*, 212−224.

(14) Chen, J. H.; Dorhout, P. K.; Ostenson, J. E. *Inorg. Chem.* **1996**, *35*, 5627−5633.

(15) (a) Kim, K. W.; Kanatzidis, M. G. *J. Am. Chem. Soc.* **1998**, *120*, 8124−8135. (b) Chondroudis, K.; Kanatzidis, M. G.; Sayettat, J.; Jobic, S.; Brec, R. *Inorg. Chem.* **1997**, *36*, 5859−5868. (c) Kanatzidis, M. G. *Phosphorus, Sulfur, and Silicon* **1994**, *93−94*, 159−172.

(16) Breshears, J. D.; Kanatzidis, M. G. Manuscript in preparation.