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Effects of alkali metal element substitution on the thermoelectric properties of $\beta$-Zn$_4$Sb$_3$

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Abstract

The effects of alkali metal elements Na, Li, and K on the electronic structure and thermoelectric properties of $\beta$-Zn$_4$Sb$_3$ were extensively studied based on first-principles electronic structure calculations and Boltzmann transport theories. We found that these alkali metal elements with s orbitals could bring resonant distortion in the electronic density of states (DOS). The effects of these resonant peaks on the thermoelectric properties of $\beta$-Zn$_4$Sb$_3$ were analyzed. And the results showed that a ~13/13/20-fold increase on the room-temperature Seebeck coefficient of $\beta$-Zn$_4$Sb$_3$ is achieved due to Na/Li/K doping respectively. Accordingly, the optimizing power factor/thermoelectric figure of merit of $\beta$-Zn$_4$Sb$_3$ gets an about 1.69/1.43-fold increase at room temperature upon Na doping. And their corresponding optimal Fermi levels of three doped compounds all lie near and below the valence band maximum of the host.

1. Introduction

Because of its potential applications of power generation or cooling environmental-friendly, thermoelectric materials have been attracted widespread attention in recent years.\cite{1–6} The energy conversion efficiency of thermoelectric materials is characterized by the dimensionless figure of merit $ZT = S \sigma T / \lambda$, where $T$ is the absolute temperature, $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\lambda$ ($= \lambda_L + \lambda_C$) is thermal conductivity with both the lattice ($\lambda_L$) and carrier ($\lambda_C$) contributions.

As is known, $\beta$-Zn$_4$Sb$_3$ exhibits a low glasslike thermal conductivity \cite{7} and good electrical properties at moderate temperatures \cite{8, 9}. This unusual combination of thermoelectric properties for $\beta$-Zn$_4$Sb$_3$ suggests that it is an ideal example of the phonon glass and electron crystal approach \cite{8}. According to the recent study on $\beta$-Zn$_4$Sb$_3$\cite{8–14}, the very low thermal conductivity of bulk $\beta$-Zn$_4$Sb$_3$ (whose actual composition should be expressed as Zn$_{13-\delta}$Sb$_{10}$ ($\delta = 0.2–0.5$) \cite{15}) is attributed to phonon scattering by various sources such as (i) disorderedly distributed Zn vacancies, (ii) interstitial Zn atoms\cite{9, 16}, and (iii) the low frequency rattling motion of the Sb dimers \cite{17}.

The standard procedure for boosting $ZT$ of $\beta$-Zn$_4$Sb$_3$ has been simultaneous optimization of carrier concentration and thermal conductivity through doping \cite{18–30}. However, the results showed that this method has reached its limits and that further significant progress will be achieved by focusing on the power factor $S^2 \sigma$. Recently, Mahan and Sofo \cite{31} theorized that the introduction of resonant distortion in the electronic density of states (DOS) could significantly enhance the Seebeck coefficient $S$ without sacrificing the electrical conductivity $\sigma$. Heremans et al.\cite{32} showed that after Tl doping, $ZT$ of PbTe is doubled due to the increase in $S$. This is ascribed to the DOS distortion of the host. Similarly, the phenomenon was also observed in Al-doped PbSe, In-doped SnTe, or Sn-doped Bi$_2$Te$_3$ \cite{33}. In this paper, we showed that alkali-metal-element doping can also cause...
resonant distortion in DOS of $\beta$-Zn$_4$Sb$_3$. These alkali metal elements all have one valence electron in $s$ orbital of the outermost layer. Thus resonant peaks close to the Femi level in DOS are formed after that the $s$ levels of these elements overlap or hybridize with the host band. Accordingly, how these resonant levels affect thermoelectric properties after doping alkali metal elements (here Na, Li and K) in $\beta$-Zn$_4$Sb$_3$ was discussed.

2. Computational details

The electronic structure of Zn-substituted compounds MZn$_{35}$Sb$_{30}$ (M = Na/Li/K) has been investigated using the Vienna ab initio simulation package (VASP) with the projector augmented wave (PAW) scheme and Perdew, Burke and Ernzerhof generalized gradient approximation (GGA-PBE) for the exchange-correlation functional [34–36]. The calculations of the undoped system has been performed within a framework of Zn$_{36}$Sb$_{30}$ (see figure 1 of supplemental material is available online at stacks.iop.org/MRX/6/1265j6/mmedia) for simplicity. Zn-substituted systems have been treated in the framework of MZn$_{35}$Sb$_{30}$ (M = Na/Li/K). Based on test calculations, the energy cutoff for the plane wave expansion is 350 eV, and the k-point density is $2 \times 2 \times 2$ for structural optimization and $4 \times 4 \times 4$ for DOS calculations with the Monkhorst-Pack method. The calculated equilibrium lattice parameters values of the undoped system ($a = 21.299$ Å, $c = 17.444$ Å) were set as the initial values for the Zn-substituted systems. The ionic coordinates and the unit cell’s size and shape were optimized simultaneously to eliminate structures with internal stress until the forces converge to less than 0.001 eV/Å.

Figure 1. (a) The total DOS of Zn$_{36}$Sb$_{30}$ with and without Na, (b) Na partial DOS of $s$-character, (c) The total DOS of Zn$_{36}$Sb$_{30}$ with and without Li, and (d) The total DOS of Zn$_{36}$Sb$_{30}$ with and without K. The energy is in respect to the host valence band maximum.
Based on the computed DOS, we used Boltzmann transport theory to calculate $\sigma$, $S$ and $\lambda_C$ of Zn-substituted compounds with MATLAB software program as follows [37]:

$$\sigma = e^2L(\varepsilon)$$  \hspace{1cm} (1a)  
$$S = -L^{(1)}(\varepsilon/TL(\varepsilon))$$  \hspace{1cm} (1b)  
$$\lambda_C = 1/TL^{(2)} - S^2\sigma T$$  \hspace{1cm} (1c)  
$$L(\varepsilon) = \int_{-\infty}^{+\infty} d\varepsilon \left( -\frac{\partial f_0}{\partial \varepsilon} \right) g(E)\nu(E)^2\tau(E)\left(E - E_f\right)^a$$  \hspace{1cm} (1d)  

where $e$, $f_0$, $E$, $F$, $g$, and $\tau$ is the electron charge, Fermi distribution function, Fermi energy, electron velocity, electron wave vector, density of states, and total relaxation time, respectively. Deformation potential scattering of acoustic and optical phonons, and polar scattering by optical phonons [38, 39] have been considered, as listed below:

$$\tau_{po} = \frac{(E + E^2/E_f)^{1/2}}{e^2(2m^*)^{1/2}k_BT(\varepsilon_{\infty}^{-1} - \varepsilon_0^{-1})(1 + 2E/E_f)}$$  \hspace{1cm} (2a)  
$$\tau_o = \frac{2\hbar^2\alpha^2\rho(\hbar\omega_0)^2(E + E^2/E_f)^{-1/2}}{\pi E_{so}^2k_BT(2m^*)^{1/2}(1 + 2E/E_f)}$$  \hspace{1cm} (2b)  
$$\tau_a = \frac{2\pi\hbar^4C_4(E + E^2/E_f)^{-1/2}}{E_{so}^2k_BT(2m^*)^{1/2}(1 + 2E/E_f)}$$  \hspace{1cm} (2c)  
$$\Theta = 1 - \frac{8E/E_f(1 + E/E_f)}{3(1 + 2E/E_f)^2}$$  \hspace{1cm} (2d)  
$$\delta = (2kr_{so})^{-2}$$  \hspace{1cm} (2e)  
$$\tau_{\infty}^{-2} = \frac{e^2}{\varepsilon_\infty}\int_{0}^{\infty} \left( -\frac{\partial f}{\partial \varepsilon} \right) g(E)dE$$  \hspace{1cm} (2f)  
$$\tau^{-1} = \tau_{po}^{-1} + \tau_o^{-1} + \tau_a^{-1}$$  \hspace{1cm} (2g)  

Values for material constants used in these equations are given in table I of supplemental material. More calculation details can be found in our earlier works [40].

### 3. Results and discussion

In consistent with the earlier model calculations, [14] the DOS of Zn$_{36}$Sb$_{30}$ system is partitioned into Sb-s and Zn-d bands, which are bonding inactive, and the valence band (VB) and conduction band (CB) primarily composed of Zn-s, p and Sb-p states as shown in figure 1. The Fermi energy is $\sim$0.35 eV below the VB top with a band gap of about 0.52 eV. The zero of energy is set at valence band maximum of Zn$_{36}$Sb$_{30}$. In order to facilitate the comparison with unsubstituted system, the DOS of MZn$_{35}$Sb$_{30}$ ($M = Na/Li/K$) was moved about 0.41/0.36/0.36 eV until their main peaks of the valence band can match perfectly with that of unsubstituted system. It can be seen clearly in figure 1(a) that Na-doping introduces a sharp band resonant peak at 0.082 eV above the VBM, which is mainly dominated by the Na s levels as shown in figure 1(b). While the cases with Li/K doping, also have a sharp peak above the VBM, and show considerable enhancement in DOS at 0.042/0.273 eV, respectively, being similar to Na doping. The formation energies $E_{form}$ of the Na/Li/K point defects are $\sim$0.829/1.098/0.4478 eV/atom which is defined as [38]:

$$E_{form} = E_{doped} + M_{Zn} - E_{undoped} - H_M - E_{VBM}$$  \hspace{1cm} (3)  

where $E_{doped}$, $E_{undoped}$, $\mu$ and $E_{VBM}$ are the total free energy for MZn$_{35}$Sb$_{30}$ ($M = Na/Li/K$), the total free energy for Zn$_{36}$Sb$_{30}$, the chemical potentials of the constituent elements and the energy of the valence band maximum (VBM).

Once the $E_p$ is known, the carrier concentration can be obtained as $n(E) = \int f_0(E)g(E)dE$, in which $f_0(E)$ and $g(E)$ are the Fermi distribution function and the carrier density of states (DOS), respectively. Thus, with the upward shift of $E_f$ from VB top into the valence bands, the carrier concentration dependence of Seebeck coefficient $S$, electrical conductivity $\sigma$, and power factor $S^2\sigma$ of MZn$_{35}$Sb$_{30}$ ($M = Na/Li/K$) could be calculated as shown in figure 2. The calculated Seebeck coefficient $S$ and electrical conductivity $\sigma$ of Zn$_{36}$Sb$_{30}$ at $T = 300$ K as a function of carrier concentration $n$ are also shown in figure 2 for comparison, which are in good agreement.
with experimentally measured values of $\beta$-Zn$_3$Sb$_3$ [7, 29, 39] (please see figure 2 of supplemental material). As shown in figure 2(a), Seebeck coefficient $S$ of four compounds increase with decreased carrier concentration. The positive Seebeck coefficient indicates p-type conduction in all four compounds. Moreover, $S$ of the three Na/Li/K-doped cases is boosted greatly when compared with that of pristine $\beta$-Zn$_3$Sb$_3$ in the interesting carrier concentration range. And their peak value of $S$ relative to that of $\beta$-Zn$_3$Sb$_3$ is nearly 13/13/20 times at $n \approx 5.6 \times 10^{27}$ m$^{-3}$, $n \approx 4.4 \times 10^{27}$ m$^{-3}$, and $n \approx 5.2 \times 10^{27}$ m$^{-3}$, respectively. According to Mott formula [39] the resonant peaks brought by Na/Li/K elements would be more and more $\delta$-function-like in the DOS as the amount of Na/Li/K elements decreases. And thus, a sharper increase in $S$ would be expected.

The electrical conductivity $\sigma$ as a function of the carrier concentration $n$ is shown in figure 2(b). As expected, with the increase of carrier concentration, $\sigma$ for three doping cases all increase monotonously and show much less than that of undoped $\beta$-Zn$_3$Sb$_3$ in the interesting carrier concentration range due to the enhancement of carrier scattering by point defects. Particularly $\sigma$ of the KZn$_{35}$Sb$_{30}$ compound is much lower, almost less than half that of $\beta$-Zn$_3$Sb$_3$ at $n \approx 8 \times 10^{27}$ m$^{-3}$. Exceptionally, $\sigma$ of Na-substituted system starts to outnumber that of pristine $\beta$-Zn$_3$Sb$_3$ as $n > 8.5 \times 10^{27}$ m$^{-3}$, and on that account, as shown in figure 2(c), Na-substituted case gains a 1.69-fold increase in optimizing power factor of $\beta$-Zn$_3$Sb$_3$ with $n \approx 5.7 \times 10^{27}$ m$^{-3}$ when $T = 300$ K. However, optimizing power factors of Li/K-substituted systems, both decrease about 9%/25% compared with that of unsubstituted case, when $n \approx 4.6 \times 10^{27}$ m$^{-3}$, and $n \approx 5.5 \times 10^{27}$ m$^{-3}$, respectively.

The carrier thermal conductivity $\lambda_C$ of MZn$_{35}$Sb$_{30}$ (M = Na/Li/K) as a function of carrier concentration $n$ is shown in figure 3(a). One can see that the carrier concentration dependence of $\lambda_C$ of MZn$_{35}$Sb$_{30}$ (M = Na/Li/K) similar to that of the electrical conductivity: (a) $\lambda_C$ of all three substituted cases increase monotonously with the increase of carrier concentration; (b) $\lambda_C$ for three substituted cases degrade largely compared with that of pristine $\beta$-Zn$_3$Sb$_3$ due to the enhancement of carrier scattering by point defects. (c) $\lambda_C$ of Na-doped system changes to outnumber that of pristine $\beta$-Zn$_3$Sb$_3$ as $n > 7.7 \times 10^{27}$ m$^{-3}$. However, despite all this, Na doping system achieves a maximum $ZT$ of 1.43 times as large as that undoped case ($ZT \approx 0.15$ at $n \approx 4.5 \times 10^{23}$ m$^{-3}$) as shown in figure 3(b).

Figure 3(b) shows that carrier concentration dependence of room temperature $ZT$ assuming $\lambda_L = 0.6$ Wm$^{-1}$K$^{-1}$ (an average experimental value for undoped $\beta$-Zn$_3$Sb$_3$) for $\beta$-Zn$_3$Sb$_3$ doped with Na/Li/K. Na-substituted system shows the best performance and its maximum $ZT$ reaches 0.22 with
\( n \approx 5.6 \times 10^{27} \text{ m}^{-3} \), attributed by the elevation of power factor coincident with the decrease of carrier thermal conductivity. As for the Li/K-substituted cases, because of the degraded power factor, their maximum \( ZT \) values are also degraded, which is 0.13 and 0.1 at \( n \approx 4.6 \times 10^{27} \text{ m}^{-3} \) or \( 5.5 \times 10^{26} \text{ m}^{-3} \) with \( T = 300 \text{ K} \), respectively. For three-substituted cases, their peaks of \( ZT \) all locate just in the range of carrier concentration for the optimizing power factors. If in conjunction with other methods (such as nanocomposite \([41]\)) to lower lattice thermal conductivity, we believe that there still has scope for \( ZT \) to improve further.

To further figure out the effects of Na/Li/K doping on thermoelectric performance, room temperature carrier concentration \( n \) as a function of the Fermi energy \( E_F \) for MZn\(_{35}\)Sb\(_{30}\) (\( M = \text{Na/Li/K} \)) is shown in the figure 4. At a fixed \( T \), carrier concentration \( n \) increases as \( E_F \) shifts upward into the deeper lying valence bands. According to the results of figure 3(b), we know that when \( n \approx 5.6 \times 10^{27} \text{ m}^{-3} \), \( n \approx 4.6 \times 10^{27} \text{ m}^{-3} \) and \( 5.5 \times 10^{26} \text{ m}^{-3} \), \( ZT \) of three Na/Li/K-substituted compounds will be maximized, respectively. And we found that their optimal \( E_F \) at this point are: \( E_F(\text{Na}) = -0.11 \text{ eV} \), \( E_F(\text{Li}) = -0.09 \text{ eV} \) and \( E_F(\text{K}) = -0.09 \text{ eV} \), being about 0.192/0.132/0.36 eV away from their resonant peak, respectively, and all lying near the maximum of the host valence band. This is in agreement with the results of recent research on resonant states \([42, 43]\).

4. Conclusions

We have investigated the effects of doping Na, Li and K on the electronic structure and thermoelectric properties of \( \beta - \text{Zn}_3\text{Sb}_3 \) and demonstrated the enhancement of the thermoelectric properties as a result of resonant doping. All three alkali metal elements could cause resonant DOS distortion, a boost in the Seebeck coefficient, and

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**Figure 3.** Carrier concentration dependence of room temperature thermoelectric parameters for \( \beta - \text{Zn}_3\text{Sb}_3 \) doped with Na/Li/K. (a) electronic thermal conductivity, (b) \( ZT \) with \( \lambda_e = 0.6 \text{ Wm}^{-1}\text{K}^{-1} \).

**Figure 4.** Fermi energy dependence of room temperature carrier concentration for MZn\(_{35}\)Sb\(_{30}\) (\( M = \text{Na/Li/K} \)). The energy is in respect to the host valence band maximum. Arrows indicate where the best thermoelectric performance is achieved.
drastic reduction of conductivity and carrier thermal conductivity. A 69%/43% increase of optimal power factor and ZT could be achieved by doping Na. The enhancement of thermoelectric performance for Na-substituted case results from the elevation of power factor and the simultaneous decrease of carrier thermal conductivity. Moreover, the optimal $E_C$ corresponding to the maximal ZT is about 0.192 eV away from its resonant peak, and near the maximum of the host valence band. These findings provide a better understanding of resonant doping and useful reference to design high-performance thermoelectric materials.

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