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$K_2Ag_3CeTe_4$: A Semiconducting Tunnel Framework Made from the Covalent "Link-Up" of $[Ag_2CeTe_4]^{3-}$ Layers with Ag

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Recently, we have studied reactions in the A/Cu/Ln/Q (Ln = Ce,U; Q = S,Se) systems which led to the discovery of $K_2Cu_2CeS_4$,[1] $KCuCe_2S_6$,[1,2] $KCuLa_2S_6$,[2] $CsCuCe_2S_6$,[2] $KCuCe_2Se_6$,[2] $CsCuCeS_3$,[2] and $KCuUSe_3$.[2] Of these, $K_2Cu_2CeS_4$[1] and $CsCuCeS_3$[2] exhibit mixed chalcogenide valency and appreciable electrical conductivity. At the same time, there has been a rapid expansion in this area by independent investigators producing compounds such as $CsCuUTe_3$,[3] $BaLnMQ_3$ (Ln = La, Ce, Nd, Er; M = Cu,Ag; Q = S,Se),[4] $BaDyCuTe_3$,[5] $K_{1.5}Dy_2Cu_{2.5}Te_5$,[5] $K_{0.5}Ba_{0.5}DyCu_{1.5}Te_3$,[5] and $KCuEu_2S_6$.[6] By combining the ionic lanthanide and actinide bonding with the more covalent transition metal bonding, one can access phases with novel structures and properties.[7] Of course, a better understanding of this newly emerging family of compounds could be achieved if a wider variety of members were available for study, including the corresponding tellurides. One important difference between Te_x^{2-} and Q_x^{2-} (Q = S,Se) ions is the greater tendency for the former to associate through Te−Te bonding interactions because of the more diffuse nature of its orbitals.[8−11] For example, in $SmTe_3$,[12] $CsCe_3Te_8$,[8] and $KCuCeTe_4$,[9] Te−Te interactions lead to superstructures. This characteristic could lead to mixed valency, which in turn can produce interesting physical phenomena.[13] Recently, we reported on the layered compound $Rb_2Cu_3CeTe_5$[14] which features Te_2^{2-} units. Here we report on $K_2Ag_3CeTe_4$, a three-dimensional tunnel framework built from the linking of $[Ag_2CeTe_4]^{3-}$ layers with Ag.

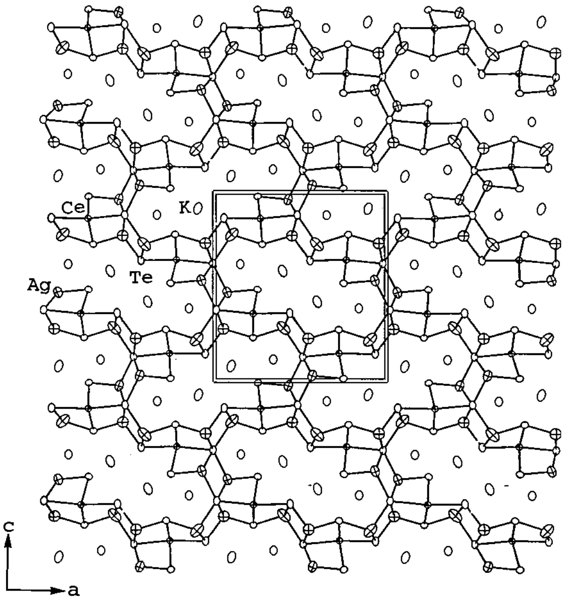

Figure 1. ORTEP representation of the structure of $K_2Ag_3CeTe_4$ viewed down the *b* axis (90% probability ellipsoids). Ellipses with octant shading represent Ce, crossed ellipses represent Ag, and open ellipses represent K and Te.

The structure of $K_2Ag_3CeTe_4$[15] is somewhat related to that of $K_2Cu_2CeS_4$,[1] see Figure 1. The basic units that make up the anionic framework in both compounds are $[CeQ_6]$ octahedra and $[MQ_4]$ (M = Cu,Ag) tetrahedra. In $K_2Cu_2CeS_4$, layers are formed when double rows of edge-sharing $[CuS_4]$ tetrahedra alternate with chains of $[CeS_6]$ octahedra, see Figure 2A. The layers in $K_2Ag_3CeTe_4$, however, are now corrugated due to the different

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(15) (a) *$K_2Ag_3CeTe_4$* was synthesized from a mixture of 0.309 g K_2Te (1.5 mmol), 0.162 g Ag (1.5 mmol), 0.070 g Ce (0.5 mmol), and 0.447 g Te (3.5 mmol) which was sealed under vacuum in a carbon coated quartz tube and heated to 850°C for 6 days. The tube was then cooled to 400 °C at −4 °C h^{-1}, and then to room temperature. The excess K_xTe_y flux was removed, under N_2 atm, with DMF to reveal black needle-shaped air/water stable crystals (57% yield, based on Ag). Phase homogeneity was confirmed by comparing the powder X-ray diffraction pattern of the product against one calculated using the crystallographically determined atomic coordinates. A Siemens SMART CCD diffractometer was used to collect data from a crystal of 0.31 × 0.02 × 0.01 mm dimensions and Mo Kα (λ = 0.710 73 Å) radiation. The SMART[15b] software was used for data acquisition and SAINT[15b] for data extraction and reduction. An absorption correction was done using SADABS.[15c] Crystal data at 93(2) K: a = 17.1985(1) Å, b = 4.6393(2) Å, c = 15.4055(3) Å, V = 1229.19(3) Å^3, Z = 8, ρ_{calc} = 5.69 g/cm^3, space group *Pnma* (No. 62), μ = 18.26 mm^{-1}, index ranges $-20 \leq h \leq 20$, $-5 \leq k \leq 5$, $-18 \leq l \leq 18$, $2\theta_{max} = 50°$, total data 5536, unique data 1221 (R_{int} = 0.03), data with $F_o^2 > 2\sigma(F_o^2)$ 1066, no. of variables 62, final R/wR2 0.032/0.066, GOF 1.06. The structure was solved (on F^2) and refined using SHELXTL-5.[15b] (b) SMART (1994), SAINT, Version 4, and SHELXTL, Vers. 5, (1994): Siemens Analytical X-ray Systems, Inc.: Madison, WI 53719. (c) Sheldrick, G. M. SADABS; University of Göttingen, Germany, to be published.

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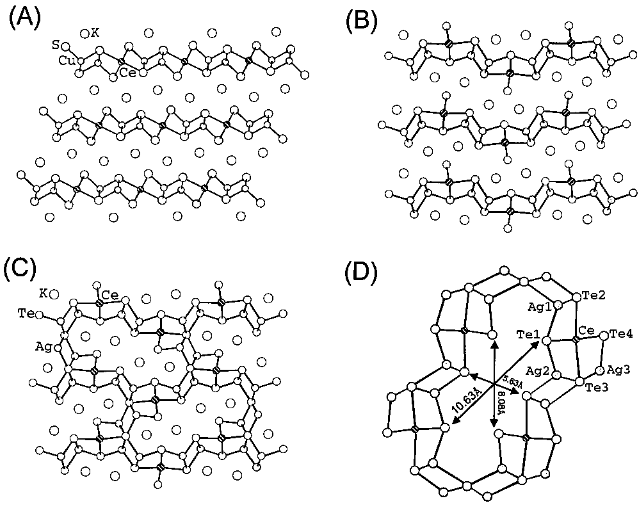

Figure 2. (A) Layers of $K_2Cu_2CeS_4$. (B) Corrugated $[Ag_2CeTe_4]^{3-}$ layers in $K_2Ag_3CeTe_4$. (C) Inclusion of the third Ag atoms, between the $[Ag_2CeTe_4]$ layers, links them together into a three-dimensional structure. (D) Tunnel window projection with corresponding dimensions. Selected distances (Å): Ce−Te1, 3.2383(8); Ce−Te2, 3.261(1); Ce−Te3, 3.303(1); Ce−Te4, 3.1898(8); Ag1−Te1, 2.906(2); Ag1−Te2, 2.785(1); Ag1−Te3, 3.182(2); Ag2−Te1, 2.813(2); Ag2−Te2, 2.828(2); Ag2−Te3, 2.974(1); Ag3−Te3, 2.922(1); Ag3−Te4, 2.778(1).

way in which the chains of $[CeTe_6]$ octahedra connect to the double rows of $[AgTe_4]$ tetrahedra, Figure 2B. In $K_2Cu_2CeS_4$ the rows of $[CuS_4]$ tetrahedra are arranged centrosymmetrically around chains of $[CeS_6]$ octahedra, while in $K_2Ag_3CeTe_4$ the edge-sharing with $[AgTe_4]$ tetrahedra involves adjacent edges of $[CeTe_6]$ octahedra. This difference creates a quadruply bridging Te atom (binding to two Ag and two Ce atoms) and leaves a trans Te atom, bonded to Ce, available to bind a third Ag atom. The latter acts to link the layers into a three-dimensional structure, Figure 2C. It is interesting that if one removes the Ce atoms, the remaining $[Ag_3Te_4]$ substructure is still contiguous and three-dimensional. In this sense, the Ce atoms occupy positions in an open silver-telluride framework. The tunnels in the structure have an oval-shaped cross section with dimensions of 10.63 Å (Te1−Te1) × 5.63 Å (Te2−Te2) × 8.08 Å (Te4−Te4), Figure 2D. If the van der Waals diameters are considered, the tunnels have an accessible opening of 7.9 Å × 2.9 Å × 5.3 Å. These dimensions are large enough to suggest that the K^+ cations may be accessible via topotactic ion-exchange.

Solid-state ion-exchange reactions were performed in which the material was pressed with a 50-fold excess of NaI and heated at 100 °C for 5 days.[16] The product was isolated by washing away the iodide matrix with methanol. The resulting material was isostructural as judged by powder X-ray diffraction. Elemental analysis (inductively coupled plasma spectroscopy) on the polycrystalline material gave $Na_{1.26}K_{0.74}Ag_3CeTe_4$. Considering that in typical ion-exchange reactions, multiple cycles are required for complete exchange, where the material has to be isolated and re-reacted with fresh reagents several times, the observed degree of ion-exchange in the first cycle for $K_2Ag_3CeTe_4$ is remarkably high. Complete exchange is expected in subsequent cycles.

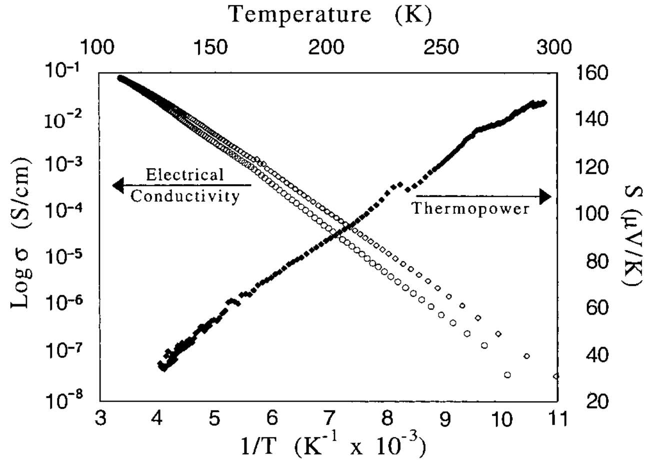

Figure 3. (A) Variable temperature, four-probe electrical conductivity data for a single crystal of $K_2Ag_3CeTe_4$. (B) Variable temperature thermopower data for a pressed pellet of $K_2Ag_3CeTe_4$.

The magnetic susceptibility of $K_2Ag_3CeTe_4$ follows Curie−Weiss Law over the range 5−300 K (at 6000 G), with only slight deviation from linearity beginning below 50 K. At temperatures above 100 K, a μ_{eff} of 2.19 μ_B has been calculated, which is in accordance with the usual range for Ce^{3+} compounds (2.3−2.5 μ_B). The presence of Ce^{3+} is confirmed by infrared spectroscopy which shows one, well defined, broad peak at 3252 cm^{-1} (0.40 eV). This absorption is electronic in origin and is attributed to an f−f or f−d transition within the f^1 configuration of Ce^{3+}.

Electrical conductivity data as a function of temperature for a single crystal of $K_2Ag_3CeTe_4$ show that this material is a narrow gap semiconductor with a room-temperature value of 0.01 S/cm, see Figure 3. A band gap of 0.36 eV is obtained by fitting the conductivity data to the semiconductor equation. The material shows a large Seebeck coefficient at room temperature of +160 μV/K. The positive sign and decreasing Seebeck coefficient with falling temperature are also consistent with a p-type narrow gap semiconductor.

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Supporting Information Available: Tables of crystallographic details, atomic coordinates, anisotropic thermal parameters, interatomic distances and angles, torsion angles, and calculated and observed X-ray powder diffraction patterns for $K_2Ag_3CeTe_4$ (16 pages). Ordering information is given on any current masthead page.

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