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New Layered Materials: Syntheses, Structures, and Optical and Magnetic Properties of $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$

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Four new quaternary selenides $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$ have been synthesized with the use of traditional high-temperature solid-state experimental methods. These compounds are isostructural with $KZrCuS_3$, crystallizing with four formula units in the orthorhombic space group *Cmcm*. Cell constants (Å) at 153 K are $CsGdZnSe_3$ 4.1684(7), 15.765(3), 11.0089(18); $CsZrCuSe_3$ 3.903(2), 15.841(10), 10.215(6); $CsUCuSe_3$ 4.1443(7), 15.786(3), 10.7188(18); and $BaGdCuSe_3$ 4.1839(6), 13.8935(19), 10.6692(15). The structure of these $ALnMSe_3$ compounds (A = Cs, Ba; Ln = Zr, Gd, U; M = Cu, Zn) is composed of ${}^{2}_{\infty}[LnMSe_3{}^{n-}]$ ($n = 1, 2$) layers separated by A atoms. The Ln atom is octahedrally coordinated to six Se atoms, the M atom is tetrahedrally coordinated to four Se atoms, and the A atom is coordinated to a bicapped trigonal prism of eight Se atoms. Because there are no Se−Se bonds in the structure, the oxidation state of A is 1+ (Cs) or 2+ (Ba), that of Ln is 3+ (Gd) or 4+ (Zr, U), and that of M is 1+ (Cu) or 2+ (Zn). $CsGdZnSe_3$ and $BaGdCuSe_3$, which are paramagnetic, obey the Curie−Weiss law and have effective magnetic moments of 7.87(6) and 7.85(5) μ_B for Gd^{3+}, in good agreement with the theoretical value of 7.94 μ_B. Optical transitions at 1.88 and 2.92 eV for $CsGdZnSe_3$ and 1.96 eV for $BaGdCuSe_3$ were deduced from diffuse reflectance spectra.

Introduction

New compounds containing a combination of d- and f-elements are of great interest in solid-state chemistry and materials science because of their physical properties. Examples include the industrially important materials Nd:YIG[1] and the permanent magnetic alloys $SmCo_5$ and $Nd_2Fe_{14}B$,[2] as well as the heavy fermion conductors $CeRu_2Si_2$[3] and $HoNi_2B_2C$.[4] The magnetic exchange energy in d/f compounds may comprise three different types of spin−spin interactions, namely, d−d, d−f, and f−f, to give materials suitable for magnetic storage.[5,6] Additionally, d-element chalcogenide semiconductors, such as MQ (M = Zn, Cd; Q = S, Se, Te), are widely used for their optical properties.[7] Traditional chalcogenide luminescent materials of this type may be doped with Cu^+, Ag^+, Mn^{2+}, or f-metal Ln^{3+} cations that act as activators and modify the luminescent and magnetic properties of such materials.[7−9] Consequently, chalcogenide compounds containing both d- and f-elements may display a host of interesting magnetic and optical properties.

Recently, many new quaternary alkaline-earth rare-earth d-element chalcogenides (A/Ln/M/Q) have been synthesized. The d-elements found in these compounds are typically coinage metals. Examples include $RbLn_2CuSe_4$ (Ln = Sm, Gd, Dy),[10] $Rb_{1.5}Ln_2Cu_{2.5}Se_5$ (Ln = Gd, Dy),[10] $RbSm_2Ag_3Se_5$,[10] $BaLnMQ_3$ (Ln = rare earth; M = Cu, Ag, Au; Q = S, Se, Te),[11−14] $Ba_2LnAg_5S_6$ (Ln = La, Y),[15] KGd_2CuS_4,[16] $K_2CeCu_2S_4$,[17] $ALnCu_2S_6$ (A = K, Cs; Ln = La, Ce, Eu),[17−19] $K_{1.5}Dy_2Cu_{2.5}Te_5$,[14] $K_{0.5}Ba_{0.5}DyCu_{1.5}Te_3$,[14] $CsUCuTe_3$,[20] $CsCeCuS_3$,[19] $K_2CeAg_3Te_4$,[21] $KCeCuTe_4$,[22] and $Rb_2CeCu_3Te_5$.[23]

The present investigation details the synthesis and physical properties of four new quaternary chalcogenides in the A/Ln/M/Q series, namely, $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$. These compounds have the simple $KZrCuS_3$ structure type.[24] The simplicity of this structure type makes more tractable the correlation of physical properties with chemical substitution.

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Experimental Section

Syntheses. The following reagents were used as obtained: Cs (Aldrich, 99.5%), Gd (Alfa, 99.9%), U (Omega, 99.7%), Zr (Aldrich, 99.9+%), Cu (Aldrich, 99.999%), Zn (Johnson Matthey, 99.99%), Se (Aldrich, 99.5%), BaSe (Alfa Aesar, 99.5%), and CsI (Aldrich, 99.99%). Cs_2Se_3, the reactive flux[25] employed in the syntheses, was prepared by the stoichiometric reaction of the elements in liquid NH_3. Reaction mixtures were loaded into fused-silica tubes under an Ar atmosphere in a glovebox. These tubes were sealed under a 10^{-4} Torr atmosphere and then placed in a computer-controlled furnace. The products of these reactions were consistent with the stated compositions, as determined by the examination of selected single crystals with an EDX-equipped Hitachi S-4500 SEM. The compounds are moderately stable in air.

$CsGdZnSe_3$ was obtained from the reaction of 0.5 mmol of Cs_2Se_3, 1.0 of mmol Gd, 1.0 mmol of Zn, and 2.0 mmol of Se with the addition of approximately 150 mg of CsI as flux. The sample was heated to 1273 K in 48 h, kept at 1273 K for 50 h, and cooled at 4 K/h to 473 K, and then the furnace was turned off. The product was washed with *N*,*N*-dimethylformamide (dmf) and water and finally dried with acetone. The product consisted of ivory flat needles and plates of $CsGdZnSe_3$ in 90−95% yield (based upon Gd).

$CsZrCuSe_3$ and $CsUCuSe_3$ were obtained from the reaction of 0.5 mmol of Cs_2Se_3, 0.5 mmol of Ln (Zr or U), 0.5 mmol of Cu, and 2.0 mmol of Se. The samples were heated to 1073 K in 24 h, kept at 1073 for 72 h, and cooled at 4 K/h to 423 K, and then the furnace was turned off. The products were washed with dmf and dried with acetone. $CsZrCuSe_3$ and $CsUCuSe_3$ crystallize as black needles. In addition to the desired products, nearly indistinguishable black needles of Cs/Ln/Se ternaries and Ln/Se binaries were also obtained. Owing to the similar appearance of these various products and the fragile nature of crystals of $CsZrCuSe_3$ and $CsUCuSe_3$, the yields of these reactions are unknown and physical measurements, other than structure determinations, could not be performed.

$BaGdCuSe_3$ was prepared from the reaction of 1.0 mmol of BaSe, 1.0 mmol of Gd, 1.0 mmol of Cu, and 2.0 mmol of Se. The sample was heated to 1223 K in 48 h, kept at 1223 K for 72 h, and cooled to 293 K at the rate of 50 K/h. The product was washed with dmf and water and finally dried with acetone. The product consisted of dark-red powder and needles of $BaGdCuSe_3$ in 90−95% yield (based on Gd).

Structure Determinations. Single-crystal X-ray diffraction data were collected with the use of graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 153 K on a Bruker Smart-1000 CCD diffractometer.[26] The crystal-to-detector distance was 5.023 cm. Crystal decay was monitored by re-collecting 50 initial frames at the end of data collection. Data were collected by a scan of 0.3° in ω in groups of 606, 606, 606, and 606 frames at φ settings of 0°, 90°, 180°, and 270° for $CsGdZnSe_3$, in groups of 606, 606, and 606 frames at φ settings of 0°, 120°, and 240° for $CsZrCuSe_3$ and $CsUCuSe_3$, and in groups of 606, 435, and 230 frames at φ settings of 0°, 90°, and 180° for $BaGdCuSe_3$. The exposure time was either 10 or 15 s/frame. The collection of the intensity data was carried out with the program SMART.[26] Cell refinement and data reduction were carried out with the use of the program SAINT,[26] and face-indexed absorption corrections were performed numerically with the use of the program XPREP.[27] Then the program SADABS[26] was employed to make incident beam and decay corrections.

The structures were solved with the direct methods program SHELXS and refined with the full-matrix least-squares program SHELXL of the SHELXTL.PC suite of programs.[28] Each final refinement included anisotropic displacement parameters and a secondary extinction correction. Additional experimental details are shown in Table 1. Table 2 presents selected bond distances.

Table 1. Crystal Data and Structure Refinements for $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$[a]

	$CsGdZnSe_3$	$CsZrCuSe_3$	$CsUCuSe_3$	$BaGdCuSe_3$
fw	592.41	524.55	671.36	595.01
a, Å	4.1684(7)	3.903(2)	4.1443(7)	4.1839(6)
b, Å	15.765(3)	15.841(10)	15.786(3)	13.8935(19)
c, Å	11.0089(18)	10.215(6)	10.7188(18)	10.6692(15)
V, Å^3	723.4(2)	631.6(7)	701.3(2)	620.19(15)
ρ_c, g cm^{-3}	5.439	5.517	6.359	6.372
μ, cm^{-1}	323.29	278.42	466.54	377.05
$R(F)$[b]	0.0196	0.0284	0.0284	0.0218
$R_w(F^2)$[c]	0.0495	0.0660	0.0717	0.0526

[a] For all structures $Z = 4$, space group = $Cmcm$, $T = 153(2)$ K, and $\lambda = 0.71073$ Å. [b] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 2\sigma(F_o^2)$. [c] $R_w(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4\}^{1/2}$ for all data. $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$ and $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 < 0$.

Table 2. Selected Bond Lengths (Å) for $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$

	$CsGdZnSe_3$	$CsZrCuSe_3$	$CsUCuSe_3$	$BaGdCuSe_3$
A−Se1 × 4	3.6816(6)	3.6061(14)	3.6592(11)	3.3228(6)
A−Se1 × 2	3.9101(7)	3.6824(18)	3.8246(11)	3.6656(8)
A−Se2 × 2	3.5993(8)	3.5373(19)	3.5825(16)	3.2289(9)
Ln−Se1 × 4	2.8831(5)	2.7119(12)	2.8611(8)	2.8997(5)
Ln−Se2 × 2	2.8894(5)	2.7158(14)	2.8265(6)	2.8359(5)
M−Se1 × 2	2.4350(7)	2.4123(15)	2.4581(14)	2.4691(10)
M−Se2 × 2	2.5663(7)	2.4463(15)	2.5256(15)	2.5250(9)

Magnetic Susceptibility Measurements. These measurements on a 30.6 mg sample of crystals of $CsGdZnSe_3$ and 116.6 mg sample of crystals of $BaGdCuSe_3$ were carried out with the use of a Quantum Design SQUID magnetometer (MPMS5 Quantum Design). The composition of each sample was verified by EDX measurements. The samples were loaded into gelatin capsules. Zero-field cooled (ZFC) and field-cooled (FC) susceptibility data were collected between 5 and 300 K. The applied field was 100 G. All measurements were corrected for core diamagnetism.[29]

UV−Vis Diffuse Reflectance Spectroscopy. A Cary 1E UV−visible spectrophotometer with a diffuse reflectance accessory was used to measure the diffuse reflectance spectra of the compounds $CsGdZnSe_3$ and $BaGdCuSe_3$ over the range 200 nm (6.20 eV) to 900 nm (1.38 eV) at 293 K.

Results and Discussion

The structure of the isostructural compounds $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$ is illustrated in Figure 1. It is composed of two-dimensional ${}^2_\infty[LnMSe_3{}^{n-}]$ ($n = 1$ for Cs, $n = 2$ for Ba) layers parallel to (101) separated by A atoms. Each A atom, which is located at a site with mm symmetry, is coordinated to a bicapped trigonal prism of eight Se atoms (Figure 2). Each bicapped trigonal prism has two face-sharing neighbors along [100] and four edge-sharing ones along [001] to form a two-dimensional ${}^2_\infty[ASe_3{}^{n-}]$ ($n = 5$ for Cs, $n = 4$ for Ba) layer, as shown in Figure 2. Each Ln atom, which is located at a site with $2/m$ symmetry, is coordinated to a slightly distorted octahedron of six Se atoms (Figure 3 and Table 2). Each M atom, which is located at a site with mm symmetry, is coordinated to a distorted tetrahedron of four Se atoms (Figure 3 and Table 2). The ${}^2_\infty[LnMSe_3{}^{n-}]$ layer is constructed from these $LnSe_6$ octahedra and MSe_4 tetrahedra, as shown in Figure 3. Each octahedron shares its edges (four Se1) with two other octahedra along [100] to form a one-dimensional ${}^1_\infty[LnSe_4]$ chain.

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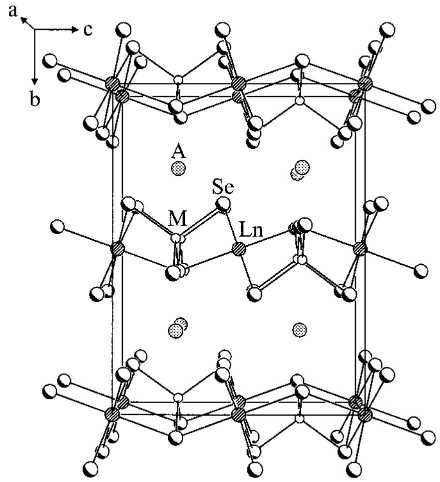

Figure 1. Unit cell of $ALnMSe_3$ viewed down [100].

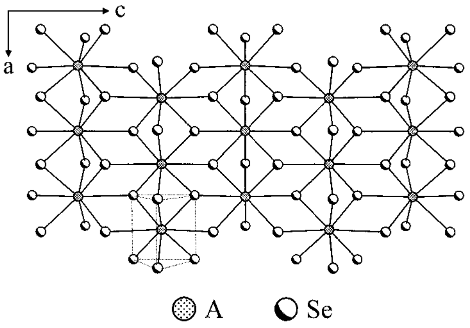

Figure 2. $^2_\infty[ASe_3^{n-}]$ ($n = 5$ for Cs, $n = 4$ for Ba) layer viewed down [010].

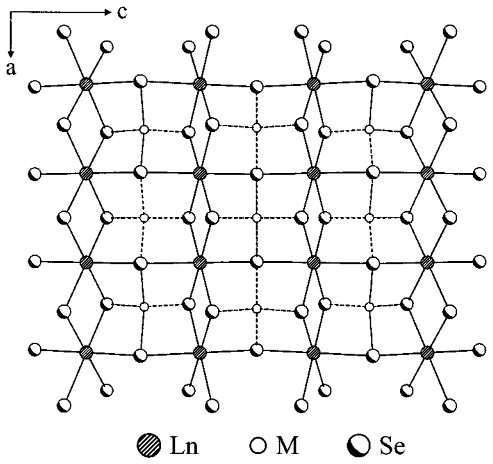

Figure 3. $^2_\infty[LnMSe_3^{n-}]$ ($n = 1$ for Cs, $n = 2$ for Ba) layer viewed down [010].

Each $LnSe_6$ octahedron in the $^1_\infty[LnSe_4]$ chain shares its vertices (two Se2) with two other octahedra in different chains to form a two-dimensional $^2_\infty[LnSe_3^{n-}]$ layer. The MSe_4 tetrahedra form one-dimensional $^1_\infty[MSe_3]$ chains along [100] by the sharing of vertices (Se2) with two neighboring tetrahedra. Each tetrahedron in the $^1_\infty[MSe_3]$ chain links with four $LnSe_6$ octahedra by edge sharing along [001] to form the $^2_\infty[LnMSe_3^{n-}]$ layers.

Selected bond distances for $ALnMSe_3$ are displayed in Table 2. These bond lengths are normal. The ranges of distances are Gd−Se, 2.8359(5)−2.8997(5) Å; Zr−Se, 2.7119(12)−2.7158(14) Å; U−Se, 2.8265(6)−2.8611(8) Å; Zn−Se, 2.4350(7)−2.5663(7) Å; and Cu−Se, 2.4123(15)−2.5256(15) Å. These ranges are consistent, for example, with those of 2.8871(1)−2.928(1) Å for Gd−Se in $BaGdAuSe_3$;[30] 2.704(1)−2.718(1) Å for Zr−Se in $KZrCuSe_3$;[24] 2.839(1)−2.848(1) Å for U−Se in $KUCuSe_3$;[19] 2.478(2)−2.577(2) Å for Cu−Se in β-$BaLaCuSe_3$;[11] and the Zn−Se distance of 2.439(1) Å in $ZnGa_{0.4}Cr_{1.6}Se_4$.[31]

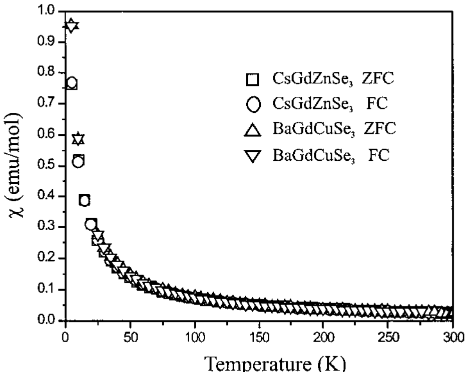

Figure 4. Plots of the molar susceptibility (χ) vs *T* for $CsGdZnSe_3$ and $BaGdCuSe_3$.

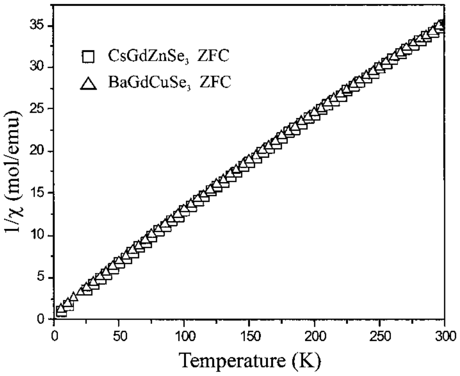

Figure 5. Plots of the inverse molar susceptibility (1/χ) vs *T* for (a) $CsGdZnSe_3$ and (b) $BaGdCuSe_3$.

Because there are no Se−Se bonds in the structure of $ALnMSe_3$ the oxidation state of A is 1+ (Cs) or 2+ (Ba), that of Ln is 3+ (Gd) or 4+ (Zr, U), and that of M is 1+ (Cu) or 2+ (Zn). Several other isostructural compounds are known with the oxidation states A/Ln/M/Q of (1+ or 2+)/(3+ or 4+)/1+/2−, such as $KZrCuQ_3$ (Q = S, Se, Te)[24] $CsUCuTe_3$,[20] $KUCuSe_3$,[19] $CsCeCuS_3$,[19] $TlZrCuTe_3$,[32] and $BaLnCuQ_3$ (Ln = rare earth, Y).[11,12,14] However, to the best of our knowledge $CsGdZnSe_3$ is the only example with M^{2+} in the $KZrCuS_3$ family.[24] This finding is significant because it implies that more substitutional chemistry can be performed within the $KZrCuS_3$ structure type.[24] $RbSbHgTe_3$, which contains Hg^{2+}, has a structure[33] that is closely related to the present one, but the Sb^{3+} atom occupies the Wyckoff *8f* site with an occupancy of 0.5 rather than the *4a* site for the Ln atom in $ALnMQ_3$.

Plots of the molar susceptibility (χ) vs temperature (*T*) for $CsGdZnSe_3$ and $BaGdCuSe_3$ are shown in Figure 4. The values of χ in both the ZFC and FC experiments for $CsGdZnSe_3$ and $BaGdCuSe_3$ are almost exactly the same. Plots of the reciprocal of the molar susceptibility (1/χ) vs *T* for $CsGdZnSe_3$ and $BaGdCuSe_3$ are shown in Figure 5. $CsGdZnSe_3$ and $BaGdCuSe_3$

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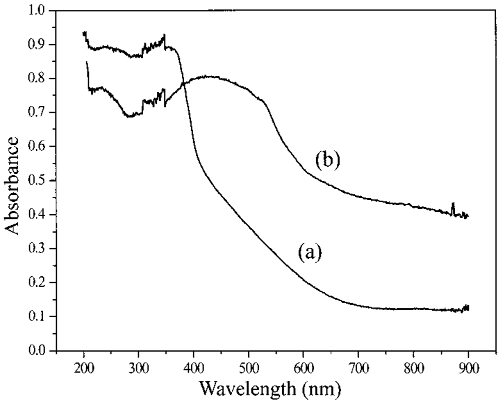

Figure 6. Diffuse reflectance spectrum of (a) $CsGdZnSe_3$ and (b) $BaGdCuSe_3$.

are paramagnetic in the range 5−300 K. The susceptibility data were fit by a least-squares method to the Curie−Weiss equation $\chi = C/(T - \theta_p)$, where C is the Curie constant and θ_p is the Weiss constant. The resulting values for C and θ_p are 7.74(4) emu K mol^{-1} and −5.12(6) K for $CsGdZnSe_3$, and 7.67(3) emu K mol^{-1} and −3.11(3) K for $BaGdCuSe_3$. The calculated effective magnetic moments of 7.87(6) and 7.85(5) μ_B agree well with the theoretical value of 7.94 μ_B for Gd^{3+}.[34]

The diffuse reflectance spectra of $CsGdZnSe_3$ and $BaGdCuSe_3$ are shown in Figure 6. The optical band gaps of 658 nm (1.88 eV) and 425 nm (2.92 eV) for $CsGdZnSe_3$ and 633 nm (1.96 eV) for $BaGdCuSe_3$ were deduced with the use of a straightforward extrapolation method.[35] The gradual slope of the optical absorption edge for both of these compounds is indicative of a complex electronic structure with the existence of indirect transitions. $CsGdZnSe_3$ absorbs minimal light from 658 nm (orange-red) to 425 nm (violet), as shown in Figure 6. These observations are consistent with the ivory color of $CsGdZnSe_3$ and the brick-red color of $BaGdCuSe_3$. Contrast these colors with that of black for $CsZrCuSe_3$ and $CsUCuSe_3$.

This study demonstrates the sensitivity of the optical properties of $ALnMSe_3$ compounds of the $KZrCuSe_3$ structure type[24] to the electronic configurations of Ln and M. Given the stability of this structure type over a wide range of Ln and M, we expect to find diverse optical properties as we prepare additional compounds. Moreover, the combination of magnetic M species with magnetic Ln species will certainly lead to new compounds with interesting magnetic properties.

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Supporting Information Available: Crystallographic files in CIF format for $CsGdZnSe_3$, $CsZrCuSe_3$, $CsUCuSe_3$, and $BaGdCuSe_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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