Ag\textsubscript{2}Se to KAg\textsubscript{3}Se\textsubscript{2}: Suppressing Order–Disorder Transitions via Reduced Dimensionality

Alexander J. E. Rettie, Christos D. Malliakas, Antia S. Botana, James M. Hodges, Fei Han, Ruiyun Huang, Duck Young Chung, and Mercouri G. Kanatzidis

Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

Center for High Pressure Science and Technology Advanced Research, Shanghai 201203, China

HPSynC, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois 60439, United States

Department of Materials Science, Northwestern University, Evanston, Illinois 60208, United States

Supporting Information

ABSTRACT: We report an order–disorder phase transition in the 2D semiconductor KAg\textsubscript{3}Se\textsubscript{2}, which is a dimensionally reduced derivative of 3D Ag\textsubscript{2}Se. At \textasciitilde695 K, the room temperature \(\beta\)-phase (CsAg\textsubscript{2}Se\textsubscript{2} structure type, monoclinic space group \(C2/m\)) transforms to the high temperature \(\alpha\)-phase (new structure type, hexagonal space group \(R\bar{3}m\), \(a = 4.5638(5)\ \text{Å}, c = 25.4109(6)\ \text{Å}\)), as revealed by in situ temperature-dependent X-ray diffraction. Significant Ag\textsuperscript{+} ion disorder accompanies the phase transition, which resembles the low temperature (\textasciitilde400 K) superionic transition in the 3D parent compound. Ultralow thermal conductivity of \textasciitilde0.4 W m\textsuperscript{-1} K\textsuperscript{-1} was measured in the “ordered” \(\beta\)-phase, suggesting anharmonic Ag motion efficiently impedes phonon transport even without extensive disordering. The optical and electronic properties of \(\beta\)-KAg\textsubscript{3}Se\textsubscript{2} are modified as expected in the context of the dimensional reduction framework. UV–vis spectroscopy shows an optical band gap of \textasciitilde1 eV that is indirect in nature as confirmed by electronic structure calculations. Electronic transport measurements on \(\beta\)-KAg\textsubscript{3}Se\textsubscript{2} yielded \(n\)-type behavior with a high electron mobility of \textasciitilde400 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} at 300 K due to a highly disperse conduction band. Our results thus imply that dimensional reduction may be used as a design strategy to frustrate order–disorder phenomena while retaining desirable electronic and thermal properties.

INTRODUCTION

Order–disorder phase transitions underlie an enormous range of physical phenomena,\textsuperscript{1} from bulk melting to shear thickening in colloidal suspensions.\textsuperscript{2} In the solid-state, order–disorder phase transitions may be subtle, i.e., vacancy ordering\textsuperscript{3} or striking as in the case of superionic conductors, where the ion-conducting phase possesses “liquid-like” electronic conductivity.\textsuperscript{4} The high ionic conductivity of these materials has traditionally found application in solid-state electrolytes\textsuperscript{5} and recently as a proposed route to low thermal conductivity.\textsuperscript{5,7} In both cases, strategies to control order–disorder phenomena are desirable, especially in thermoelectric energy conversion where operation in the superionic state eventually results in device failure.\textsuperscript{8–10}

It is convenient to classify superionic transitions by their abruptness after Boyce and Huberman.\textsuperscript{11} Type I compounds are exemplified by AgI, where a sharp, first-order structural phase transition coincides with a dramatic increase in the ionic conductivity. In Type II, a continuous phase transition is observed (e.g., PbF\textsubscript{2}) and in Type III, no obvious phase transition is present and superionic conductivity is gradually approached with increasing temperature as in Na\textsuperscript{+}–\(\beta\)-alumina.

The Type I superionic conductors are dominated by copper and silver chalcogenides, M\textsubscript{3}Q (M = Cu, Ag; Q = Se, Te), which transform to their ion-conducting phases abruptly just above room temperature, between 400 and 450 K. Strategies to tune these solid–solid transitions are limited to nanoscale confinement which depresses the superionic state to lower temperature,\textsuperscript{12–14} and the nontrivial effects of applied pressure, which decreases the transition temperature in some Type I materials (AgI and Cu\textsubscript{2}Se)\textsuperscript{15,16} and increases it in others (Ag\textsubscript{2}Se).\textsuperscript{17}

With respect to our interest in layered materials with emergent structural and electronic properties we recently reported KCu\textsubscript{1–x}Se\textsubscript{x}, which was shown to be a \(p\)-type semiconductor with a low hole mobility arising from a relatively flat valence band.\textsuperscript{18} Electronic structure calculations revealed a dispersive conduction band and thus light, mobile electrons. By analogy with the binary Ag\textsubscript{2}Se, which is commonly electron-doped,\textsuperscript{19–21} we hypothesized that \(n\)-type material with high electron mobility could be produced by replacing the Cu\textsuperscript{+} ions...
with Ag⁺ in this 2D structure type. In evaluating KAg₃Se₂ (β-phase), we discovered an order–disorder phase transition that produces a new form α-KAg₃Se₂ at high temperature, behavior that is absent in KCu₃Se₂.

KAg₃Se₂ can be viewed as a dimensionally reduced 2D form of 3D Ag₂Se, represented by the formula, \((K₂Se)ₙ(\text{Ag}_2\text{Se})_{n-3}\) where \(K₂Se\) is the dimension reduction agent, \(n = 1\) and \(n = 3\). Within the \([\text{Ag}_2\text{Se}]_n\) layers, the Ag-Se coordination geometries (bent trigonal planar and distorted tetrahedral) and connectivity are preserved. Dimensional reduction has been applied to dismantle the covalent networks of binary compounds, progressively widening band gaps and flattening bands as network connectivity is decreased from 3D to 0D. This raises the interesting question whether the 3D Ag sublattice which is prone to such behavior could be susceptible to such behavior confined in 2D, and if so how? Although the crystal structures of several AAg₃Q₃ (A = K, Rb, Cs, Q = S, Se, Te) are known, no physical or chemical properties have been reported in detail.

We report here the synthesis and physical properties of β-KAg₃Se₂, showing that it is an n-type semiconductor with an ~1 eV band gap and high electron mobility measured by the Hall effect. Electronic structure calculations indicate a highly dispersive conduction band and low effective mass electrons in agreement with this observation. The blue-shifted band gap and lower carrier mobility relative to β-Ag₃Se are consistent with the dimensional reduction framework. We also report a high temperature Ag⁺ ion order–disorder phase transition to a very different 2D structure, α-KAg₃Se₂, that bears the hallmarks of a Type I superionic phase transition based on structural and thermal analyses. This occurs at ~700 °C, about 300 °C higher than the relevant transition in the parent compound. Finally, we measured an ultralow thermal conductivity in the “ordered” phase and preliminarily attribute this to anharmonic thermal motion of Ag ions. Thus, we highlight dimensional reduction as a potential route to suppress Type I order–disorder phase transitions, while retaining desirable electronic and thermal properties. By analogy with the binary copper and silver chalcogenides, the room temperature phase will be designated β-KAg₃Se₂ and the high temperature phase α-KAg₃Se₂ (cf., Table 2 in ref 4).

## Experimental Section

### Reagents

The following reagents were used as received: potassium metal (99%, Sigma-Aldrich) and selenium beads (99.999%, Plasmateals, Inc.). Silver shot (99.99%, Alfa Aesar) was reacted with nitric acid (98%, Strem Chemicals) to produce silver powder for the preparation of KAg₃Se₂. Before use, the Ag powder was loaded into fused-silica tube and heated with a sharp tip, flame sealed under 10⁻⁴ mbar in a vertical three-zone furnace and preheated at 700 °C prior to growth. The top and middle zones were set at 725 and 400 °C respectively, with these temperatures being informed by thermal analysis. A growth rate of ~5 mm hr⁻¹ was used. Phase-pure Ag₃Se₂ for the heat capacity measurements was synthesized from Ag and Se powders, which were homogenized in a mortar and pestle before being sealed under vacuum in a fused-silica ampule. This mixture was heated to 400 °C in 3 h and soaked for 12 h before natural cooling to room temperature in a muffle furnace. Subsequently, the powder was ressealed in an evacuated fused-silica ampule and held at 950 °C for 10 min before natural cooling to form a polycrystalline ingot.

### Powder X-ray Diffraction

Phase purity was routinely determined by powder X-ray diffraction (PXRD). Data were collected using a Panalytical XPert Pro diffractometer with a Ni filtered Cu Kα source operating at 45 mA and 40 kV. Continuous scanning was utilized with a step size of 0.0167°. Materials were finely ground and uniformly coated on a flat plate sample holder. KAg₃Se₂ powder was mildly sensitive to ambient air (evidenced by a loss of intensity of known peaks after several hours), so it was sealed under a dry Ar atmosphere with vacuum grease Kapton film for PXRD.

### Scanning Electron Microscopy

A Hitachi S-4700-II scanning electron microscope with an energy-dispersive X-ray spectrometer (EDX) was used to inspect crystal morphology and composition. The spectrometer utilizes a Li-drifted Si detector with an ultrathin window, and a beam current of 20 μA at 15 kV accelerating potential were used for data collection.

### Optical Properties

The optical band gap was determined using UV–vis diffuse reflectance spectroscopy on KAg₃Se₂ powder. Data were collected under flowing N₂ at room temperature using a Shimadzu UV-3600 UV–vis-NIR spectrophotometer. BaSO₄ was used as a 100% reflectance standard. The data were transformed using the Kubelka–Munk equation (eq 1),

\[ f(R) = \frac{(1 - R)^2}{2R} = \alpha/\varepsilon, \]

where, \(R\) is absolute reflectance, \(\alpha\) is the absorption coefficient, and \(\varepsilon\) is the scattering coefficient. ²²

### Charge Transport Properties

Temperature-variable conductivity and Hall effect measurements on polycrystals (approximate diameters: 1.5 x 1 x 0.3 mm) were conducted on a Quantum Design Dynacool Physical Property Measurement System (PPMS) between 1.8 and 300 K. Conductivity was measured by placing the sample perpendicular to the axis of current flow. The magnetic field was applied perpendicular to the axis of current flow from −9 to + 9 T. Temperature and field were cycled multiple times to confirm data reproducibility. Electronic conductivity and Hall effect measurements were performed simultaneously on the same sample in all cases. Silver paste contacts were found to result in unstable contact resistances. Stable, Ohmic contact was achieved using colloidal graphite paste (Ted Pella). Melted hydrocarbon grease (Apiezon N) was used to encapsulate the sample for transport to the PPMS. All sample preparation and contact fabrication was done in an Ar-filled glovebox.

### Electronic Structure Calculations

The electronic structure calculations were performed within DFT using the all-electron, full potential code WIEN2k ²³ based on the augmented plane wave plus local orbitals (APW+lo) basis set. We have studied the electronic structure of KAg₃Se₂ by using the modified Becke Johnson exchange potential which does not contain any system-dependent parameter. This is a local approximation to an atomic exact-exchange potential and (a screening term) + LDA-correlation (from hereon mBJ) that allows the calculation of band gaps with an accuracy similar to the much more expensive GW or hybrid methods.³⁵—³⁷ Spin orbit coupling (SOC) was introduced in a second variational procedure. ²⁴

\[ R_{\text{Kmax}} = 7.0, \]
chosen for all the calculations. A k-mesh of $19 \times 19 \times 10$ was used for $\beta$-KAg$_3$Se$_2$ and $26 \times 26 \times 4$ for $\alpha$-KAg$_3$Se$_2$. Muffin-tin radii of 2.49, 2.37 and 2.5 au were used for Ag, Se, and K, respectively. From the calculated band structure, carrier effective masses ($m^*$) at the band edges were calculated using eq 2,
\[
\frac{1}{m^*_\parallel} = \frac{1}{h^2} \frac{\partial^2 E}{\partial k^2}_|_{k^*}
\]
where, $E(k)$ is the energy as a function of $k$, the wavevector.

**High Temperature Powder X-ray Diffraction.** A Stoe STADI-MP high-resolution diffractometer with oven attachment was used to obtain data for Rietveld structure refinements at room temperature and 823 K. KAg$_3$Se$_2$ powder was finely ground and sieved to < 40 µm particle size before being diluted in a ~5:1 volume ratio with carbon powder (99.9%, Aldrich) and sealed under vacuum in a 0.5 mm O.D. fused-silica capillary. The capillary was spun during collection. Rietveld refinements were carried out using GSAS-II software (version 0.2.0). The $\beta$-phase was refined from the single crystal structure of Bensch and Duriche.\textsuperscript{22} The crystal structure of the high temperature $\alpha$-phase was solved by analogy with a related compound discovered in our laboratory, NaCu$_3$S$_2$. The single crystal structure of NaCu$_3$S$_2$ was used to refine the crystal structure of $\alpha$-KAg$_3$Se$_2$.

**Synchrotron X-ray Diffraction.** Temperature-dependent synchrotron X-ray diffraction (SXRD) data from room temperature to 600 °C were collected on beamline 11-ID-C at the Advanced Photon Source (APS) at Argonne National Laboratory. Undiluted KAg$_3$Se$_2$ powder was loaded into a fused-silica capillary (0.3 mm O.D.) and flame-sealed in under < 10$^{-3}$ mbar. Integration of the 2D images was performed using Dioptas software (version 0.2.4) using CeO$_2$ as a standard. Le Bail refinements were carried out using GSAS-II software (version 0.2.0). The linear coefficients of thermal expansion, $\alpha_x$, were calculated from the unit cell parameters using eq 3,
\[
\alpha_x = 1/L \times \frac{\partial L}{\partial T},
\]
where $L$ is length.

**Thermal Analysis and Heat Capacity.** Differential thermal analyses (DTA) were carried out with a Shimadzu DTA-50 thermal analyzer. The sample (~20 mg total mass) was sealed in a fused-silica ampule under vacuum. A fused-silica ampule containing alumina powder was used as a reference. The sample was heated to 923 at 5 K min$^{-1}$, followed by cooling at the same rate to 343 K. Residues of the DTA experiments were examined with PXRD. High temperature heat capacity ($C_p$) data were collected according to the standard procedure ASTM E1269 on a Netzsch 404 Differential Scanning Calorimetry (DSC) cell under flowing He gas with Proteus software (version 6.0.0). The sample (~20 mg total mass) was loaded in an alumina crucible with a lid and heated to 973 K at a rate of 20 K min$^{-1}$. Thermogravimetric analysis indicated a negligible (<0.1%) weight change under these experimental conditions. Prior to sample measurement, several baseline runs and calibration with a sapphire standard of comparable mass (Netzsch) were performed using the experimental heating profile. Transition temperatures were measured from the peak onset. The entropy change of transition, $\Delta S_T$, was determined using eq 4,
\[
\Delta S_T = \Delta H_T / T_p = (1/T_p) \int C_p(T) \, dT
\]
where $\Delta H_T$ is the enthalpy change of the transition, and $T_p$ is the peak temperature of the relevant thermal feature. Low temperature $C_p$ was measured on a Quantum Design Dynacool Physical Property Measurement (PPMS) System between 1.8 and 300 K. A piezoelectric N grease was used to fix samples to the heat capacity stage. Data were collected on warming.

**Thermal Diffusivity.** KAg$_3$Se$_2$ powder was densified by spark plasma sintering (SPS, Dr. Sinter) at 623 K in a graphite die and samples were shaped by hand polishing in a nitrogen-filled glovebox. Samples were fabricated such that $x$ was measured both parallel ($\parallel$) and perpendicular ($\perp$) to the SPS pressing direction as preferred orientation may occur during SPS processing of anisotropic materials. Thermal diffusivity ($D$) was measured using a Netzsch LFA457 laser flash diffusivity instrument. Samples were spray coated with a thin layer of graphite to minimize radiative heat loss from the material. The total thermal conductivity was calculated from $\kappa = D \times C_p \times \rho$ where the specific heat capacity ($C_p$) was measured as a function of temperature in a DSC and the density ($\rho$) was determined using the dimensions and mass of the sample to be ~5.99 g cm$^{-3}$ or ~90% of the theoretical density. The uncertainty of the thermal conductivity is estimated to be ~10%.

**RESULTS AND DISCUSSION**

**Synthesis.** Phase pure KAg$_3$Se$_2$ powder was synthesized from a stoichiometric mixture of K$_2$Se$_3$, Ag, and Se. Polyselenide precursors were used to avoid the exothermic reaction between K and Se. Room temperature unit cell parameters from Rietveld refinements ($a = 3.44\%$, $\chi^2 = 2.16$) on the PXRD data (Figure S1a in the Supporting Information, SI) were in good agreement with those from the layered single crystal structure solution of Bensch and Duriche.\textsuperscript{22} $a = 16.613(1) \, \text{Å}$, $b = 4.39149(7) \, \text{Å}$, $\alpha = 8.7768(4) \, \text{Å}$, $\beta = 115.546(2)\, ^\circ$, $Z = 4$, and $V = 577.71(1) \, \text{Å}^3$. Scanning electron microscopy (SEM) showed a layered crystal morphology (Figure S1b in the SI) and elemental analysis by EDX yielded K$_{0.05}$Ag$_{0.95}$Se$_{3.05}$O$_{0.6}$ close to the expected 1:3:2 atomic ratios. Vertical Bridgman crystal growth was utilized to produce crystal samples for property measurements. The crystal boule produced was easily cleaved into visually polycrystalline samples (see Figure S2 in the SI). This is likely due to the formation of multiple domains while cooling through the phase transition.

**Optical Properties.** (K$^+$)(Ag$^{+}$)$_2$(Se$^{2-}$)$_3$ is a valence-precise compound and therefore expected to be a semiconductor. Indeed the sample exhibits a sharp optical transition at ~1 eV, consistent with the black color of KAg$_3$Se$_2$ powder (Figure 1).

![Figure 1. Tauc plot (allowed direct) showing a band gap transition at ~1.0 eV. Inset: photograph of black KAg$_3$Se$_2$ powder in a glass vial (27.5 mm diameter).](image-url)
Bridgman-grown boule was measured from 2 to 300 K, with current flow approximately parallel to the layers. The temperature-dependent electronic conductivity, $\sigma$, is shown in Figure 2a. The modest room temperature $\sigma$ of $\sim 0.1$ S cm$^{-1}$ is reasonable for a semiconductor. A weak, negative temperature-dependence of $\sigma$ was observed—decreasing by a factor of about 2 over this temperature range—indicating degenerate semiconducting behavior.

Hall effect data showed a linear dependence with field (Figure S3 in the SI) and were negative at all temperatures implying that electrons are the majority carriers ($n$-type). Calculation of electron concentration ($n_{\text{Hall}}$) yielded a value of $10^{15}$ cm$^{-3}$ that was effectively constant with temperature (Figure 2b). Degenerate behavior can result from defects that have a negligible ionization energy or the formation of impurity bands. Due to the low concentration of carriers in our samples we prefer the former explanation, which was also suggested to explain the electronic transport of Ag$_2$Se and Ag$_2$Te at low temperatures.\cite{40} Defect energy calculations for KAg$_3$Se$_2$ would be very interesting as doping in the binary silver chalcogenides is notoriously difficult to control, usually being self-doped $n$-type at levels $> 10^{18}$ cm$^{-3}$ during synthesis.\cite{41,42} By analogy with Ag$_2$Se we attribute $n$-type doping in our samples to a small Ag excess.\cite{35,44} The Hall mobility for electrons was estimated at $\sim 400$ cm$^2$ V$^{-1}$ s$^{-1}$ at room temperature and rose to $\sim 700$ cm$^2$ V$^{-1}$ s$^{-1}$ at 5 K (Figure 2b). These results were reproducible on additional samples (Figure S4 in the SI).

**Band Structure Calculations.** Electronic structure calculations showed semiconducting behavior, which was expected from the valence-precise nature of the compound (Figure 3a). It can be seen that our calculations reproduce the experimental band gap well, giving a value of 0.9 eV. Although the band gap is formally indirect at $\Gamma$-$L$, the direct transition at $\Gamma$ is extremely close in energy ($< 0.05$ eV), hence we justify the use of Tauc analysis for direct transitions in the analysis above.

Monoclinic KAg$_3$Se$_2$ has a highly disperse conduction band around $\Gamma$, mainly comprised of Ag $s$ and Se $p$ orbitals (Figure 3b). The calculated effective masses of $\sim 0.4 m_e$ and $0.5 m_e$ for $\Gamma$-$N$ and $\Gamma$-$Z$, respectively, are consistent with the high electron mobility measured by the Hall effect. It is noteworthy to point out the almost linear dispersion of the conduction band along $\Gamma$-$N$. Conversely, a relatively flat valence band, consisting of Ag $d$ and Se $p$ orbitals in equal contribution, suggests holes should have high effective masses and low intrinsic mobility. Indeed, this has been recently observed in the $p$-type copper analogue, KCu$_3$S$_2$, which is isometrically similar and shares a similar band structure.\cite{18} The corresponding Brillouin zone is given in the SI (Figure S5 in the SI). Decreased carrier mobility due to flatter bands and the larger optical band gap of $\beta$-KAg$_3$Se$_2$ relative to $\beta$-Ag$_2$Se (Table 1) agree with the expected trends for dimensional reduction.

**Order–Disorder Phase Transition.** DTA indicates that KAg$_3$Se$_2$ melts congruently at $\sim 890$ K and crystallizes at $\sim 885$ K (see Figure S6 in the SI). An additional set of reproducible exothermic and endothermic features, however, appear below bulk melting/crystallization transitions at $\sim 700$ and 670 K, respectively.

These thermal events raised the possibility of a phase transition, and this was investigated by high temperature XRD. At 823 K a clear change in the diffraction pattern was observed (Figure 4a). The high temperature structure was solved by analogy with a related compound previously discovered by our group: NaCu$_3$S$_2$ (hexagonal space group R-3m, $a = 3.9346(6)$ Å, $c = 21.971(4)$ Å, $Z = 3$, $R_{\text{all}} = 0.0573$, $wR_{\text{all}} = 0.1359$). This structure was used as a starting point for subsequent refinements. Rietveld refinements yielded a structural model (Figure 4b) with very good agreement with the data ($wR = 2.63\%$, $\chi^2 = 2.05$). Details of the structure refinement and comparison with $\beta$-KAg$_3$Se$_2$ are located in Table 2. Atomic coordinates, anisotropic displacement parameters, selected bond lengths and angles for $\alpha$-KAg$_3$Se$_2$ are presented in Tables 3, 4, 5, and 6 with full refinement details given in the SI. Crystallographic information for $\beta$-KAg$_3$Se$_2$ (Beta_KAg3Se2.cif) is provided in the SI.
trigonal planar and distorted tetrahedral (2 + 2) Ag-Se arrangements also describe the two unique Ag atoms in β-Ag2Se,46,47 evidencing the structural relationship between these phases (Figure S7 in the SI).

As illustrated in Figure 5a, the high temperature structure also consists of infinite $[\text{Ag}_3\text{Se}_2]^-$ layers, $\sim$4.1 Å thick, spaced $\sim$4 Å apart by K$^+$ ions. The uneven Se atoms that cap the layers in β-KAg$_3$Se$_2$ have flattened into 2D hexagonal sheets in α-KAg$_3$Se$_2$. On the basis of the small ADPs and analogy with other Ag ionic conductors,46,47 the Se ions comprise the immobile sublattice. Transformation from the initial combination of trigonal and near-square motifs to the purely trigonal can be accomplished by each trigonal Se chain translating by $\sim$1 Å in the y-direction relative to each other (Figure 5c). Sandwiched between the Se sheets are two unique Ag sites. Ag1 is 3-fold coordinated with Se in (red) sheets which are separated by K ions (light blue). Thermal ellipsoids are shown at 50%.

It is instructive to first summarize the main structural details of the room temperature structure. β-KAg$_3$Se$_2$ crystallizes in the CsAg$_3$S$_2$ structure type (monoclinic space group C2/m),28,45 with corrugated infinite $[\text{Ag}_3\text{Se}_2]^-$ layers separated by K$^+$ ions (Figure 5a). Briefly, these layers can be visualized as Ag$_3$Se$_4$ columns that run along the b-axis, bridged by Ag atoms in a distorted tetrahedral environment. Three unique Ag atoms stabilize this network. Ag(1) and Ag(3) form the periodic “throwing star” columns (shaded in Figure 5a and b) and are 3-fold coordinated with Se in a bent planar geometry. Joining each column are two Ag(2) atoms in a 2 + 2 distorted tetrahedral environment with Se. It is worth noting that in the original room temperature single crystal refinement40 the anisotropic displacement parameters (ADPs) for the Ag ions are significant—the largest being $U_{22}$(Ag(2)): the bridging Ag ion between columns—which can be indicative of static or dynamic disorder. Bent...
Table 2. Crystal Data and Rietveld Refinement for \(\beta\)- and \(\alpha\)-KAg\(_3\)Se\(_2\), at 823 K with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>label</th>
<th>(\beta)-KAg(_3)Se(_2)</th>
<th>(\alpha)-KAg(_3)Se(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>empirical formula</td>
<td>KAg(_3)Se(_2)</td>
<td>520.62</td>
</tr>
<tr>
<td>formula weight</td>
<td>1.54059 Å</td>
<td>823 K</td>
</tr>
<tr>
<td>wavelength</td>
<td>C 2/m</td>
<td>R – 3 m</td>
</tr>
<tr>
<td>temperature</td>
<td>a = 16.613(1) Å, (\alpha = 90^\circ)</td>
<td>a = 4.5638(5) Å, (\alpha = 90^\circ)</td>
</tr>
<tr>
<td>crystal system</td>
<td>b = 4.39149(7) Å, (\beta = 115.546(2)^\circ)</td>
<td>b = 4.5638(5) Å, (\beta = 90^\circ)</td>
</tr>
<tr>
<td>space group</td>
<td>c = 8.7768(4) Å, (\gamma = 90^\circ)</td>
<td>c = 25.4109(6) Å, (\gamma = 120^\circ)</td>
</tr>
<tr>
<td>unit cell dimensions</td>
<td>volume = 577.71(1) Å(^3)</td>
<td>volume = 458.36(6) Å(^3)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>density (calculated)</td>
<td>5.986 g/cm(^3)</td>
<td>5.658 g/cm(^3)</td>
</tr>
<tr>
<td>goodness-of-fit</td>
<td>1.47</td>
<td>1.43</td>
</tr>
<tr>
<td>profile R indices</td>
<td>wR = 0.03442</td>
<td>wR = 0.02633</td>
</tr>
</tbody>
</table>

Table 3. Atomic Coordinates (\(\times 10^4\)) and Equivalent Isotropic Displacement Parameters (Å\(^2\)\(\times 10^3\)) for \(\alpha\)-KAg\(_3\)Se\(_2\), at 823 K with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>label</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>occupancy</th>
<th>(U_{eq})</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.000</td>
<td>82(9)</td>
</tr>
<tr>
<td>Ag(1)</td>
<td>0</td>
<td>0</td>
<td>4390(2)</td>
<td>0.750</td>
<td>131(4)</td>
</tr>
<tr>
<td>Ag(2)</td>
<td>0</td>
<td>0</td>
<td>1444(2)</td>
<td>0.750</td>
<td>275(2)</td>
</tr>
<tr>
<td>Se</td>
<td>0</td>
<td>0</td>
<td>2472(2)</td>
<td>1.000</td>
<td>59(4)</td>
</tr>
</tbody>
</table>

\(U_{eq}\) is defined as one-third of the trace of the orthogonalized \(U_{ij}\) tensor.

Table 4. Anisotropic Displacement Parameters (Å\(^2\)\(\times 10^3\)) for \(\alpha\)-KAg\(_3\)Se\(_2\), at 823 K with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>label</th>
<th>(U_{11})</th>
<th>(U_{22})</th>
<th>(U_{33})</th>
<th>(U_{12})</th>
<th>(U_{13})</th>
<th>(U_{23})</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>103(9)</td>
<td>103(9)</td>
<td>39(9)</td>
<td>51(4)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ag(1)</td>
<td>124(4)</td>
<td>124(4)</td>
<td>148(3)</td>
<td>62(2)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ag(2)</td>
<td>386(2)</td>
<td>386(2)</td>
<td>55(3)</td>
<td>193(1)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Se</td>
<td>68(4)</td>
<td>68(4)</td>
<td>39(3)</td>
<td>34(2)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

The anisotropic displacement exponent factor exponent takes the form: \(-2\pi^2[h^2a^2U_{11} + \ldots + 2hka^bU_{ij}].\)

Table 5. Bond Lengths [Å] for \(\alpha\)-KAg\(_3\)Se\(_2\), at 823 K with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>bond</th>
<th>distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>K-Se × 6</td>
<td>3.4250(23)</td>
</tr>
<tr>
<td>Ag(1)-Se × 3</td>
<td>2.6813(12)</td>
</tr>
<tr>
<td>Ag(2)-Se</td>
<td>2.614(5)</td>
</tr>
<tr>
<td>Ag(1)-Se × 3</td>
<td>3.022(3)</td>
</tr>
<tr>
<td>Se-Se</td>
<td>4.5638(4)</td>
</tr>
</tbody>
</table>

Table 6. Bond Angles [°] for \(\alpha\)-KAg\(_3\)Se\(_2\), at 823 K with Estimated Standard Deviations in Parentheses

<table>
<thead>
<tr>
<th>label</th>
<th>angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se-K-Se × 3</td>
<td>83.56(7)</td>
</tr>
<tr>
<td>Se-K-Se × 3</td>
<td>96.44(7)</td>
</tr>
<tr>
<td>Se-Ag(1)-Se × 3</td>
<td>116.65(9)</td>
</tr>
<tr>
<td>Se-Ag(2)-Se × 3</td>
<td>119.32(10)</td>
</tr>
<tr>
<td>Se-Ag(2)-Se × 3</td>
<td>98.06(13)</td>
</tr>
</tbody>
</table>

The structural cues for fast Ag\(^+\) ion conduction in \(\alpha\)-KAg\(_3\)Se\(_2\) and the occasional growth of actual Ag metal whiskers in high temperature annealing experiments of the KAg\(_3\)Se\(_2\) samples or even during slow cooling from the melt (Figure S12 in the SI) strongly suggested that the Ag\(^+\) ions in the structure are highly mobile. Fast ion or “superionic” conductors are defined by ionic conductivities or ionic diffusivities that approach those observed in liquids, \(\sim0.1–1 \text{ S cm}^{-1}\) or \(10^{-12} \text{ cm}^2 \text{s}^{-1}\), respectively. Experiments aimed at determining the Ag\(^+\) ion contribution to the conductivity by AC or DC techniques were inconclusive due to the lack of suitable electron-blocking electrodes (see Section S4 in the SI). Spectroscopic techniques such as solid-state NMR\(^{53}\) or quasielastic neutron scattering\(^{52}\) may be of use to determine the mobility of Ag\(^+\) ions but these are out of the scope of the current study.

Heat Capacity. The thermal events revealed by DTA were quantified with heat capacity (\(C_p\)) measurements in a DSC. A sharp, symmetrical peak (onset at \(\sim695\) K) in the heat capacity and hysteresis between heating and cooling (Figure 7) were observed. Taken together with the discontinuous change in unit cell volume (Figure 6a), these are strong evidence for the order–disorder transition being first-order. Thus, the order–disorder transition in KAg\(_3\)Se\(_2\) at \(\sim695\) K most closely resembles a Type I superionic phase transition.\(^{4,11}\)

Comparative changes in entropy at the solid transition and the melting point have been suggested previously to indicate “melting” of a sublattice in superionic conductors.\(^{33}\) The thermodynamic properties of the solid and melting transitions of KAg\(_3\)Se\(_2\) (calculated using eq 4) and known Type I superionic conductors are given in Table 7. KAg\(_3\)Se\(_2\) is unique among these compounds as the transition temperature is high and the 2D character is retained in the new structure of the high temperature phase. Comparison shows that the entropy change of the transition (\(\Delta S_\text{f}\)) is comparable to that of AgI and Ag\(_2\)Se, but that the entropy of fusion was markedly greater. Taking \(\Delta S_\text{f}\) as a fraction of the total entropy change implies that \(\sim1/2\) of the Ag\(^+\) ions are highly mobile at the \(\beta \rightarrow \alpha\) transition.

As shown in Figure 7a, the heat capacity is in good agreement with the Dulong–Petit limit (\(\sim150\) J mol\(^{-1}\) K\(^{-1}\)) below 675 K. Between 750 K and the bulk melting point there is a significant increase of \(C_p\) up to \(\sim350\) mol\(^{-1}\) K\(^{-1}\) at 850 K. This is not typically observed in related disordered phases—in superionic AgI and Ag\(_2\)Se \(C_p\) only slightly increased (<10%) with increasing temperature.\(^{55,56}\) We speculate that the elevated \(C_p\) post-
transition may be a broad peak associated with a subsequent, subtler order—disorder transition in the α-phase, e.g., gradual changes in Ag site occupancy with increasing temperature as seen in AgCr\(_Q\)\(_2\) (\(Q = S, Se\))\(^{58,59}\) compounds, convoluted with the melting peak.

Low temperature \(C_p\) data were measured for both \(\beta\)-KAg\(_3\)Se\(_2\) and \(\beta\)-Ag\(_2\)Se between 1.8 and 300 K in a Dynacool PPMS (Figure S13 in the SI). Qualitative analysis indicated the presence of low energy phonon modes in both materials, with those in \(\beta\)-KAg\(_3\)Se\(_2\) being even lower in energy than \(\beta\)-Ag\(_2\)Se (Section S5 in the SI). As low energy phonon modes and large thermal expansion coefficients are often correlated with efficient scattering of phonons, we measured the thermal conductivity of this material.

**Thermal Conductivity.** The thermal conductivity measured on the SPS processed pellet sample of \(\beta\)-KAg\(_3\)Se\(_2\) is \(\sim 0.4\) W m\(^{-1}\) K\(^{-1}\) at room temperature and reaches a minimum of \(\sim 0.3\) W m\(^{-1}\) K\(^{-1}\) between 325 and 700 K (Figure 8). This compares well with the estimated range of lattice thermal conductivity for \(\beta\)-Ag\(_2\)Se (\(\sim 0.3–0.5\) W m\(^{-1}\) K\(^{-1}\) at room temperature)\(^{41,61,62}\) indicating that ultralow thermal conductivity is retained after dimensional reduction. In \(\beta\)-KAg\(_3\)Se\(_2\), the difference in thermal conductivity perpendicular and parallel to the pressing direction was \(<20\%\), indicating that anisotropy does not play a strong role in the low thermal conductivity. A steep increase in \(\kappa\) occurred above the phase transition, roughly doubling from 725 to 825 K. This increase was driven by the larger heat capacity in this phase (Figure 7a) as the density decreases a little (Table 1) and the diffusivity, \(D\), is approximately constant (Figure S14 in the SI). The weak temperature dependence of \(D\) is consistent with high levels of disorder and has been observed in a number of Ag\(^+\)-ion superionic phases.\(^{41,61,62}\) For the SPS processed sample of the α-phase the values of \(\kappa\) for different pressing directions converge. This is likely due to microstructural evolution (Figure 6c) eliminating the small difference in crystallite orientation with pressing direction.

We attribute the ultralow thermal conductivity to efficient scattering of phonons by Ag\(^+\) ions even in the “ordered” \(\beta\)-KAg\(_3\)Se\(_2\), similar to the rattling mechanism proposed in CsAg\(_5\)Te\(_3\), which shares the structural motif of columns bridged by distorted Ag-Q tetrahedra.\(^{63}\) Our results highlight that an order—disorder transition is not necessary for ultralow \(\kappa\). Indeed,
a recent study attributes the low thermal conductivity of Cu$_2$Se to Cu$^+$ ion anharmonicity and not the quasi-molten Cu$^+$ sublattice.\textsuperscript{64} Therefore, structures that facilitate anharmonic thermal motion (i.e., those with all the ingredients for superionic conduction but are inhibited in some way) may yield desirable functional properties without superionic conductivity that leads to eventual material failure under dc operating conditions.

**Related Materials.** A comparison to KCu$_{3-x}$Se$_2$ is apt due to the similarities between the parent and derivative compounds; KCu$_{3-x}$Se$_2$ is also layered and isostructural with $\beta$-KAg$_3$Se$_2$. The parent binary phase is Cu$_{2-x}$Se, another Type-I superionic conductor with an order–disorder transition at 395 K,\textsuperscript{65} where the unique Cu-Se environments are distorted tetrahedral and trigonal planar. The relevant physical properties of Cu$_{2-x}$Se are: band gap\textsuperscript{66,67} \(\sim 1.2\) eV and hole mobility\textsuperscript{68} of \(\sim 15\) cm$^2$/V$\cdot$s$^{-1}$ at a carrier concentration of \(10^{20}\) cm$^{-3}$). We showed recently\textsuperscript{18} that KCu$_{3-x}$Se$_2$ is a $p$-type semiconductor with a wider band gap (~1.35 eV) and lower hole mobility (on the order of \(\sim 1\) cm$^2$/V$\cdot$s$^{-1}$ for a carrier concentration of \(10^{19}\) cm$^{-3}$) relative to the parent. These trends in physical properties are in agreement with the dimensional reduction framework. In that report, DTA indicated no phase transition prior to the melting point of the material (~1030 K), consistent with the order–disorder transition at 395 K in Cu$_{2-x}$Se also being suppressed.

Additional known members of the homologous series (K$_2$Se)$_m$(Ag$_2$Se)$_n$ are as follows: K$_2$Ag$_{12}$Se$_7$ \((m = 6, n = 1)\), a 3D-open-framework structure with K$^+$ filling the channels,\textsuperscript{69} K$_2$Ag$_4$Se$_3$ \((m = 2, n = 1)\) and KAgSe \((m = 1, n = 1)\), which are 2D like $\beta$-KAg$_3$Se$_2$ but with Ag in either distorted tetrahedral or trigonal planar coordination, respectively.\textsuperscript{70,71} Relevant physical properties, e.g., thermal analysis, optical, and transport properties, are currently unknown. Thus, thorough characterization studies of these compounds will be necessary to include them in this framework, in addition to the discovery of 1D and 0D members.
The monochinal 2D semiconductor $\beta$-KAg$_3$Se$_2$ exhibits a first-order phase transition to a higher symmetry phase ($\alpha$-KAg$_3$Se$_2$) at high temperature. The $\beta$-phase is a dimensionally reduced derivative of $\beta$-Ag$_2$Se, with a band gap of $\sim$1 eV and features a high room temperature electron mobility of $\sim$400 cm$^2$ V$^{-1}$ s$^{-1}$ at a carrier concentration of $\sim$10$^{15}$ cm$^{-3}$ which is attributed to a highly disperse conduction band. Above $\sim$695 K, the system transforms to a new hexagonal layered structure (R3m), and this is accompanied by extensive Ag ion disorder confined in infinite layers $\sim$4 Å thick. This order–disorder transition is found to strongly resemble a Type I superionic phase transition based on our structural and thermal analyses. Interestingly, the solid transition temperature is significantly higher than its 3D parent compound, a known Type I superionic conductor. Finally, ultralow thermal conductivity in the “ordered” $\beta$-phase was ascribed to anharmonic thermal motion of the Ag ions. Our results hint that the concept of dimensional reduction may include order–disorder transitions and thermal conductivity, while also revealing a family of layered chalcogenide compounds where functional properties can be chemically tuned in this context.

CONCLUSIONS

The symbols “$\perp$” and “$\parallel$” represent measurements perpendicular and parallel to the SPS pressing direction, respectively.

Table 7. Comparison of Thermodynamic Data with Type-I Superionic Conductors

<table>
<thead>
<tr>
<th>compound</th>
<th>solid transition</th>
<th>melting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_f$ (K)</td>
<td>$\Delta T$ (J mol$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>AgI</td>
<td>420</td>
<td>15.0</td>
</tr>
<tr>
<td>Ag$_2$Se</td>
<td>406</td>
<td>16.8</td>
</tr>
<tr>
<td>KAg$_3$Se$_2$</td>
<td>704</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Figure 8. Total thermal conductivity of KAg$_3$Se$_2$ from 325 to 825 K. The symbols “$\perp$” and “$\parallel$” represent measurements perpendicular and parallel to the SPS pressing direction, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b04888.

Crystallographic data (CIF)

Details of Rietveld refinements, additional transport and structural data, electronic structure calculations and thermal diffusivity data (PDF)

AUTHOR INFORMATION

Corresponding Author

m-kanatzidis@northwestern.edu

ORCID

Alexander J. E. Rettie: 0000-0002-2482-9732

Mercouri G. Kanatzidis: 0000-0003-2037-4168

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was primarily performed in the Materials Science Division of Argonne National Laboratory and supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. We gratefully acknowledge the computing resources provided on Blues, the high-performance computing clusters operated by the Laboratory Computing Resource Center at Argonne National Laboratory. We are indebted to S.M. Haile for the generous use of electrochemical apparatus and thank K. Selkregg of Monofrax LLC for the donation of Na$_2$β-alumina material for preliminary experiments. A.J.E.R. acknowledges fruitful discussions with M. Agne, M. Murphy, and J. Bao. High temperature XRD measurements were performed at the IMSEC at Northwestern University, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the State of Illinois and International Institute for Nanotechnology (IIN). Use of the Center for Nanoscale Materials, an Office of Science user facility, for SEM/EDX analysis was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. J.M.H. acknowledges support from The Midwest integrated Center for Computational Materials (No. SJ-30161-0010A) for thermal conductivity measurements.

REFERENCES
