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$Rb_2Cu_3CeTe_5$: a quaternary semiconducting compound with a two-dimensional polytelluride framework

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$Rb_2Cu_3CeTe_5$ has been synthesized from the reaction of Cu and Ce in a molten alkali metal/polytelluride flux. The compound crystallizes in the monoclinic space group, $C2/m$ (no. 12) with $a = 18.6884(1)$ Å, $b = 6.2384(2)$ Å, $c = 12.5264(3)$ Å, $\beta = 112.795(1)°$, $V = 1346.34(5)$ Å^3, and $Z = 4$. $Rb_2Cu_3CeTe_5$ is two-dimensional with $\frac{1}{\infty}$ $[Cu_3CeTe_5]^{2-}$ layers built from one-dimensional $\frac{1}{\infty}$ $[Cu_2CeTe_5]^{3-}$ chains that are 'stitched' together by distorted tetrahedral Cu atoms; the compound is paramagnetic and a narrow-gap p-type semiconductor.

Over the past decade, the polychalcogenide flux method has become an established technique for discovering new solid state chalcogenides.[1] Although many of the compounds form completely new structure types, others are reminiscent of, or can be considered derivatives of known chalcogenides. This is particularly true when lanthanide and actinide metals are involved. The binary LnQ_3 phases ($NdTe_3$[2] and $ZrSe_3$[3] type), for example, are quite stable. Several new ternary phases have recently been reported in which the structural motifs are related to these LnQ_3 binaries. While $NaLnS_3$ (Ln = La,Ce)[4] and ATh_2Q_6 (A = Cs,Rb,K; Q = Se,Te)[5] represent two different variations of the $ZrSe_3$ structure type, ALn_3Te_8 (A = Cs,Rb,K; Ln = Ce,Nd)[6] is closely related to the structure of $NdTe_3$. In an effort to access quaternary phases which are less structurally related to the LnQ_3 binaries, another element was introduced into the synthesis. Copper proved to be well behaved in this respect and we were able to isolate several compounds, whereas other elements gave phase-separated ternary compounds. Reactions in the A/Cu/Ln/Q (Q = S,Se) system have produced several quaternary compounds, including $K_2Cu_2CeS_4$,[7] $KCuCe_2S_6$,[7,8] $KCuLa_2S_6$,[8] $CsCuCe_2S_6$,[8] $CsCuCeS_3$[8] and $KCuUSe_3$.[8] Other investigators have identified such compounds as $BaErAgS_3$,[9] $CsCuUTe_3$,[10] $BaLnMQ_3$ (Ln = La,Ce,Nd; M = Cu,Ag; Q = S,Se)[11] and $KCuEu_2S_6$.[12] Although many of these phases are structurally unique, some still retain the components of the LnQ_3 motif. It is apparent that the greater the amount of copper in the framework, the more profound the effect of breaking up the LnQ_3 structure. Along these lines, we examined the A/M/Ln/Te (M = Cu,Ag) system using polytelluride fluxes and discovered several novel compounds including $KCuCeTe_4$,[13] $K_2Ag_3CeTe_4$[14] and $K_{2.5}Ag_{4.5}Ce_2Te_9$.[15] We report here on $Rb_2Cu_3CeTe_5$,[16] a low-dimensional compound in which the basic LnQ_3 structure is substantially disrupted.

$Rb_2Cu_3CeTe_5$ consists of $\frac{1}{\infty}[Cu_3CeTe_5]^{2-}$ layers separated by Rb^+ cations (Fig. 1.) The Ce atom is seven coordinate, exhibiting a distorted pentagonal bipyramidal geometry in which one η^2-(Te_2^{2-}) unit[17] and three Te^{2-} anions comprise the pentagon and two Te^{2-} anions occupy the axial positions [Fig. 2(A)]. The pentagonal bipyramids share monotelluride ions, forming $\frac{1}{\infty}$ $[CeTe_5]^{5-}$ chains parallel to the b-axis.

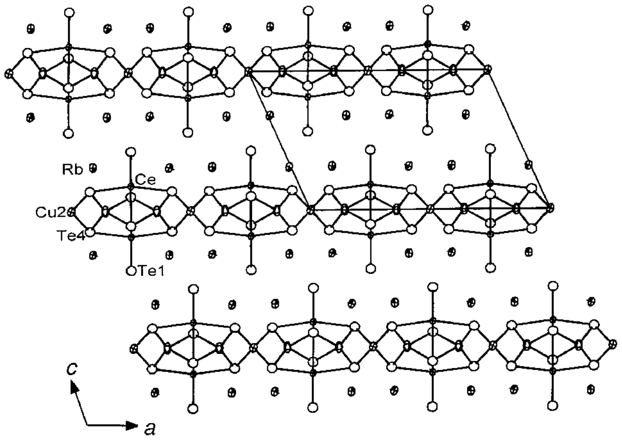

Fig. 1 ORTEP representation of the structure of $Rb_2Cu_3CeTe_5$ as seen down the b-axis (90% ellipsoids). The ellipses with octant shading represent Ce and Rb, the crossed ellipses represent Cu and the open ellipses represent Te.

Conceptually, these one-dimensional chains derive from the $ZrSe_3$ structure type. By replacing one (Q_2^{2-}) unit in the $ZrSe_3$ framework with a Q^{2-} unit, the coordination environment of the metal changes from bicapped trigonal prismatic to pentagonal bipyramidal. This change in coordination is accompanied by a conversion from two-dimensional layers to one-dimensional chains. Within the $\frac{1}{\infty}$ $[CeTe_5]^{5-}$ chains exist empty distorted tetrahedral pockets of Te atoms which are large enough to accommodate Cu atoms. Each Cu atom is bonded at two points to the axial positions of two neighboring pentagonal bipyramids, and at the remaining sites to the closest edge between these axial positions. The chains, once extended to include the Cu atom, can be written as $\frac{1}{\infty}$ $[Cu_2CeTe_5]^{3-}$. Finally, the layers are formed when the second type of Cu atom 'stitches' these chains together in the a-direction by coordinating to neighboring chains in a distorted tetrahedral arrangement. A view perpendicular to the layers is shown in Fig. 2(B). It is interesting that if one removes the Ce atoms from the structure, the remaining $[Cu_3Te_3]$ substructure remains contiguous. In this sense, the Ce atoms are situated on both sides of a two-dimensional $[CuTe]^-$ substrate. In fact, this copper telluride framework, albeit distorted, bears a close resemblance to the layers of NaCuTe[18] [Fig. 2(C)].

The magnetic susceptibility of $Rb_2Cu_3CeTe_5$ was measured over the range 5–300K at 6000 G, and a plot of $1/\chi_m$ *vs.* T shows that the material exhibits nearly Curie–Weiss behavior with only slight deviation from linearity beginning below 50 K. Such deviation has been reported for several Ce^{3+} compounds and has been attributed to crystal field splitting of the $^3F_{5/2}$ ground state of the cation.[19] At temperatures above 150 K,

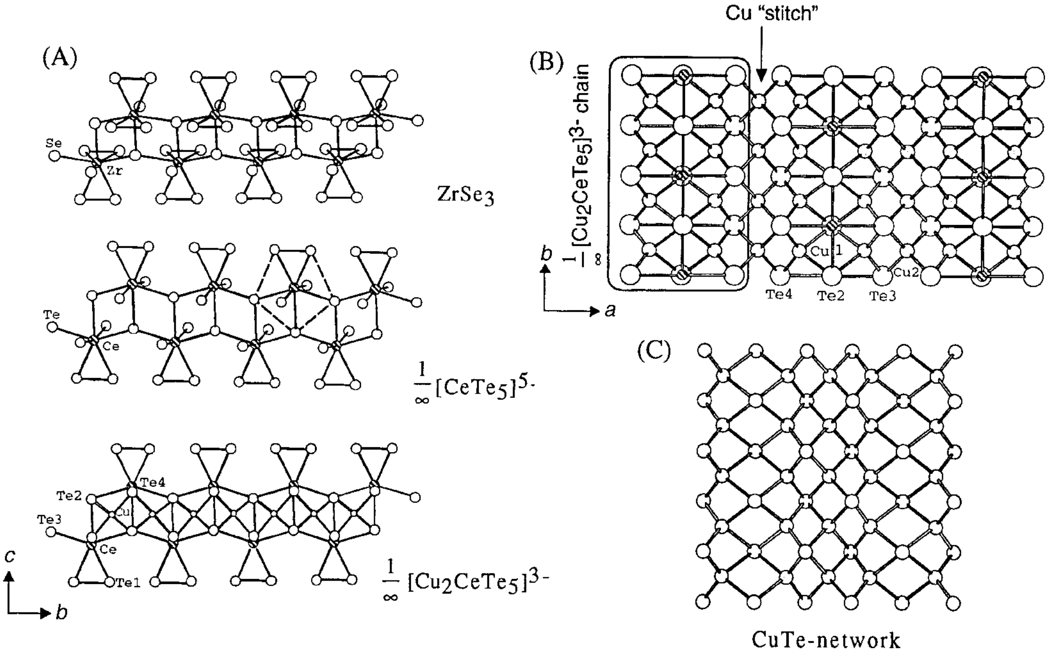

Fig. 2 (A) Schematic comparison of the two-dimensional layers of $ZrSe_3$, the one-dimensional $\frac{1}{\infty}[CeTe_5]^{5-}$ chains and the $\frac{1}{\infty}[Cu_2CeTe_5]^{3-}$ chains in $Rb_2Cu_3CeTe_5$. The dotted line highlights the pentagonal bipyramidal coordination around Ce. Selected distances (Å) are as follows: Ce–Te1 3.161(1), Ce–Te2 3.2538(5), Ce–Te3 3.246(2), Ce–Te4 3.253(2) and Te1–Te1 2.771(2). (B) View perpendicular to the layers of $Rb_2Cu_3CeTe_5$, illustrating how the second Cu atom stitches together the $\frac{1}{\infty}[Cu_2CeTe_5]^{3-}$ chains to form two-dimensional layers. The ditelluride groups above and below the anionic layers are omitted for clarity. Selected distances (Å): Cu1–Te2 2.820(2), Cu1–Te3 2.591(2), Cu1–Te4 2.593(2), Cu1–Ce1 3.332(2), Cu1–Cu2 2.650(2), Cu2–Te3 2.721(2), Cu2–Te4 2.721(2) and 2.593(2). (C) The distorted $[CuTe]^-$, PbO-like layer in $Rb_2Cu_3CeTe_5$.

a μ_{eff} of 2.64 μ_B has been calculated, which is in accord with the usual range for Ce^{3+} compounds (2.3–2.5 μ_B). The presence of Ce^{3+} is confirmed by IR spectroscopy with shows one well defined, broad peak at *ca.* 3420 cm^{-1} (0.42 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+}. From this we can conclude that $Rb_2Cu_3CeTe_5$ is a valence precise compound, and thus we expect semiconducting properties. The formal oxidation states are $(Rb^{1+})_2(Cu^{1+})_3(Ce^{3+})(Te^{2-})_3(Te_2{}^{2-})$.

The electrical conductivity of $Rb_2Cu_3CeTe_5$ as a function of temperature measured on single crystals suggests that the material is indeed a narrow gap semiconductor with a room temperature conductivity value of 0.05 S cm^{-1} [Fig. 3(A)]. The log σ *vs.* $1/T$ plot is non-linear over the entire temperature range of 8–300 K, suggesting the conduction mechanism varies in different temperature regions, possibly due to different types of mid-gap states. Thermoelectric power data as a function of temperature show a large Seebeck coefficient at room temperature of +275 μV K^{-1} [Fig. 3(B)]. The increasing Seebeck coefficient with decreasing temperature and its positive sign are consistent with a p-type semiconductor.

Note added in proof. By the time we received proofs of this manuscript we became aware of the syntheses of $BaDyCuTe_3$, $K_{1.5}Dy_2Cu_{2.5}Te_5$ and $K_{0.5}Ba_{0.5}DyCu_{1.5}Te_3$ (F. Q. Huang, W. Choe, S. Lee and J. S. Chu, *Chem. Mater.*, 1998, **10**, 1320). These compounds are not structurally related to the one reported here; however, they do belong in the broad quaternary family of A/Cu/Ln/Q compounds.

Acknowledgments

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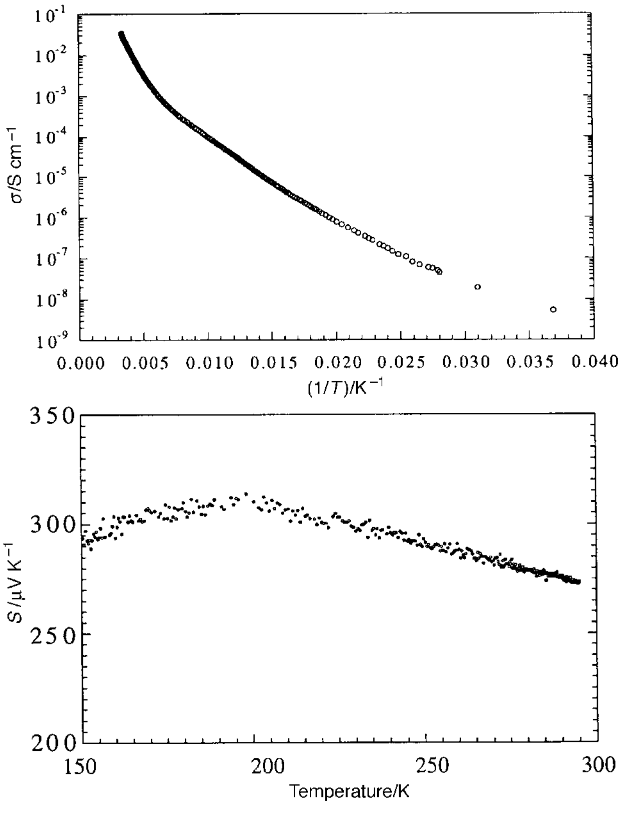

Fig. 3 (A) Variable temperature, four-probe electrical conductivity data for a single crystal of $Rb_2Cu_3CeTe_5$. (B) Variable temperature thermopower data for a single crystal of $Rb_2Cu_3CeTe_5$.

crystal X-ray data set. M.G.K. is a Henry Dreyfus Teacher Scholar 1993–1998. This work made use of the SEM facilities of the center for Electron Optics at Michigan State University. At Northwestern University, this work made use of the Central Facilities supported by NSF through the Materials Research Center (DMR-9632472).

Notes and references

1 M. G. Kanatzidis and A. C. Sutorik, *Prog. Inorg. Chem.*, 1995, **43**, 151 and references therein; M. G. Kanatzidis, *Curr. Opin. Solid State Mater. Sci.*, 1997, **2**, 139; M. A. Pell and J. A. Ibers, *Chem. Ber./Recueil*, 1997, **130**, 1.

2 B. K. Norling and H. Steinfink, *Inorg. Chem.*, 1966, **5**, 1488.

3 V. W. Krönert and K. Plieth, *Z. Anorg. Allg. Chem.*, 1965, **336**, 207.

4 A. C. Sutorik and M. G. Kanatzidis, *Chem. Mater.*, 1997, **9**, 387.

5 J. A. Cody and J. A. Ibers, *Inorg. Chem.*, 1996, **16**, 3273; E. J. Wu, M. A. Pell and J. A. Ibers, *J. Alloys Compd.*, 1997, **255**, 106; K.-S. Choi, R. Patschke, S. J. L. Billinge, M. J. Waner, M. Dantus and M. G. Kanatzidis, *J. Am. Chem. Soc.*, in press.

6 R. Patschke, J. Heising, J. Schindler, C. R. Kannewurf and M. G. Kanatzidis, *J. Solid State Chem.*, 1998, **135**, 111.

7 A. C. Sutorik, J. Albritton-Thomas, C. R. Kannewurf and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 1994, **116**, 7706.

8 A. C. Sutorik, J. Albritton-Thomas, T. Hogan, C. R. Kannewurf and M. G. Kanatzidis, *Chem. Mater.*, 1996, **8**, 751.

9 P. Wu and J. A. Ibers, *J. Solid State Chem.*, 1994, **110**, 156.

10 J. A. Cody and J. A. Ibers, *Inorg. Chem.* 1995, **34**, 3165.

11 A. E. Christuk, P. Wu and J. A. Ibers *J. Solid State Chem.*, 1994, **110**, 330; P. Wu and J. A. Ibers, *J. Solid State Chem.*, 1994, **110**, 337.

12 W. Bensch and P. Dürichen, *Chem. Ber.*, 1996, **129**, 1489.

13 R. Patschke, J. Heising, P. Brazis, C. R. Kannewurf and M. G. Kanatzidis, *Chem. Mater.*, 1998, **10**, 695.

14 R. Patschke, P. Brazis, C. R. Kannewurf and M. G. Kanatzidis, *Inorg. Chem.*, in press.

15 R. Patschke, P. Brazis, C. R. Kannewurf and M. G. Kanatzidis, submitted for publication.

16 (*a*) $Rb_2Cu_3CeTe_5$ was synthesized from a mixture of 0.448 g Rb_2Te (3.0 mmol), 0.095 g Cu (3.0 mmol), 0.070 g Ce (1.0 mmol) and 0.447 g Te (7.0 mmol) which was sealed under vacuum in a carbon coated quartz tube and heated to 850 °C for 10 days. The tube was then cooled to 400 °C at -3 °C h^{-1}, and then quenched to room temperature. The excess Rb_xTe_y flux was removed, under nitrogen atmosphere, with dimethylformamide to reveal black needle-shaped crystals in 45% yield (based on Cu). The crystals are air and water stable. Phase homogeneity was confirmed by comparing the power X-ray diffraction pattern of the product against that calculated using the crystallographically determined atomic coordinates. Microprobe analysis carried out on randomly selected crystals gave an average composition of $Rb_{2.46}Cu_{3.29}Ce_{1.0}Te_{5.55}$. A Siemens SMART Platform CCD diffractometer was used to collect data from a crystal of $0.160 \times 0.035 \times 0.010$ mm dimensions using Mo-Kα ($\lambda = 0.71073$ Å) radiation. SMART[16b] software was used for data acquisition and SAINT[16c] for data extraction and reduction. An absorption correction was performed using SADABS.[16d]

Crystal data at 173 K: $a = 18.6884(1)$, $b = 6.2384(2)$, $c = 12.5264(3)$ Å, $\beta = 112.795(1)°$, $V = 1346.34(5)$ Å^3, $Z = 4$, $D_c = 5.623$ g cm^{-3}, monoclinic, space group $C2/m$ (no. 12), $\mu = 25.741$ mm^{-1}, index ranges $-22 \leqslant h \leqslant 20$, $0 \leqslant k \leqslant 7$, $0 \leqslant l \leqslant 14$, $2\theta_{max} = 50°$, total data 3427, unique data 1307 ($R_{int} = 0.044$), data with $F_o{}^2 > 2\sigma(F_o{}^2)$ 1087, no. of variables 60, final $R/wR2 = 0.0461/0.1182$, GOF 1.041. The structure was solved and refined using the SHELXTL-5 package of crystallographic programs;[16e] SHELXTL refines on F^2. (*b*) SMART: 1994, Siemens Analytical Xray Systems, Inc., Madison, WI 53719 USA; (*c*) SAINT: Version 4, 1994–1996, Siemens Analytical Xray Systems, Inc., Madison, WI 53719 USA; (*d*) SADABS: G.M. Sheldrick, University of Göttingen, Germany, to be published. (*e*) SHELXTL: Version 5, 1994, G.M. Sheldrick, Siemens Analytical X-ray Instruments, Inc. Madison, WI 53719. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/124.

17 The Te–Te stretch exhibits a Raman shift at *ca.* 160 cm^{-1}.

18 G. Savelsberg and H. Schäfer, *Z. Naturforsch.*, *Teil B.* 1978, **33**, 370.

19 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, New York, 1984, p. 1443.

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