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Synthesis and Characterization of a Series of Quaternary Chalcogenides Ba*LnMQ*$_3$ (*Ln* = Rare Earth, *M* = Coinage Metal, *Q* = Se or Te)

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The compounds $BaGdAuSe_3$, $BaLaCuTe_3$, $BaYCuTe_3$, $BaYAgTe_3$, $BaLaAgTe_3$, $BaYbCuTe_3$, $BaGdAgTe_3$, $BaNdCuTe_3$, and $BaPrCuTe_3$ were prepared by the reaction in a $BaBr_2$/KBr flux at 850°C of a rare earth, a coinage-group metal, a chalcogen, and BaSe or BaTe. The unit cells of all of the compounds and the crystal structures of the first four compounds were determined by single-crystal X-ray diffraction methods. With the exception of $BaLaCuTe_3$, which crystallizes with four formula units in the orthorhombic space group *Pnma*, all of these compounds crystallize with four formula units in the orthorhombic space group *Cmcm*. $BaLaCuTe_3$, isostructural with β-$BaLaCuSe_3$ and Eu_2CuS_3 (i.e., $Eu^{2+}Eu^{3+}Cu^{+}(S^{2-})_3$), and $BaGdAuSe_3$, $BaYCuTe_3$, and $BaYAgTe_3$, isostructural with $KZrCuS_3$, crystallize in a layered structure in which there are $^2_\infty[LnMQ_3^{2-}]$ layers separated by Ba^{2+} ions. *Ln* atoms are coordinated by six *Q* atoms at the corners of a distorted octahedron, and *M* atoms are coordinated by four *Q* atoms at the corners of a tetrahedron. The layers are formed by the connection of edge-sharing octahedral chains and corner-sharing tetrahedral chains. Ba atoms are coordinated by seven *Q* atoms in $BaLaCuTe_3$ and by eight *Q* atoms in $BaGdAuSe_3$, $BaYCuTe_3$, and $BaYAgTe_3$. $BaNdAgTe_3$ shows temperature-dependent paramagnetism. Its magnetic susceptibility follows the Curie–Weiss law. The effective magnetic moment of 3.4(3) μ_B is in agreement with the theoretical value of 3.6 μ_B for Nd^{3+}. © 1999 Academic Press

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INTRODUCTION

A variety of quaternary rare-earth chalcogenides have been synthesized recently (1–7). Among these are the compounds Ba*LnMQ*$_3$ (*Ln* = rare earth; *M* = Cu, Ag; *Q* = S, Se) (1, 2). In this series there are two structural types. One, typified by $BaLaCuS_3$ and α-$BaLaCuSe_3$ crystallizing in space group *Pnma*, consists of a three-dimensional framework of $LaSe_7$ monocapped trigonal prisms and $CuSe_4$ tetrahedra. It also exhibits a one-dimensional character in the form of channels that extend along the *b* axis. Ba^{2+} ions are accommodated in these channels. The other, typified by β-$BaLaCuSe_3$ crystallizing in space group *Pnma* and other Ba*LnMQ*$_3$ compounds crystallizing in space group *Cmcm*, has a layered structure in which there are $^2_\infty[LnMQ_3^{2-}]$ layers separated by Ba^{2+} ions. *Ln* atoms are coordinated by six *Q* atoms at the corners of a distorted octahedron, and *M* atoms are coordinated by four *Q* atoms at the corners of a tetrahedron. The layers are formed by the connection of edge-sharing octahedral chains and corner-sharing tetrahedral chains. The two structures are closely related. Thus β-$BaLaCuSe_3$ undergoes a phase transformation to α-$BaLaCuSe_3$ upon mechanical grinding (1). The reverse phase transition occurs when α-$BaLaCuSe_3$ is annealed at elevated temperatures.

The present work extends these earlier studies to the tellurides and to gold. Only the second structural type is found.

EXPERIMENTAL

Syntheses

The compound $BaGdAuSe_3$ was prepared from the elements and BaSe (elemental ratio Ba : Gd : Au : Se = 1 : 1 : 1 : 3) in a $BaBr_2$/KBr (1.1 : 1) flux at 850°C. The other compounds, all tellurides, were prepared from the elements and BaTe (elemental ratio Ba : *Ln* : *M* : Te = 1 : 1 : 1 : 3) in a $BaBr_2$/KBr (1.1 : 1) flux at 850°C. Used were La (Reacton, 99.9%), Pr (Alfa Aesar, 99.9%), Gd (Alfa Aesar, 99.9%), Nd (Alfa Aesar, 99.9%), Yb (Alfa Aesar, 99.9%), Y (Aldrich, 99.9%), Cu (Alfa Aesar, 99.999%), Ag (Alfa Aesar, 99.99%), Au (Alfa Aesar, 99.96%), Se (Aldrich, 99.5%), Te (Aldrich 99.8%), BaSe (Alfa Aesar, 99.5%), and BaTe (Alfa Aesar, 99.5%). The starting materials were loaded in a glove box into fused silica tubes that were subsequently evacuated to 10^{-4} Torr and sealed. The tubes were heated at 650°C for 50 h, 850°C for 150 h, then cooled at 3°C/h to 300°C, and then the furnace was shut off. Black crystals of tellurides and red crystals of $BaGdAuSe_3$ formed in good yields ranging from 35–65%, as judged by the morphology and color of the products that include binary Ln_2Q_3 impurities. The

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quaternaries are easily isolated from the flux by washing with water and acetone. Their composition Ba : *Ln* : *M* : *Q* of approximately 1 : 1 : 1 : 3 was established by EDAX with the use of a Hitachi S-4500 scanning electron microscope. The tellurides are modestly stable in air; the selenide is stable. In the absence of the flux, only binary compounds of *Ln*/Te formed.

Crystallography

The unit cells and space groups for all compounds synthesized were obtained at 115 K from suitable single crystals with the use of a Picker X-ray diffractometer. These results are presented in Table 1. Diffraction data were obtained from suitable crystals of $BaGdAuSe_3$, $BaLaCuTe_3$, $BaYCuTe_3$, and $BaYAgTe_3$, and their structures were determined. Table 2 provides details. Common features not detailed in Table 2 are the diffractometer—computer-controlled Picker (8); radiation—Mo$K\alpha$ ($\lambda = 0.71073$ Å); temperature of data collection—115 K; scan technique—θ–2θ; scan speed—3 deg/min in 2θ; standards—six measured every 100 reflections; decay—none; absorption correction —face-indexed, analytical (9).

The initial data processing for all four compounds was carried out with programs and methods standard in this laboratory. The structures were solved with the use of the direct methods program SHELXS and refined by full-matrix least-squares methods with the program SHELXL in the SHELXTL-PC suite of programs (10). Table 3 lists positional and displacement parameters.

Magnetic Susceptibility

Magnetic susceptibility (χ) measurements on the compound $BaNdAgTe_3$ were made at 500 G over the temperature range 5–300 K with a Quantum Design SQUID magnetometer. Data were corrected for the diamagnetic contributions of the atomic cores (11).

TABLE 1
Unit Cells and Space Groups for the Compounds Ba$LnMQ_3$ at 115 K

Compound	Space group	a (Å)[a]	b (Å)	c (Å)	V (Å^3)[b]
$BaLaCuTe_3$	*Pnma*	11.786(2)	4.5133(9)	14.710(3)	782.5(3)
$BaYCuTe_3$	*Cmcm*	4.4010(9)	14.706(3)	11.287(2)	730.5(3)
$BaYAgTe_3$	*Cmcm*	4.4773(9)	14.856(3)	11.336(2)	754.0(3)
$BaGdAuSe_3$	*Cmcm*	4.2120(8)	14.036(3)	10.657(2)	630.0(2)
$BaLaAgTe_3$	*Cmcm*	4.576(6)	14.96(2)	11.71(2)	801(3)
$BaYbCuTe_3$	*Cmcm*	4.360(7)	14.65(2)	11.15(1)	712(3)
$BaGdAgTe_3$	*Cmcm*	4.477(7)	14.87(2)	11.38(2)	758(4)
$BaNdCuTe_3$	*Cmcm*	4.462(6)	14.67(2)	11.50(2)	753(3)
$BaPrCuTe_3$	*Cmcm*	4.466(4)	14.69(1)	11.56(1)	758(2)

[a] Unit-cell parameters were determined from high-angle peaks for the first four compounds and from low-angle peaks for the others.

[b] All cells contain four formula units.

TABLE 2
Crystal Data and Experimental Details

Compound	$BaLaCuTe_3$	$BaYCuTe_3$	$BaYAgTe_3$	$BaGdAuSe_3$
Formula weight	722.59	672.59	716.92	728.44
Crystal vol. (mm^3)	1.4×10^{-4}	3.9×10^{-5}	1.9×10^{-5}	3.8×10^{-5}
Lin. abs. coeff. (cm^{-1})	239.6	278.2	267.0	568.2
Transmission factors	0.495–0.558	0.249–0.300	0.383–0.448	0.125–0.188
2θ limits (deg)	2–62	2–62	2–55	2–62
No. unique data	1398	685	515	596
No. $I > 2\sigma(I)$	1096	565	433	526
No. of variables	38	24	24	24
R_w[a]	0.0710	0.0586	0.0539	0.0641
R[b]	0.0311	0.0249	0.0230	0.0288

[a] $R_w(F_o^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04 \times F_o^2)^2$ for $F_o^2 \geq 0$; and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

[b] $R(F_o) = \sum||F_o| - F_c||/|F_o|$; $F_o^2 > 2\sigma(F_o^2)$.

TABLE 3
Positional Parameters and Equivalent Isotropic Displacement Parameters

Atom	x	y	z	U_{eq}[a]	Wyckoff Position
			$BaLaCuTe_3$		
La	0.01185(4)	0.2500	0.75699(4)	0.00766(14)	4c
Ba	0.26917(5)	0.2500	0.00178(4)	0.0093(2)	4c
Cu	0.24174(9)	0.2500	0.28251(9)	0.0079(2)	4c
Te(1)	0.05617(5)	0.2500	0.38735(4)	0.0063(2)	4c
Te(2)	0.25858(5)	0.2500	0.67771(4)	0.0071(2)	4c
Te(3)	0.41619(5)	0.2500	0.39744(4)	0.0071(2)	4c
			$BaYCuTe_3$		
Y	0.0000	0.0000	0.0000	0.0066(2)	4a
Ba	0.0000	0.74997(5)	0.2500	0.0087(2)	4c
Cu	0.0000	0.4673(1)	0.2500	0.0095(3)	4c
Te(1)	0.0000	0.36220(3)	0.05915(4)	0.0064(1)	8f
Te(2)	0.0000	0.07094(5)	0.2500	0.0057(2)	4c
			$BaYAgTe_3$		
Y	0.0000	0.0000	0.0000	0.0064(3)	4a
Ba	0.0000	0.75483(5)	0.2500	0.0080(2)	4c
Ag	0.0000	0.46833(7)	0.2500	0.0093(2)	4c
Te(1)	0.0000	0.36053(4)	0.05033(6)	0.0061(2)	8f
Te(2)	0.0000	0.07954(5)	0.2500	0.0060(2)	4c
			$BaGdAuSe_3$		
Gd	0.0000	0.0000	0.0000	0.0038(2)	4a
Ba	0.0000	0.75136(6)	0.2500	0.0055(2)	4c
Au	0.0000	0.46505(4)	0.2500	0.0096(2)	4c
Se(1)	0.0000	0.36044(7)	0.05137(1)	0.0043(2)	8f
Se(2)	0.0000	0.07916(1)	0.2500	0.0044(3)	4c

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

RESULTS

BaGdAuSe$_3$, BaYCuTe$_3$, and BaYAgTe$_3$

These compounds crystallize in space group *Cmcm* in a layered structure in which there are $^{2}_{\infty}[LnCuQ_3^{2-}]$ layers separated by Ba^{2+} ions (Fig. 1). *Ln* atoms (site symmetry = 2/*m*) are coordinated by six *Q* atoms at the corners of a distorted octahedron and *M* atoms (site symmetry = *mm*) are coordinated by four *Q* atoms at the corners of a tetrahedron (Fig. 2). The layers are formed by the connection of edge-sharing octahedral chains and corner-sharing tetrahedral chains (Fig. 3). These compounds are isostructural with KZrCuS$_3$ (12). Bond distances and angles (Table 4) are normal. In BaYCuTe$_3$, Y–Te bond lengths range from 3.0084(6) to 3.0650(5) Å; Cu–Te distances range from 2.651(1) to 2.677(1) Å. In BaYAgTe$_3$, Y–Te distances range from 3.0705(6) to 3.1032(6) Å; Ag–Te range from 2.773(1) to 2.782(1) Å. In BaGdAuSe$_3$, Gd–Se distances range from 2.887(1) to 2.928(1) Å; Au–Se distances range from 2.576(1) to 2.646(1) Å. These bond lengths are normal and agree, for example, with those of 2.60(1)–2.77(1) Å for Cu–Te in Cu$_{0.28}$LaTe$_2$ (13), 2.806(2)–2.817(2) Å for Ag–Te in Cs$_2$Ag$_2$ZrTe$_4$ (14), and 2.832–3.032 Å for Gd-Se in Cs$_3$Gd$_7$Se$_{12}$ (15).

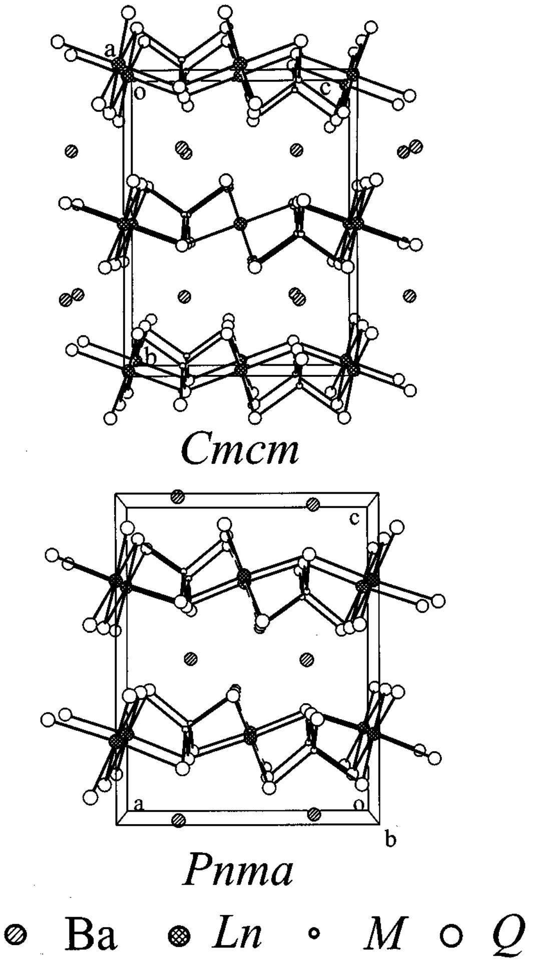

FIG. 1. Structure of Ba*LnMQ*$_3$.

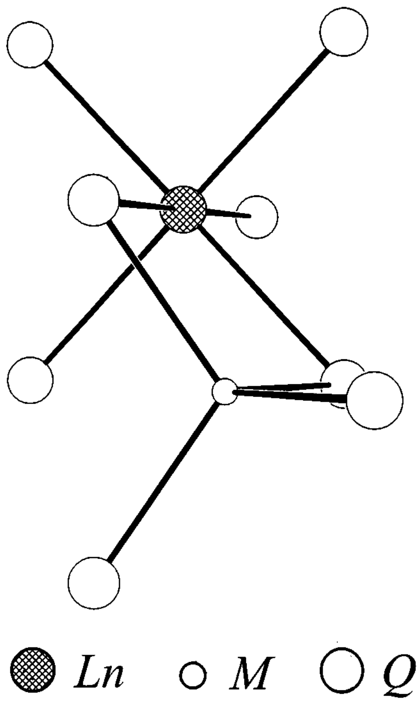

FIG. 2. The coordination environment in Ba*LnMQ*$_3$.

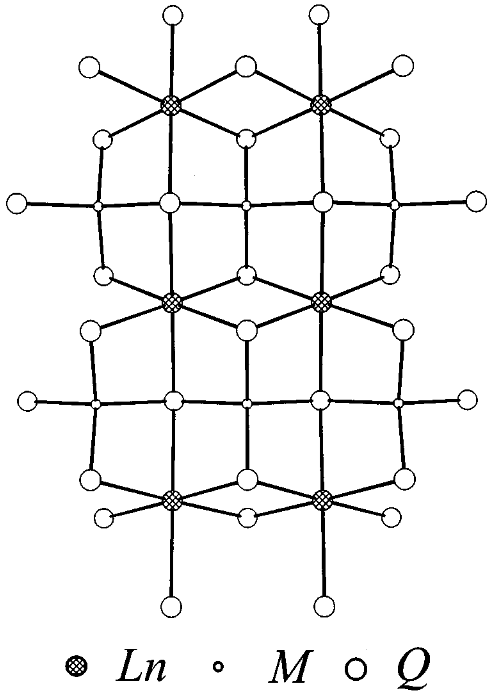

FIG. 3. Layered structure of [*LnMQ*$_3$] in the *a*–*c* plane.

TABLE 4
Bond Lengths (Å) and Bond Angles (deg)

$BaLaCuTe_3$					$BaYCuTe_3$	$BaYAgTe_3$	$BaGdAuSe_3$
La–Te(1)	×2	3.2005(7)	Ln–*Q*(1)	×4	3.0650(5)	3.103(1)	2.9278(8)
La–Te(2)		3.133(1)	Ln–*Q*(2)	×2	3.0084(6)	3.071(1)	2.8866(7)
La–Te(2)		3.136(1)	*M*–*Q*(1)	×2	2.651(1)	2.773(1)	2.576(1)
La–Te(3)	×2	3.1750(7)	*M*–*Q*(2)	×2	2.677(1)	2.782(1)	2.646(1)
Cu–Te(1)		2.676(1)	Ba–*Q*(1)	×4	3.4939(7)	3.550(1)	3.356(1)
Cu–Te(2)	×2	2.733(1)	Ba–*Q*(1)	×2	3.8596(9)	3.812(1)	3.574(1)
Cu–Te(3)		2.662(1)	Ba–*Q*(2)	×2	3.4313(9)	3.434(1)	3.206(2)
Ba–Te(1)		3.755(1)					
Ba–Te(1)	×2	3.4876(8)					
Ba–Te(2)	×2	3.4492(8)					
Ba–Te(3)	×2	3.4958(8)					
Te(3)–La–Te(3)		90.59(3)	*Q*(1)–*Ln*–*Q*(1)	×2	180.0	180.0	180.0
Te(3)–La–Te(1)	×2	178.76(2)	*Q*(1)–*Ln*–*Q*(1)	×2	88.23(2)	87.66(2)	88.01(4)
Te(3)–La–Te(1)	×2	89.86(2)	*Q*(1)–*Ln*–*Q*(1)	×2	91.77(2)	92.34(2)	91.99(4)
Te(1)–La–Te(1)		89.67(3)	*Q*(2)–*Ln*–*Q*(1)	×4	88.57(1)	84.99(2)	85.12(3)
Te(2)–La–Te(3)	×2	89.67(2)	*Q*(2)–*Ln*–*Q*(1)	×4	91.43(1)	95.01(2)	94.88(3)
Te(2)–La–Te(3)	×2	93.15(2)	*Q*(2)–*Ln*–*Q*(2)		180.0	180.0	180.0
Te(2)–La–Te(1)	×2	89.17(2)	*Q*(1)–*M*–*Q*(1)		108.68(6)	109.44(5)	110.50(6)
Te(2)–La–Te(1)	×2	87.98(2)	*Q*(1)–*M*–*Q*(2)	×4	109.39(1)	110.06(1)	110.18(2)
Te(2)–La–Te(2)		175.99(2)	*Q*(2)–*M*–*Q*(2)		110.59(6)	107.14(5)	105.49(7)
Te(3)–Cu–Te(1)		105.38(5)					
Te(3)–Cu–Te(2)	×2	111.06(3)					
Te(1)–Cu–Te(2)	×2	108.90(3)					
Te(2)–Cu–Te(2)		111.32(5)					

$BaLaCuTe_3$

$BaLaCuTe_3$, isostructural with β-$BaLaCuSe_3$ and crystallizing in space group *Pnma*, possesses a slightly distorted Eu_2CuS_3 (i.e., $Eu^{2+}Eu^{3+}Cu^{+}(S^{2-})_3$) structure (16). $BaLaCuTe_3$ also consists of layers formed by the connection of edge-sharing octahedral chains and corner-sharing tetrahedral chains (Figs. 1 and 3). Similarly, La atoms (site symmetry $= m$) are coordinated by six Te atoms at the corners of a distorted octahedron and Cu atoms (site symmetry $= m$) are coordinated by four Te atoms at the corners of a tetrahedron. Figure 2 displays the structure. Bond distances and angles (Table 4) are normal with La–Te distances ranging from 3.133(1) to 3.200(1) Å and Cu–Te distances ranging from 2.676(1) to 2.733(1) Å.

The inverse mass magnetic susceptibility of $BaNdAgTe_3$ as a function of temperature (Fig. 4) was fitted to the Curie–Weiss expression $\chi = C/(T - \theta)$. The resultant parameters are: $C = 1.97(2)\ 10^{-3}$ emu K g^{-1} G^{-1}; $\theta = -5.79(8)$ K. The calculated value of the effective magnetic moment of 3.4(3) μ_B is in agreement with the theoretical value of 3.6 μ_B for Nd^{3+} (17). The magnetic properties of the isostructural selenide and sulfide compounds were measured previously (1, 2). Since the representative telluride $BaNdAgTe_3$ shows similar magnetic properties, no further magnetic measurements were made.

DISCUSSION

In the structure of $BaLaCuTe_3$, each La atom is coordinated by six Te atoms of an octahedron, whereas in $BaLaCuS_3$ each La atom is coordinated by seven sulfur atoms of a monocapped trigonal prism. Interestingly, $BaLaCuSe_3$ has two phases: each La atom in the α-phase is coordinated by seven Se atoms as in $BaLaCuS_3$; and each La atom in the β-phase is coordinated by six Se atoms as in $BaLaCuTe_3$. Obviously, this change in coordination around La from six in the telluride to seven in the sulfide, with the selenide exhibiting each of these coordination numbers in separate phases, is a manifestation of the decrease in anionic radius as one progresses from Te^{2-} to Se^{2-} to S^{2-}.

Given these changes in coordination number and the fact that all three $BaLaCuQ_3$ compounds crystallize in *Pnma*, it is difficult to predict the space group for a given $BaLnMQ_3$ compound (Table 5). Independent of the chalcogen, it does appear that *Pnma* is favored in those systems where the Ln^{3+} ion is large and the coinage-metal ion is small. (The ionic radii of Cu^{+}, Ag^{+}, and Au^{+} are 0.60, 1.00, and 1.22 Å, respectively (18), with the radius for four-coordinate Au^{+} being deduced from that for six-coordinate Au^{+}.) The edge sharing of the *Ln* and *M* polyhedra could lead to more distortions in this instance; the site symmetries of *Ln* and *M* are lower in the *Pnma* structure than they are in the

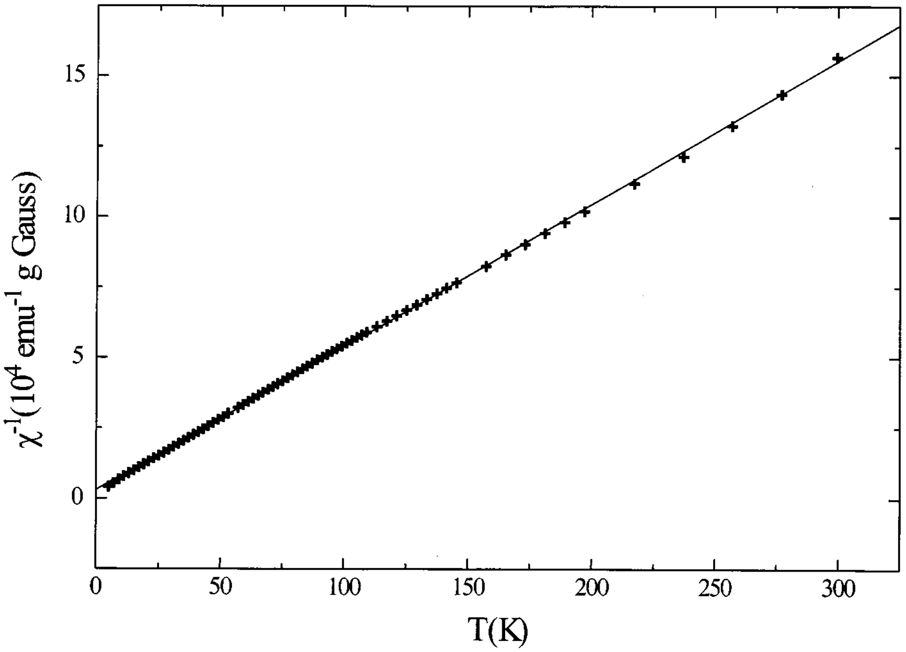

FIG. 4. Plot of χ^{-1} vs T for $BaNdAgTe_3$.

Cmcm structure. Zn^{2+} is smaller than Cu^+, but both commonly are tetrahedrally coordinated. Thus "$KLaZnTe_3$" should show more distortion than $BaLaCuTe_3$. Thus far, attempts to synthesize "$KLaZnTe_3$" have been unsuccessful.

The structure types typified by these $BaLnMQ_3$ compounds allow cations to distribute in an ordered manner in three different kinds of chalcogen polyhedra: octahedra for medium-sized cations, tetrahedra for small-sized cations and those cations preferring tetrahedral coordination, and monocapped or bicapped trigonal prisms for large cations. It is thus not surprising that a number of compounds crystallize in these structural types. These include Eu_2CuS_3 (16), $KZrCuS_3$ (12), $CsCuUTe_3$ (19), $TlCuTiTe_3$ (20), $RbHgSbTe_3$ (21), and $BaDyCuTe_3$ (22).

TABLE 5
Space Groups of Known $BaLnMQ_3$ Compound[a,b] Together with $r(Ln^{3+})$[c] (Å)

		M = Cu			M = Ag		
Ln	$R(Ln^{3+})$ (Å)[c]	Q = S	Q = Se	Q = Te	Q = S	Q = Se	Q = Te
La	1.032	*Pnma*	*Pnma* (α and β)	*Pnma*		*Cmcm*	*Cmcm*
Ce	1.01	*Pnma*	*Pnma*				
Pr	0.99			*Cmcm*			
Nd	0.983	*Pnma*		*Cmcm*	*Cmcm*		
Gd	0.938	*Cmcm*					*Cmcm*
Y	0.90	*Cmcm*	*Cmcm*	*Cmcm*		*Cmcm*	*Cmcm*
Er	0.890	*Cmcm*	*Cmcm*			*Cmcm*	
Yb	0.868			*Cmcm*			
Sc	0.745	*Cmcm*					

[a] The space groups of the sulfides and selenides are taken from Refs. 1 and 2.

[b] Not tabulated is the only example of M = Au, namely, $BaGdAuSe_3$, which crystallizes in *Cmcm*.

[c] Ref. 18.

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REFERENCES

1. A. E. Christuk, P. Wu, and J. A. Ibers, *J. Solid State Chem.* **110,** 330 (1994).
2. P. Wu, A. E. Christuk, and J. A. Ibers, *J. Solid State Chem.* **110,** 337 (1994).
3. P. Wu and J. A. Ibers, *J. Alloys Compd.* **229,** 206 (1995).
4. S.-J. Hwu, C. K. Bucher, J. D. Carpenter, and S. P. Taylor, *Inorg. Chem.* **34,** 1979 (1995).
5. J. D. Carpenter and S.-J. Hwu, *Inorg. Chem.* **34,** 4647 (1995).
6. A. C. Sutorik, J. Albritton-Thomas, T. Hogan, C. R. Kannewurf, and M. G. Kanatzidis, *Chem. Mater.* **8,** 751 (1996).
7. W. Bensch and P. Dürichen, *Chem. Ber.* **129,** 1489 (1996).
8. J. C. Huffman and W. E. Streib, unpublished work (1990).
9. J. de Meulenaer and H. Tompa, *Acta Crystallogr.* **19,** 1014 (1965).

10. G. M. Sheldrick, SHELXTL PC Version 5.0 An Integrated System for Solving, Refining, and Displaying Crystal Structures from Diffraction Data. Siemens Analytical X-Ray Instruments, Inc. Madison, WI, 1994.
11. L. N. Mulay and E. A. Boudreaux, Eds., "Theory and Applications of Molecular Diamagnetism," Wiley-Interscience, New York, 1976.
12. M. F. Mansuetto, P. M. Keane, and J. A. Ibers, *J. Solid State Chem.* **101,** 257 (1992).
13. N.-H. Dung, M.-P. Pardo, and P. Boy, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **39,** 668 (1983).
14. M. A. Pell and J. A. Ibers, *J. Am. Chem. Soc.* **117,** 6284 (1995).
15. M. Folchnandt and T. Schleid, *Z. Anorg. Allg. Chem.* **624,** 1595 (1998).
16. P. Lemoine, D. Carré, and M. Guittard, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **42,** 390 (1986).
17. J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1932.
18. R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **32,** 751 (1976).
19. J. A. Cody and J. A. Ibers, *Inorg. Chem.* **34,** 3165 (1995).
20. M. A. Pell and J. A. Ibers, *J. Alloys Compd.* **240,** 37 (1996).
21. J. Li, Z. Chen, X. Wang, and D. M. Proserpio, *J. Alloys Compd.* **262–263,** 28 (1997).
22. F. Q. Huang, W. Choe, S. Lee, and J. S. Chu, *Chem. Mater.* **10,** 1320 (1998).