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Syntheses, Structures, and Theoretical Study of LaCuSTe and SmCuSTe

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Two mixed-chalcogen compounds LaCuSTe and SmCuSTe have been synthesized by the reactions of the elements at 1123 K. LaCuSTe crystallizes in a cell of dimensions $a = 6.4955(8)$ Å, $b = 7.7692(9)$ Å, $c = 7.4665(9)$ Å, and $\beta = 95.045(2)°$ ($T = 153$ K) with four formula units in space group C_{2h}^5-$P2_1/c$ of the monoclinic system. Its structure is closely related to that of $LaCuS_2$. SmCuSTe crystallizes as a new structure type in a cell of dimensions $a = 7.5195(8)$ Å, $b = 12.6370(14)$ Å, and $c = 7.5287(8)$ Å ($T = 153$ K) with eight formula units in space group D_{2h}^{15}-$Pbca$ of the orthorhombic system. In LaCuSTe, the La atom is coordinated by a bicapped trigonal prism of four S atoms and four Te atoms; in SmCuSTe, the Sm atom is coordinated by a monocapped trigonal prism of four S atoms and three Te atoms. In both structures, the Cu atom is coordinated by a tetrahedron of one S atom and three Te atoms, These structures are built from $(CuSTe)_n$ sheets that are separated by the rare-earth-metal atoms. In LaCuSTe, a sheet comprises edge-sharing dimers of $CuSTe_3$ tetrahedra ($Cu_2S_2Te_4$) that share each of their Te atoms with four neighboring dimers to form a mixed octagonal/quadrilateral net. In SmCuSTe, a sheet comprises a single tetrahedral $CuSTe_3$ unit that shares each of its Te atoms with three neighboring tetrahedra to form a hexagonal net. The band structures of these two compounds indicate that they should be semiconductors. The calculations also show that the substitution of Te atoms for S atoms lowers the energy gap compared with those of unsubstituted systems.

Introduction

Ternary sulfides of the general formula $MCuS_2$, where M is a trivalent metal such as Sc, Cr, or a rare-earth metal (Ln), exhibit interesting structures and a variety of optical, magnetic, electrical, and thermoelectric properties.[1−13] $ScCuS_2$ and $CrCuS_2$ possess hexagonal and rhombohedral structures, respectively; in each, the trivalent metal atom is octahedrally coordinated.[3,6] Most $LnCuS_2$ compounds crystallize in one of three structure types: monoclinic $LaCuS_2$ (Ln = La to Tb),[2,5,7,9,11,12] orthorhombic $ErCuS_2$ (Ln = Y, Dy to Lu),[5,7,12] and trigonal $ScCuS_2$.[6,12] In each structure, the Ln atom has trigonal prismatic coordination and the Cu atom has tetrahedral coordination. Some attempts have been made to modify the physical properties of these compounds,[4,6,9,12] but not by partial substitution of the chalcogen.

A few ordered mixed-metal chalcogenides are known. These include USSe,[14] USTe,[14] USeTe,[14] $Ho_2S_2Te_{1.3}$,[15] $Dy_2S_2Te_{1.4}$,[16] $Re_4S_4Te_4$,[17] Bi_2Te_2S,[18] and Ga_2S_2Te.[19] The parent compounds β-US_2[20] and β-USe_2[21] contain two crystallographically independent chalcogen atoms from which USSe, USTe, and USeTe are derived conceptually by the substitution of only one such chalcogen by a heavier one. The mixed chalcogenides and their parents belong to the orthorhombic $PbCl_2$ structure type.[22] These mixed compounds show ferromagnetic and pseudo-semimetallic behavior, whereas β-US_2 and UTe_2 are paramagnetic[21] and semiconducting.[20,21]

The $LaCuS_2$ structure type also has two crystallographically distinct S positions.[8] If one of these could be substituted by Te, which is heavier and less electronegative than S, then the

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Table 1. Crystal Data and Structure Refinement for LaCuSTe and SmCuSTe

	LaCuSTe	SmCuSTe
fw	362.11	747.10
space group	C_{2h}^5-$P2_1/c$ (No. 14)	D_{2h}^{15}-$Pbca$ (No. 61)
a (Å)	6.4955(8)	7.5195(8)
b (Å)	7.7692(9)	12.6370(14)
c (Å)	7.4665(9)	7.5287(8)
β (deg)	95.045(2)	90
V (Å^3)	375.34(8)	715.41(13)
Z	4	8
T (K)	153 (2)	153 (2)
λ(Mo Kα) (Å)	0.710 73	0.710 73
d_{calcd} (g/cm^3)	6.408	6.936
cryst dimens (mm)	0.023 × 0.127 × 0.140	0.040 × 0.134 × 0.215
lin abs coeff (cm^{-1})	248.8	305.0
transm factors	0.108−0.570	0.031−0.298
$R(F)^a$ ($F_o^2 > 2\sigma(F_o^2)$)	0.025	0.023
$R_w(F_o^2)^b$ (all data)	0.069	0.068

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.04F_o^2)^2$ for $F_o^2 \geq 0$; $w^{-1} = \sigma^2(F_o^2)$ for $F_o^2 \leq 0$.

resultant material might show physical properties different from those of the parent. We have investigated the La/Cu/S/Te and Sm/Cu/S/Te systems and report here the syntheses, structures, and band structures of the ordered compounds LaCuSTe and SmCuSTe.

Experimental Details

Synthesis. The compounds LaCuSTe and SmCuSTe were prepared by the reactions of La (Reacton, 99.9%) or Sm (Alfa, 99.9%) with Cu (Alfa, 99.999%), S (Alfa, 99.8%), and Te (Aldrich, 99.8%) in a flux of KI (Aldrich, 99%). Mixtures of Ln, Cu, S, Te, and KI in the molar ratio 1:1:1:1:5 were loaded into fused-silica tubes under an argon atmosphere in a glovebox. 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 at 1 K/min, kept at 1123 K for 3 days, cooled at 0.05 K/min to 573 K, and then cooled to room temperature. The products were washed free of iodide salts with water and then dried with acetone. The major products were black plates of the mixed chalcogenides. Analysis of these plates with an EDX-equipped Hitachi S-4500 SEM showed only the presence of Ln, Cu, S, and Te approximately in the ratio 1:1:1:1. These compounds are modestly stable in air.

Structure Determinations. Single-crystal X-ray diffraction data were obtained with the use of graphite-monochromatized MoKα radiation (λ = 0.710 73 Å) at 153 K on a Bruker Smart-1000 CCD diffractometer.[23] Intensity data were collected with the program SMART.[23] Cell refinement and data reduction were carried out with the use of the program SAINT,[23] and face-indexed absorption corrections were carried out numerically with the program XPREP.[24]

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.[24] Each final refinement included anisotropic displacement parameters and a secondary extinction correction. Additional experimental details are shown in Table 1. Tables 2 and 3 give positional parameters and equivalent isotropic displacement parameters, and Tables 4 and 5 present selected bond distances for LaCuSTe and SmCuSTe, respectively..

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for LaCuSTe

atom	x	y	z	U_{eq}^a (Å^2)
La	0.35383(4)	0.03108(3)	0.22166(3)	0.00766(15)
Cu	0.06688(10)	0.66396(8)	0.04289(8)	0.01180(19)
S	0.59187(17)	0.27128(14)	0.00154(14)	0.0052(2)
Te	0.12498(5)	0.39784(4)	0.27801(4)	0.00764(15)

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

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for SmCuSTe

atom	x	y	z	U_{eq} (Å^2)
Sm	0.24131(3)	0.43130(2)	0.02448(4)	0.00773(15)
Cu	0.07143(9)	0.21024(5)	0.17008(8)	0.01092(19)
S	0.00131(12)	0.03815(9)	0.24116(11)	0.0051(3)
Te	0.27797(5)	0.30785(2)	0.39212(5)	0.00737(15)

Table 4. Selected Bond Lengths (Å) for LaCuSTe

La−S	2.8882(11)	La−Te	3.5527(6)
La−S	2.9195(11)	Cu−S	2.3250(13)
La−S	2.9236(11)	Cu−Te	2.6337(7)
La−S	3.0035(11)	Cu−Te	2.6456(7)
La−Te	3.2582(5)	Cu−Te	2.7170(7)
La−Te	3.2781(5)	Cu−Cu	2.7491(12)
La−Te	3.5399(6)		

Table 5. Selected Bond Lengths (Å) for SmCuSTe

Sm−S	2.8206(9)	Sm−Te	3.4468(6)
Sm−S	2.8233(9)	Cu−S	2.3008(13)
Sm−S	2.8688(10)	Cu−Te	2.5709(8)
Sm−S	2.8748(10)	Cu−Te	2.5938(7)
Sm−Te	3.1891(5)	Cu−Te	2.6161(7)
Sm−Te	3.1941(5)		

TB-LMTO Calculations. First-principles self-consistent local density approximation (LDA)[25] calculations of electronic structures for $LaCuS_2$, LaCuSTe, $ScCuS_2$, and SmCuSTe were performed with the use of the tight-binding (TB) linear muffin-tin orbital (LMTO) method in the atomic sphere approximation (ASA), including the combining correction.[26−28] This method splits the crystal space into overlapping atomic spheres (Wigner−Seitz spheres) whose radii are chosen to fill completely the crystal volume. In the present calculations, space-filling is achieved without overlapping atomic spheres with one another by more than 15%, without overlapping atomic spheres with interstitial (or empty) spheres (ES) by more than 20%, and without overlapping interstitial spheres with one another by more than 25%. All k-space integrations were performed with the tetrahedron method.[29,30] Within the irreducible Brillouin zone, calculations for the isostructural $LaCuS_2$ and LaCuSTe compounds both used 170 irreducible k-points and those for $ScCuS_2$ and SmCuSTe used 248 and 75 k-points, respectively. The basis sets consisted of 6s, 5d, and 4f for La; 4s, 4p, and 3d for Cu; 3s and 3p for S; 5s and 5p for Te; and 1s for ES. The 6p orbitals for La, the 3d orbitals for S, the 5d orbitals for Te, and ES p−d states were downfolded by means of Löwdin's technique.[29−31] In the calculations on SmCuSTe, the Sm atoms were replaced by La atoms because of program limitations.

Results and Discussion

The structure of LaCuSTe is closely related to that of $LaCuS_2$. The latter structure may be thought of as consisting of CuS_2 layers separated by La atoms along the a axis.[8] Each La atom is coordinated by a monocapped trigonal prism of seven S atoms

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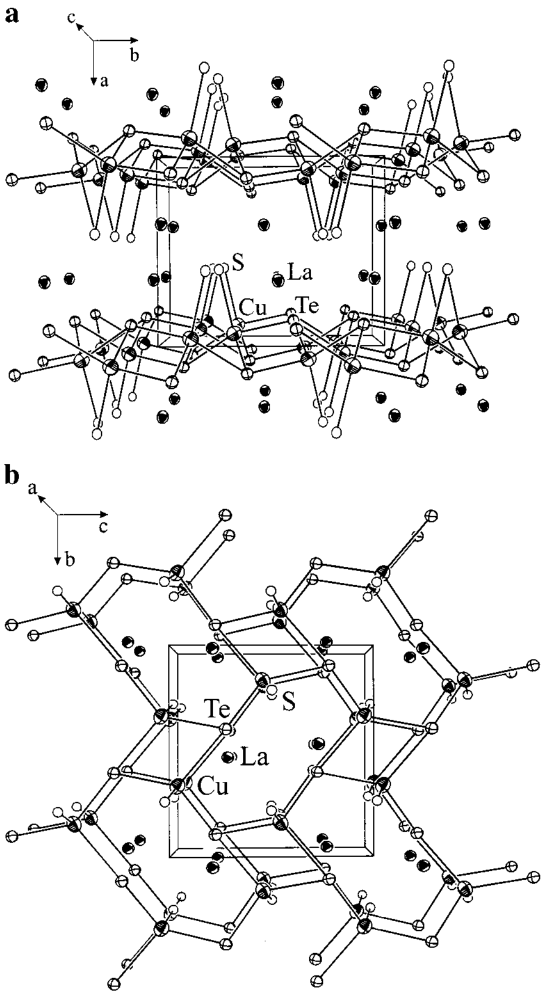

Figure 1. Unit cell of LaCuSTe viewed down (a) *c** and (b) *a**. The 90% displacement ellipsoids are displayed here. For the sake of clarity, no La−S or La−Te interactions are shown. Here the S and Te positions are replaced by the S1 and S2 atoms to obtain the closely related $LaCuS_2$ structure.

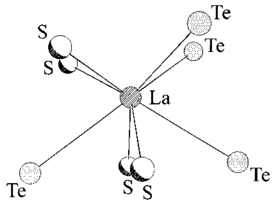

Figure 2. Coordination of La in LaCuSTe.

(4 S1 and 3 S2), and each Cu atom is coordinated by a tetrahedron of four S atoms (1 S1 and 3 S2). The LaCuSTe structure is formed conceptually by the substitution of the S2 atom by a Te atom, but the resultant structure differs from that of $LaCuS_2$. Figure 1 displays the structure of LaCuSTe; for clarity, the La−S and La−Te bonds are not shown. The La atoms in this structure are coordinated by four S and four Te atoms at the vertices of a bicapped trigonal prism with two of the four Te atoms as caps (Figure 2). The Cu atoms are coordinated by a tetrahedron of one S atom and three Te atoms, as shown in Figure 1. As may be seen in Figure 1a, there is a single CuSTe sheet in the unit cell. This sheet comprises edge-sharing dimers of $CuSTe_3$ tetrahedra ($Cu_2S_2Te_4$). Each dimer shares each of its Te atoms with four neighboring dimers to form a mixed octagonal/quadrilateral net (Figures 1b and 3), and these nets are stacked parallel to one another to form infinite channels. Each octagonal channel is filled with a pair of La atoms 3.9875(6) Å away from each other. One CuSTe sheet viewed down the *a* axis is displayed in Figure 1b. The sheet is composed of equal numbers of octagons and quadrilaterals.

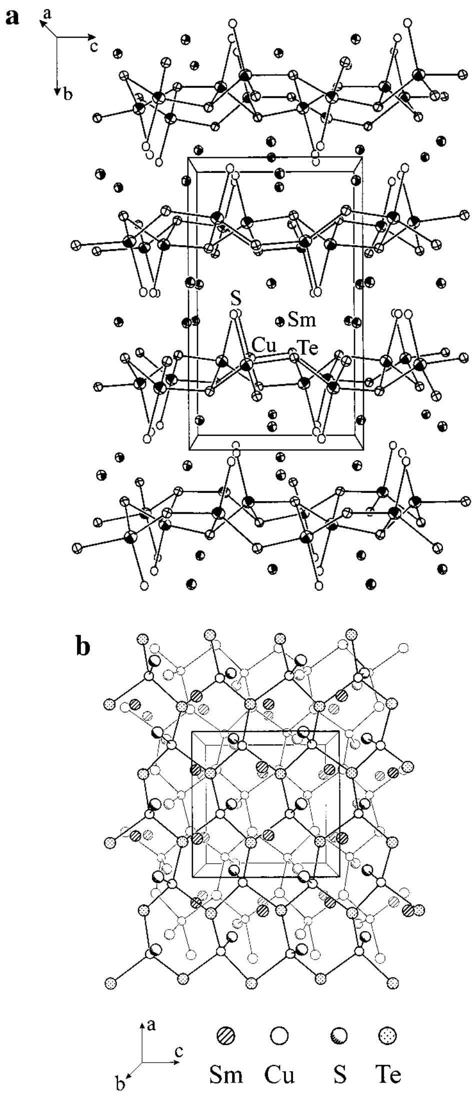

Figure 3. Unit cell of SmCuSTe viewed down (a) *a* and (b) *b*, where there are two sheets in the unit cell related by a 2_1 symmetry operation. The 90% displacement ellipsoids are displayed here. For the sake of clarity, no Sm−Te interactions are shown.

In LaCuSTe, the bond distances (Table 4) are reasonable: the La−S distances range from 2.8882(11) to 3.0035(11) Å compared with 2.891(4)−3.081(4) Å in $LaCuS_2$;[8] the La−Te distances range from 3.2582(5) to 3.5527(6) Å compared with 3.3157(6)−3.3585(5) Å in $LaCu_{0.4}Te_2$;[32] the Cu−Te distances range from 2.6337(7) to 2.7170(7) Å compared with 2.611(3)−2.781(4) Å in $LaCu_{0.4}Te_2$; the Cu−S distance of 2.3250(13) Å is comparable to those of 2.337(5)−2.537(5) Å in $LaCuS_2$. The Cu−Cu distance of 2.7491(12) Å in LaCuSTe is longer than those of 2.644(6) Å in $LaCuS_2$ and 2.557(1) Å in metallic Cu.[33] In $LaCuS_2$ and LaCuSTe, the formal oxidation states of La, Cu, S, and Te are +3, +1, −2, and −2 so that the probable Cu−Cu interaction comprises d^{10} Cu^+ species. This interaction has been discussed elsewhere.[34−38]

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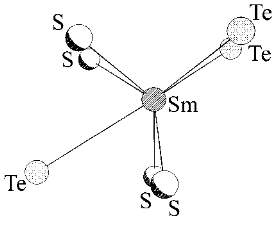

Figure 4. Coordination of Sm in SmCuSTe.

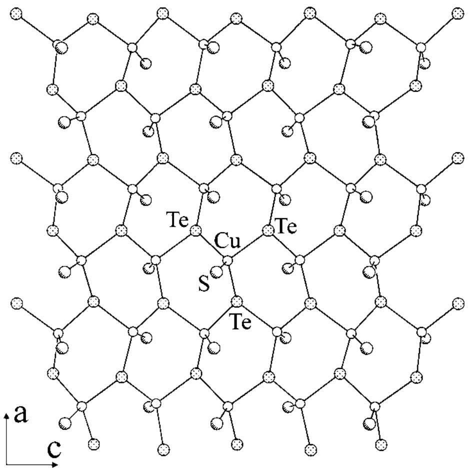

Figure 5. The CuSTe sheet of SmCuSTe.

The structure of SmCuSTe is displayed in Figure 4, and bond distances are given in Table 5. These distances are reasonable. SmCuSTe consists of CuSTe sheets, separated by Sm atoms. Figure 3a and Figure 1a show very similar patterns. However, SmCuSTe and LaCuSTe are not isostructural as is clear by comparing Figures 4b and Figure 1b and from the fact that SmCuSTe has eight formula units in an orthorhombic unit cell whereas LaCuSTe has four formula units in a monoclinic unit cell. In SmCuSTe, the Sm atom is coordinated by a monocapped trigonal prism (4 S and 3 Te atoms) (Figure 4) whereas, in LaCuSTe, the La atom is coordinated by a bicapped trigonal prism (Figure 2). In both coordination polyhedra, the trigonal prism consists of four S atoms and two Te atoms. In each structure, the Cu atoms are coordinated tetrahedrally by one S and three Te atoms. The single CuSTe sheet in SmCuSTe (Figure 5) is built from these tetrahedral $CuSTe_3$ units. The Te atoms at the vertices are shared with three neighboring units to form a distorted hexagonal net, as shown in Figures 3b and 6. The unit cell contains two sheets related by the 2_1 axis along *b*, as shown in Figure 3b. A similar hexagonal net is found in the structure of hexagonal $ScCuS_2$ (Figure 6),[6] where the Sc atoms are at the centers of hexagonal channels. As in $LaCuS_2$, there are two crystallographically distinct S atoms (S1 and S2) in $ScCuS_2$. Each S1 atom makes only one bond to a Cu atom, and the Cu−S1 bonds extend out of the same side of the sheet. In contrast, in SmCuSTe along *c*, the S atoms successively are above and below the sheet, and they alternate up and down in a given Cu_3Te_3 hexagon (Figure 5). The disposition of S atoms in LaCuSTe is different from either of these arrangements.

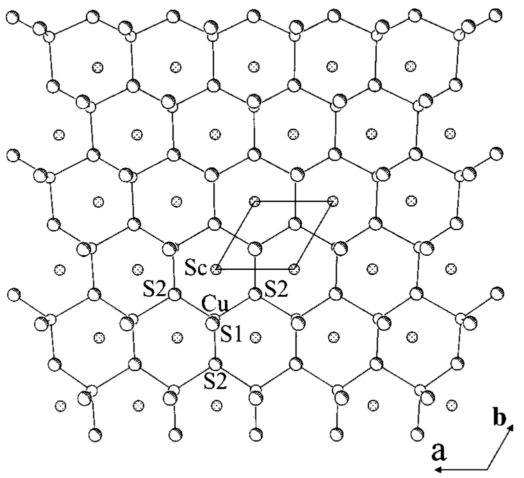

Figure 6. The hexagonal net in the structure of $ScCuS_2$.

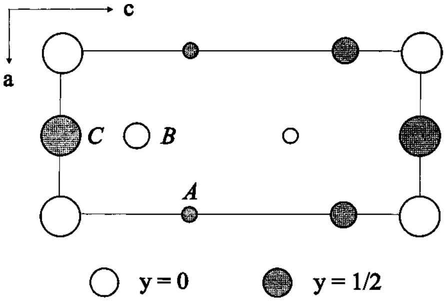

Figure 7. Unit cell of ABC of the Cu_2Sb type. These atoms are at A (0, $^{1}/_{2}$, z_1), B (0, $^{1}/_{2}$, z_2), and C (0, 0, 0).

In going from $LaCuS_2$ to LaCuSTe, why does Te substitute only for the S2 atom in the ring and not for the S1 atom out of the ring? To answer this question, let us first discuss the ABC ternary compounds of the Cu_2Sb structure type.[22] These structures can be considered to be layered compounds with distorted rocksalt AB slabs separated by layers of four-coordinated C atoms, as shown in Figure 7. Examples are KAgSe[39] and UAsSb.[40] In these structures, K or U occupies the A site, Se or As occupies the B site, and Ag or Sb occupies the C site. In each instance the A atom, the metal, is the most electropositive one; it loses electrons most easily and becomes the electron donor in the structure. In each instance, the B atom, the non-metal, is the most electronegative one; it most readily gains electrons from the A atom and becomes the electron acceptor. The C atom may be a metal or a non-metal. Stronger ionic bonds may be formed between A and B atoms than between A and C atoms. So, if the electronegativities of A, B, and C decrease in that order, the A atom will always be as close as possible to the B atom, and the C atoms in the sheet may make some covalent bonds with four neighboring C atoms. In this way, the total energy is minimized. Almost all ABC compounds follow this rule, including those in different structural families such as $ThCr_2Si_2$ and $CeNiSi_2$.[22] Let us now apply this rule to $LaCuS_2$. Here La, the most electropositive atom, is coordinated by a bicapped trigonal prism of four S1 and three S2 atoms (Figure 2). The S1 atoms occupy four vertices of the trigonal prism. Two of the three S2 atoms are

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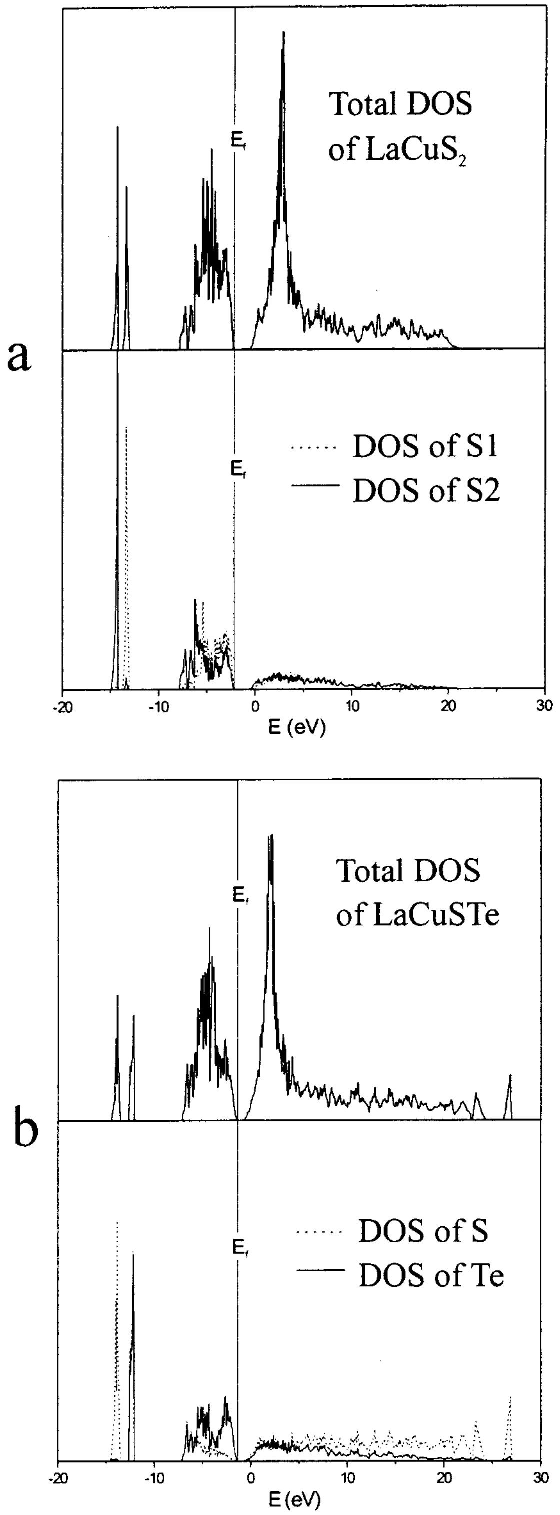

Figure 8. Density of states (DOS): (a) total, S1, and S2 of $LaCuS_2$; (b) total, S, and Te of LaCuSTe. The scale of the total DOS is half that of the partial DOS.

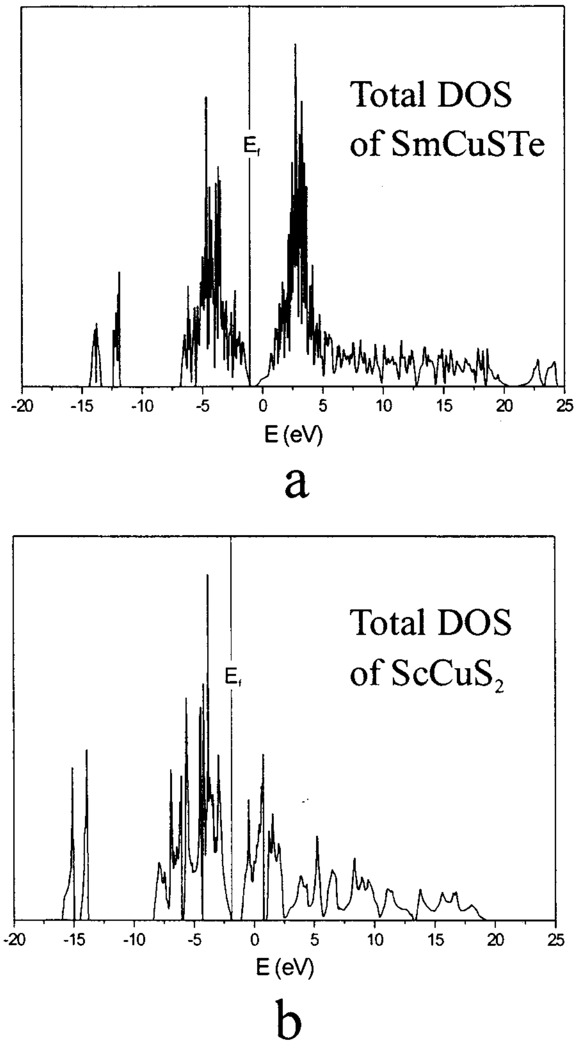

Figure 9. Total DOS of (a) $ScCuS_2$ and (b) SmCuSTe.

at the other two vertices of the prism, and the other is at the cap position. Each S1 atom bonds to four La atoms and one Cu atom whereas each S2 atom bonds to three La atoms and three Cu atoms. The four La−S1 bond distances are 2.891(4), 2.902(4), 2.937(4), and 2.946(4) Å. The three La−S2 bond distances are 2.915(4, 2.926(4), and 3.081(4) Å. It is clear that the S1 atom forms more and generally stronger bonds to the most electropositive atom, La. Extended Hückel calculations show that the S1 atom is more ionic than the S2 atom, carrying more negative charge.[41] Thus the less electronegative Te atom is able to replace the more loosely bound S2 atom and not the S1 atom in $LaCuS_2$. In the resultant LaCuSTe and SmCuSTe compounds, the S atom, being the most electronegative, forms more and stronger bonds with the most electropositive Ln atom rather than with the Cu atom. In both structures, each Cu atom forms one bond with an S atom and three bonds with Te atoms.

$LaCuS_2$ and LaCuSTe, which have similar crystal structures, have similar band structures. The band dispersion is larger in the (101) plane (the layer plane) than in the direction of the *b* axis. Both compounds are predicted to be semiconductors. The energy levels of the HOMOs (Fermi energy levels) are −2.161 and −1.367 eV, the energy levels of the LUMOs are −0.619 and −0.750 eV, and the band gaps are 1.542 and 0.616 eV for $LaCuS_2$ and LaCuSTe, respectively. The energy difference (0.794 eV) between the HOMOs is large compared with the difference (0.131 eV) between the LUMOs, so the smaller band gap in LaCuSTe is mainly the result of the higher energy level of the HOMO. To clarify further the effect of the substitution of a Te atom for the S2 atom in $LaCuS_2$ to form LaCuSTe, the

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(41) Extended Hückel results for $LaCuS_2$ show that the S1 atom carries −0.28 net charge and the S2 atom −0.16 charge, where the atomic parameters of La, Cu, and S are from the YAeHMO package.[42] The calculations for the two-dimensional $[CuS_2]^{3-}$ layer show that the S1 atom carries −1.5 charge and the S2 atom −1 charge.

(42) Landrum, G. *Yet Another Extended Hückel Molecular Orbital Package (YAeHMOP)*, Version 2.0; 1997.

density of states (DOS) of S1 and S2 of $LaCuS_2$ and of S and Te of LaCuSTe were calculated and are displayed in Figure 8. In $LaCuS_2$, both S1 and S2 contribute to the DOS near the Fermi level whereas in LaCuSTe the Te atom but not the S atom contributes. Obviously, the valence orbitals of the Te atom elevate the Fermi level and narrow the band gap. Figure 9 displays the total DOS of $ScCuS_2$ and SmCuSTe, respectively. In SmCuSTe, the Te atoms play the same role. These calculations predict that both $ScCuS_2$ and SmCuSTe should be semiconductors.

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

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