Syntheses, Structure, Some Band Gaps, and Electronic Structures of CsLnZnTe₃ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Y)

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Eleven new quaternary rare-earth tellurides, CsLnZnTe₃ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Y), were prepared from solid-state reactions at 1123 K. These isostructural materials crystallize in the layered KZrCuS₃ structure type in the orthorhombic space group Cmcm. The structure is composed of LnTe₆ octahedra and ZnTe₄ tetrahedra that share edges to form ∞[LnZnTe₃] layers. These layers stack perpendicular to [010] and are separated by layers of face- and edge-sharing CsTe₈ bicapped trigonal prisms. There are no Te−Te bonds in the structure of these CsLnZnTe₃ compounds so the formal oxidation states of Cs/Ln/Zn/Te are 1+/3+2+/2−. Optical band gaps of 2.13 eV for CsGdZnTe₃ and 2.12 eV for CsTbZnTe₃ were deduced from single-crystal optical absorption measurements. A first-principles calculation of the density of states and the frequency-dependent optical properties was performed on CsGdZnTe₃. The calculated band gap of 2.1 eV is in good agreement with the experimental value. A quadratic fit for the lanthanide contraction of the Ln−Te distance is superior to a linear one if the closed-shell atom is included.

Introduction

Ternary and quaternary rare-earth chalcogenides containing a combination of d- and f-elements have been reviewed recently.¹ These compounds are of interest in solid-state chemistry and materials science because of their physical properties and their rich structural chemistry.

Recently, we reported the syntheses, structure, selected physical properties, and theoretical calculations of a series of CsLnMSe₃ compounds (Ln = rare earth or Y; M = Mn, Zn, Cd, Hg).²⁻⁵ These compounds, which possess the KZrCuS₃ structure type,⁶ are a new class of transparent magnetic semiconductors that exhibit interesting variations of their optical properties as a function of M and Ln and also display some unusual magnetic properties. Also, one of these studies reported the first extension to the analogous tellurides, namely to RbYbZnTe₃ and CsYbZnTe₃.⁵ In keeping with predictions from theory,⁴ these Te compounds are darker in color and hence possess narrower band gaps than their Se analogues. However, no measurements of optical properties were made. Here we extend these preliminary studies of the tellurides and report the syntheses, structure, selected band gaps, and electronic structures of CsLnZnTe₃.

Experimental Section

Syntheses. The following reagents were used as obtained: La (Cerac, 99.9%), Pr (Strem, 99%), Nd (Cerac, 99.9%), Sm (Alfa Aesar, 99.9%), Gd (Alfa Aesar, 99.9%), Tb (Alfa Aesar, 99.9%), Dy (Alfa Aesar, 99.9%), Ho (Alfa Aesar, 99.9%), Er (Strem, 99.9%), Tm (Strem, 99.9%), Y (Alfa Aesar, 99.9%), Zn (Johnson Matthey, 99.9%), Te (Aldrich, 99.9%), and CsCl (Aldrich, 99.9%). The starting materials were 0.5 mmol of Zn, 1.0 mmol of Ln, 2.0 mmol of Te, and 200 mg of CsCl. The reactants were loaded into fused-silica tubes under an Ar atmosphere in a glovebox.

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Table 1. Crystal Data and Structure Refinements for CsLnZnTe₃

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<tr>
<th>CsLaZnTe₃</th>
<th>CsPrZnTe₃</th>
<th>CsNdZnTe₃</th>
<th>CsSmZnTe₃</th>
<th>CsGdZnTe₃</th>
<th>CsTbZnTe₃</th>
<th>CsDyZnTe₃</th>
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<td>4.4702(5)</td>
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<td>4.3992(4)</td>
<td>4.3838(4)</td>
<td>4.3761(4)</td>
<td>4.3604(8)</td>
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<tr>
<td>b (Å)</td>
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<td>6.164(7)</td>
<td>6.1664(7)</td>
<td>6.1684(10)</td>
<td>6.1714(15)</td>
<td>6.1704(14)</td>
<td>6.1709(14)</td>
<td>6.1721(5)</td>
<td>6.1706(3)</td>
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<td>c (Å)</td>
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<td>V (Å³)</td>
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<td>883.93(16)</td>
<td>871.44(16)</td>
<td>863.55(14)</td>
<td>857.10(12)</td>
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<td>847.5(5)</td>
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<tr>
<td>µ (µm⁻¹)</td>
<td>205.09 216.33 221.83 232.81 243.74 250.71 257.17 263.46 271.46 278.36 237.91</td>
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<tr>
<td>R (F²)</td>
<td>0.0242 0.0354 0.0287 0.0282 0.0192 0.0229 0.0237 0.0268 0.0319 0.0309 0.0169</td>
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<tr>
<td>R,w(F²)</td>
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These tubes were sealed under a 10⁻⁴ Torr atmosphere and then placed in a computer-controlled furnace. The samples were heated to 1123 K for 30 h, kept at 1123 K for 96 h, slowly cooled at 4 K/h to 737 K, and then cooled to room temperature. The CsLnZnTe₃ compounds crystollized as dark-red needles or plates. Yields varied from 20% to 40% based on Ln. Analyses of these compounds with an EDX-equipped Hitachi S-3500 SEM showed the presence of all. Although this open-care treatment was used in which the potential was shifted by a constant. The resulting eigenvalues were also shifted by this constant. The electron density was not affected at all. Although this open-care treatment eliminates the problem that 4f states show around the Fermi energy level, it makes impossible the study of the optical transitions related to the 4f states. Brillouin-zone integrations with self-consistency cycles were performed by means of a tetrahedron method with the use of 200 k points throughout the Brillouin zone. For the calculation of the optical properties, 800 k points throughout the Brillouin zone were used. The frequency-dependent optical properties were obtained with the use of the joint density of states (JDOS) weighted by the dipole matrix elements of the optical transitions. In this calculation the allowed and forbidden optical transitions were taken into account.

Results and Discussion

Syntheses. The quaternary metal tellurides CsLnZnTe₃ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Y) were prepared at 1123 K by the reactive flux method with a CsCl flux added to aid crystallization. Efforts to synthesize CsCeZnTe₃ were unsuccessful. The synthesis of CsYbZnTe₃ was reported previously. In the CsLnMSe₄ compounds it was found that as the atomic radius of the transition metal increased so did the radius of the rare earth in order to maintain the anionic framework of edge-sharing MSe₄ tetrahedra and LnSe₆ octahedra and hence the stability of the structure. Thus, the CsLnZnSe₃ compounds could not be synthesized for the Ln elements lighter and hence larger.
than Sm, whereas the CsLnHgSe₃ compounds could not be synthesized for the Ln elements heavier and hence smaller than Ho. Obviously, the larger tetrahedral and octahedral holes in the Te layers are more accommodating compared with the Se layers because the present CsLnZnTe₃ compounds have been synthesized over the entire range of Ln elements.

**Structures.** The structure of these isostructural CsLnZnTe₃ compounds is illustrated in Figure 1. It is the layered KZrCuS₃ structure type and is composed of LnTe₆ octahedra and ZnTe₄ tetrahedra that share edges to form [LnZnTe₃] layers. These layers stack perpendicular to [010] and are separated by layers of face- and edge-sharing CsTe₈ bicapped...
trigonal prisms. The Ln atoms are coordinated to a slightly distorted octahedron of six Te atoms, whereas the Zn atoms are coordinated to a distorted tetrahedron of four Te atoms (Table 2). The structural details have been illustrated earlier.\textsuperscript{2-4} Selected bond distances for these 11 compounds as well as for Ln\textsuperscript{3+}Yb\textsuperscript{5+} are listed in Table 2. These bond lengths are normal. The ranges of distances are La–Te, 3.1739(3)–3.2039(3) Å; Pr–Te, 3.1394(4)–3.1616(4) Å; Nd–Te, 3.1245(3)–3.1467(3) Å; Sm–Te, 3.1032(3)–3.1188(4) Å; Gd–Te, 3.1032(3)–3.1188(4) Å; Tb–Te, 3.0755(3)–3.0874(3) Å; Dy–Te, 3.0672(3)–3.0727(3) Å; Ho–Te, 3.0583(9)–3.0653(7) Å; Er–Te, 3.0462(5)–3.0525(5) Å; Tm–Te, 3.0414(5)–3.0426(5) Å; Y–Te, 3.0644(2)–3.0732(2) Å; Zn–Te, 2.6336(9)–2.8063(7) Å; and Cs–Te, 3.7933(8)–4.2665(6) Å. These ranges are consistent, for example, with those of 3.133(1)–3.2005(7) Å for La–Te in BaLa\textsubscript{2}CuTe\textsubscript{3};\textsuperscript{17} 3.377(1)–3.379(2) Å for Pr–Te in PrSeTe\textsubscript{2};\textsuperscript{18} 3.1496(4)–3.2732(5) Å for Nd–Te in Nd\textsubscript{2}Te\textsubscript{3};\textsuperscript{19} 3.0756(5)–3.1388(7) Å for Sm–Te in BaSm\textsubscript{2}Te\textsubscript{4};\textsuperscript{20} 2.9987(8)–3.0715(9) Å for Tm–Te in BaTm\textsubscript{2}Te\textsubscript{4};\textsuperscript{20} 3.0462(5)–3.0525(5) Å for Y–Te in BaYCuTe\textsubscript{3};\textsuperscript{17} 2.6819(5) Å for Zn–Te in KCuZnTe\textsubscript{2};\textsuperscript{21} and 3.693(1)–4.155(2) Å for Cs–Te in Cs\textsubscript{3}Tb\textsubscript{7}Te\textsubscript{12}.\textsuperscript{22} Because there are no Te–Te bonds in the structure, oxidation states of 1\textsuperscript{+}, 3\textsuperscript{+}, 3\textsuperscript{+}, and 2\textsuperscript{−} can be assigned to Cs, Ln, Zn, and Te, respectively.

**Lanthanide Contraction.** The lanthanide contraction is clearly evident in the lattice constants and the Ln–Te bond distances. For the RbLnSe\textsubscript{2} compounds,\textsuperscript{23} a quadratic expression $d(Ln–Se) = A_0 – A_1n + A_2n^2$, where 0 ≤ n ≤ 14 is the number of f electrons, provides a better fit to the lanthanide contraction than does a linear one $d(Ln–Se) = B_0 – B_n$, although not if the closed-shell atoms La and Lu are excluded (i.e., 1 ≤ n ≤ 13). Such a nonlinear relationship was described previously,\textsuperscript{24,25} where it was ascribed to crystal-
Electronic Structures of CsLnZnTe₃

field contractions of those rare earths lacking spherical symmetry. The nonlinear relationship was recently rediscovered. A similar analysis was performed on the Ln–Te distances (Table 2) in these CsLnZnTe₃ compounds. Results for the Ln–Te1 distances are shown in Figure 2. The results for the Ln–Te2 distances are similar. Once again, a quadratic fit of \( d(\text{Ln–Te}) \) versus \( n \) is superior to a linear one if the closed-shell atom, in this case La, is included.

**Optical Properties and Electronic Structures.** The optical absorption spectra of the (010) and (001) crystal planes for CsTbZnTe₃ are shown in Figure 3. The optical band gap is about 2.12 eV, consistent with the color of the crystal. There is no significant difference between the band gaps along the two different orientations for this compound. For CsGdZnTe₃, the band gap of the (010) crystal plane is 2.13 eV.

The total and partial densities of states (DOS) of CsGdZnTe₃ are shown in Figure 4a. The contributions from the Gd (4f) orbitals are not shown in the total DOS. The Zn (3d) orbitals are highly localized, as can be seen from the sharp peak near \(-7\) eV. The Gd, Zn, and Te orbitals are hybridized in the valence and conduction bands, which can be seen from the overlap among them around the Fermi level. The valence band primarily consists of Te1 (5p) and Te2 (5p) orbitals, whereas the conduction band has most contributions from Gd (5d and 6s) orbitals, Zn (4s and 4p) orbitals, and less significantly from Te (5s and 5p) orbitals. Because Cs has almost no contributions in the DOS, the electronic properties are mainly determined by the two-dimensional \( 2\text{[GdZnTe₃]} \) anionic framework. The band structure of CsGdZnTe₃ (not shown) indicates that the valence-band maximum and conduction-band minimum are both located at the same \( k \) point. Thus, the CsLnZnTe₃ compounds are direct band-gap semiconductors, and for each, the lowest optical transition is simply from the valence-band maximum to the conduction-band minimum.

To calculate optical absorption, we considered the interband transitions, with the initial states being the occupied valence-band states and the final states being the unoccupied conduction-band states. Interband transitions are the most important part of optical transitions in direct band-gap semiconductors. The joint density of states (JDOS) is related to a convolution over the valence-band and conduction-band density of states functions. It corresponds to the optical transitions between the valence-band and conduction-band states. The JDOS is zero if the transitions are forbidden or if no initial or final states are present at the transition energy. It is large for allowed transitions between bands with a large DOS at the transition energy. The JDOS of CsGdZnTe₃ is shown in Figure 4b. An optical transition at 2.1 eV can be deduced from this figure. Although the muffin-tin radii were optimized to avoid electron leakage from the Zn and Te cores, the small peaks in the JDOS around 2.0 eV arise from 0.002 electrons leaking from every Zn core and 0.003 electrons leaking from every Te core. Although the LDA is known to underestimate optical band gaps, the value obtained from the JDOS is in surprisingly close agreement with the experimental value of 2.13 eV.

Previous density functional theory calculations on the CsYMSe₃ (M = Zn, Cd, Hg) compounds indicate that the 4p orbitals of Se also contribute mainly to the valence band. Because the sequence of energy levels of p orbitals is \( 4p(\text{Se}) < 5p(\text{Te}) \), the band gaps for the CsLnZnTe₃ compounds should be smaller than those of the CsLnZnSe₃ analogues. This is demonstrated by both the colors and the band gaps obtained for these two series of compounds. The CsLnZnSe₃ compounds are yellow, gray, or red, whereas the CsLnZnTe₃ reported here are all dark red. The band gaps measured for selected CsLnZnSe₃ compounds along [010] are around 2.4–2.6 eV, whereas the band gaps measured

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for the present CsLnZnTe$_3$ compounds are around 2.1 eV. A similar shift of band gaps in the RbLnSe$_2$ compounds has also been noted.\textsuperscript{23}

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**Supporting Information Available:** Crystallographic files in CIF format for CsLnZnTe$_3$ (Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Y). This material is available free of charge via the Internet at http://pubs.acs.org.

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