Rare earth chalcogenide \( \text{Ce}_3\text{Te}_4 \) as high efficiency high temperature thermoelectric material

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The electronic band structures of \( \text{Ce}_3\text{Te}_4 \) have been studied using the first-principles density-functional theory calculations. It is found that the density of states of \( \text{Ce}_3\text{Te}_4 \) has a very high delta-shaped peak appearing 0.21 eV above the Fermi level, which mainly comes from the \( f \) orbital electrons of the rare-earth element Ce. Using the simple theory proposed by Mahan and Sofo, we predict the \( zT \) of \( \text{Ce}_3\text{Te}_4 \) material in an ideal condition. Our calculation yields an equilibrium lattice constant \( a_0 = 9.466 \) Å for \( \text{Ce}_3\text{Te}_4 \), which agrees well with the experimental result (9.553 Å).11

Figure 2(a) shows the Brillouin zone (BZ) of \( \text{Ce}_3\text{Te}_4 \) for the band structure calculations, where the coordinates of the high symmetry points are given by \( \Gamma = (0,0,0) \), \( H = (1/2, -1/2, 1/2) \), \( P = (1/4, 1/4, 1/4) \), \( N = (0,0,1/2) \), expressed in units of the reciprocal vectors. The BZ integration is done using an \( 8 \times 8 \times 8 \) Monkhorst–Pack k-point mesh.12 We have tested the total energy convergence to be within 0.01% difference with respect to the energy cutoff and the number of k points. Figure 2(b) shows the electronic band structures of \( \text{Ce}_3\text{Te}_4 \) in an energy range from \(-6\) to 2 eV along high symmetry directions \( \Gamma-H-N-P \) of the BZ, without including the spin–orbit interaction. On this figure, the Fermi level is set to be at 0 eV. First, there is an overlap between the two lowest conduction bands that are partially occupied (near the Fermi level). This indicated that \( \text{Ce}_3\text{Te}_4 \) is a semimetal. Second, there is a direct band gap at the \( \Gamma \) point between the bottom of the partially occupied conduction band and the top of the fully occupied valence band, which is 1.06 eV. Most importantly, Fig. 2 clearly shows that there is a very high

There have been strong interests in developing high efficiency thermoelectric materials over the past two decades for both refrigeration and power generation applications. Rare-earth chalcogenides was identified in Wood’s review for both refrigeration and power generation applications. Rare-earth chalcogenides has, we expect a potentially higher \( zT \) of \( \text{Ce}_3\text{Te}_4 \) than that of \( \text{La}_3\text{Te}_4 \) and \( \text{Th}_3\text{P}_4 \) structures, as shown in Fig. 1, which includes 6 Ce atoms and 16 Te atoms. In all our calculations, we use a primitive super cell of the \( \text{Th}_3\text{P}_4 \) structure, as shown in Fig. 1, which includes 6 Ce atoms and 8 Te atoms, with \( a_1 = a_0 (-1/2, 1/2, 1/2) \), \( a_2 = a_0 (1/2, -1/2, 1/2) \), and \( a_3 = a_0 (1/2, 1/2, -1/2) \), where \( a_0 \) is the lattice constant of the cubic unit cell. The optimization of the atomic structures was performed by using the conjugate-gradient technique.\(^{10}\) The atomic structure is fully relaxed until the forces on all the atoms are less than 0.02 eV/Å.

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density of states located at about 0.21 eV above the Fermi level. Such high density of electron states sitting close to the Fermi level could be very beneficial for high temperature thermoelectricity.

Figure 3 shows the calculated total electronic density of states (TDOS) and partial electronic density of states (PDOS) for the Ce₃Te₄. The TDOS is found to be very high between −0.28 and 0.69 eV around the Fermi-level (the Fermi level is at 0 eV), as shown in Fig. 3(a). The very high DOS peak, 200 states/(eV unit cell), is located at 0.21 eV above the Fermi level with a \( \delta \)-function shape. At high temperature with \( k_B T > 0.21 \) eV, a high \( zT \) value in Ce₃Te₄ could potentially be expected because these \( \delta \)-function shaped DOS peaks electrons with very narrow energy distribution participate in the transport process. A 1.06 eV band gap is clearly located at the energy ranging from −1.42 to −0.36 eV in the TDOS plot. Figure 3(b) shows the PDOS of the Ce atom in Ce₃Te₄. It clearly shows that the strong peak in the TDOS mainly comes from the \( 4f \) orbit with slightly hybridization with the \( 5d \) orbit of the Ce atoms. This phenomenon (the \( \delta \)-function shape peak in DOS) is due to the strong localization character of the \( 4f \) orbit. For Ce atom, the contribution of the \( s, p, \) and \( d \) orbits are far smaller than that of the \( 4f \) orbit, and are practically invisible in the PDOS plot in Fig. 3(b). Figure 3(c) shows that the valence band is dominated by the \( 5p \) orbit of the Te atoms. The contribution of the \( s, d, \) and \( f \) orbits are much lower than the \( p \) orbit and are almost invisible in Fig. 3(c).

As discussed above, the very interesting feature for the electronic band structures of Ce₃Te₄ is that there is a high-density band lines located at only 0.21 eV above the Fermi level. According to the analytic model proposed by Mahan and Sofo that relates electrical conductivity, thermopower, and electronic thermal conductivity to a common transport distribution function \( s(x) \), where \( x \) is the dimensionless electron energy scaled by \( k_B T \) and measured from Fermi level and, the figure of merit \( zT \) for a thermoelectric material is optimized when \( s(x) \) has the form of a Dirac \( \delta \)-function and peaks at \( x_0 \sim \pm 2.4 k_B T \) above the Fermi level. If a thermoelectric material is operated at \( T = 1200 \) K, the optimal value for \( x_0 \) would be about 0.25 eV.

We apply the simple theory from Ref. 3 to estimate the ideal \( zT \) values at 1200 K for Ce₃Te₄, using the following equations:

\[
zT = \frac{k_\text{b}}{k_\text{f}}, \tag{1}
\]

\[
D(x) = e^x/(e^x + 1)^2, \tag{2}
\]

\[
k_\text{b} = (k_B/e)^2\sigma_0 D(b)/b^2, \tag{3}
\]

where \( k_\text{b} \) is electronic thermal conductivity, \( k_\text{f} \) is the lattice thermal conductivity, \( T \) is the mean operating temperature of the device, and \( b \) indicates the position of the peak with respect to the Fermi level in \( k_B T \). Using some idealistic parameters such as \( k_\text{b}=1 \) W/m·K, mean-free-path \( l=a =0.3 \) nm, and \( b= \pm 2.4k_B T \), Mahan and Sofo arrived at a maximum value of \( (zT)_{\text{max}} = 14 \). If assuming that the deviation from this maximum value is caused only by the variation in \( D(b)/b^2 \) and take the TDOS peak as the major contributor, we obtain the ideal \( zT=13.5 \) for Ce₃Te₄ at \( T = 1200 \) K.

The above results do not include the spin–orbit interaction. When the spin–orbit interaction is included in the band structure calculation, the single \( \delta \)-function shape peak at 0.21 eV in the DOS (without spin–orbit interaction) is split into two \( \delta \)-function shape peaks which locate at 0.29 eV and 0.82 eV, respectively. While the peak locating at 0.82 eV is too far away (\( >3k_B T \) from the Fermi level) to make contributions on \( zT \), the shift in the location of the \( \delta \)-function shape peak in DOS from 0.21 to 0.29 eV only slightly change the estimate of idealized \( zT \) value. Finally, we note that the real \( zT \) of Ce₃Te₄ could be much lower than the estimate because of the following: (1) the lattice thermal conductivity could be \( 3–5 \) W/m·K for Ce₃Te₄, similar to the measured value of La₃Te₄.\(^4\) As shown in Eq. (1), the ultimate limit of the idealistic \( zT \) is essentially the ratio of the electronic thermal conductivity over the lattice thermal conductivity. High lattice thermal conductivity lowers the \( zT \). (2) The background DOS due to the non-\( f \) electrons shown in Fig. 3 could have a negative effect on \( zT \).

In summary, the first-principles density functional theory calculations have been employed to study the electronic structures of the rare-earth chalcogenide Ce₃Te₄. This study shows that there is a high \( \delta \)-function shaped peak in the conduction band DOS above the Fermi level, mainly coming from the \( f \)-level electrons of the rare-earth element Ce. Such high density of electron states at the proximity of the Fermi level is highly desirable for high temperature thermoelectricity. Using the simple theory proposed by Mahan and Sofo, we estimate an ideal \( zT=13.5 \) for Ce₃Te₄ at \( T = 1200 \) K, which indicates that rare-earth chalcogenide Ce₃Te₄ could be a promising high efficiency high temperature thermoelectric materials.

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