Rare earth chalcogenide Ce_3Te_4 as high efficiency high temperature thermoelectric material

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The electronic band structures of Ce_3Te_4 have been studied using the first-principles density-functional theory calculations. It is found that the density of states of Ce_3Te_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, [Proc. Natl. Acad. Sci. U.S.A. **93**, 7436 (1996)], we obtain an ideal value of zT=13.5 for Ce_3Te_4 at T =1200 K, suggesting that the rare-earth chalcogenide Ce_3Te_4 could be a promising high efficiency high temperature thermoelectric material. © *2011 American Institute of Physics*. [doi:10.1063/1.3597409]

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[1] in 1986 as one of high efficiency thermoelectric material systems for high temperature applications, due to the excellent thermal stability[2] and the potential contributions of *d*- and *f*-level electrons in rare-earth elements for high Seebeck coefficient.[3] Recently May *et al.* synthesized lanthanum telluride (La_3Te_4) via mechanical alloying and reported the dimensionless figure of merit zT ∼ 1.1 at 1275 K.[4]

Considering that both cerium telluride (Ce_3Te_4) and La_3Te_4 have Th_3P_4 structure but cerium atom has one $4f$ electron in addition to the $5d$ electrons that lanthanum atom has, we expect a potentially higher zT of Ce_3Te_4 than that of La_3Te_4 recently reported. The first-principles density functional theory is used in this work to study the electronic band structures of the thermoelectric material Ce_3Te_4. We then use the simple analytical model proposed by Mahan and Sofo[3] to predict zT of Ce_3Te_4 material in an ideal condition.

The electronic band structure calculations are carried out using the Vienna *ab initio* simulation package (VASP), which uses a plane-wave basis and projector augmented wave potentials.[5–7] The exchange-correlation is treated with the generalized gradient approximation.[8,9] The plane wave kinetic energy cutoff is selected to be 23 Ry. The $4f$, $5d$, and $6s$ electron orbits of the Ce atom and the $5s$ and $5p$ electron orbits of the Te atom are treated as valence electrons. The conventional Ce_3Te_4 super cell has the cubic Th_3P_4 structure (space group *I*-43*d*) with 12 Ce atoms and 16 Te atoms. In all our calculations, we use a primitive super cell of the Th_3P_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. Our calculation yields an equilibrium lattice constant a_0 =9.466 Å for Ce_3Te_4, which agrees well with the experimental result (9.553 Å).[11]

Figure 2(a) shows the Brillouin zone (BZ) of Ce_3Te_4 for the band structure calculations, where the coordinates of the high symmetry points are given by Γ=(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 $8\times8\times8$ 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 Ce_3Te_4 in an energy range from −6 to 2 eV along high symmetry directions Γ-H-N-Γ-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 Ce_3Te_4 is a semimetal. Second, there is a direct band gap at the Γ 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
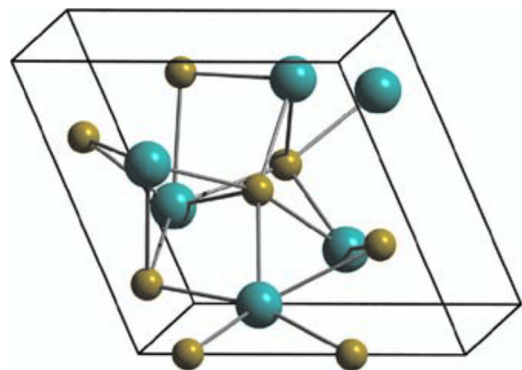

FIG. 1. (Color online) The primitive cell of Ce_3Te_4. Large and small spheres represent cerium and tellurium atoms, respectively.
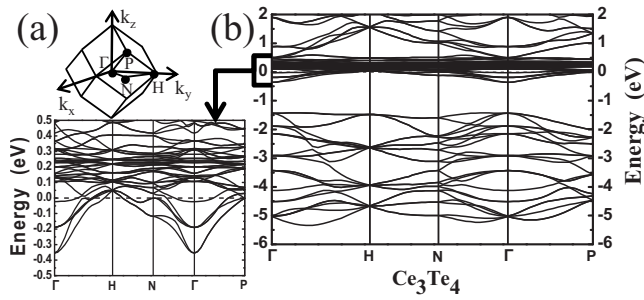
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FIG. 2. The calculated electronic band structures of Ce_3Te_4 along high symmetry lines of the BZ, in an energy window from −6 to 2 eV, where the Fermi level is set to 0 eV.

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.[3]

Figure 3 shows the calculated total electronic density of states (TDOS) and partial electronic density of states (PDOS) for the Ce_3Te_4. 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 δ-function shape. At high temperature with 3 $k_B T > 0.21$ eV, a high zT value in Ce_3Te_4 could potentially be expected because these δ-function shaped DOS peak electrons with very narrow energy distribution participate in the transport process.[3] 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 Ce_3Te_4. 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 δ-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 Ce_3Te_4 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
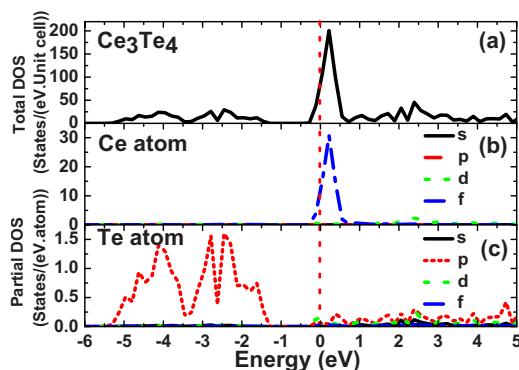

FIG. 3. (Color online) (a) Calculated total DOS for bulk Ce_3Te_4. [(b) and (c)] Partial DOS for Ce atom and Te atom, respectively. Fermi level is at the 0 eV.

and Sofo[3] 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 δ-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 Ce_3Te_4, using the following equations:

$$zT = k_0/k_l, \tag{1}$$

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

$$k_0 = (k_B/e)^2 T\sigma_0 D(b)b^2, \tag{3}$$

where k_0 is electronic thermal conductivity, k_l 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_l=1 W/m·K, mean-free-path l=a =0.3 nm, and b= ± 2.4$k_B T$, Mahan and Sofo arrived at a maximum value of $(zT)_{max}$=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 Ce_3Te_4 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 δ-function shape peak at 0.21 eV in the DOS (without spin–orbit interaction) is spitted into two δ-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 ($\gg 3k_B T$ from the Fermi level) to make contributions on zT, the shift in the location of the δ-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 Ce_3Te_4 could be much lower than the estimate because of the following: (1) the lattice thermal conductivity could be 3–5 W/m K for Ce_3Te_4, similar to the measured value of La_3Te_4.[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.[3]

In summary, the first-principles density functional theory calculations have been employed to study the electronic structures of the rare-earth chalcogenide Ce_3Te_4. This study shows that there is a high δ—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 Ce_3Te_4 at T=1200 K, which indicates that rare-earth chalcogenide Ce_3Te_4 could be a promising high efficiency high temperature thermoelectric materials.

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