Optimizing thermoelectric properties of filled MPt$_4$Ge$_{12-x}$Sb$_x$ skutterudites by band engineering

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On the basis of density functional theory (DFT) calculations thermoelectric properties are derived for Sb-doped skutterudites MPt$_4$Ge$_{12-x}$Sb$_x$ with M=Ba,La,Th. It is predicted that the originally very small absolute values of Seebeck coefficients |$S$| of the undoped compounds is increased by factors of 10 or more for suitable dopings. The optimal dopings correspond to a “magic” valence electron number for which all electronic states up to a (pseudo)gap are filled. The theoretical findings are corroborated by measurements of $S$ for LaPt$_4$Ge$_{12-x}$Sb$_x$ skutterudites. DFT derived vibrational rattling-like modes for LaPt$_4$Ge$_{12}$ indicate a small value for the lattice thermal conductivity which in combination with a large value of $S^2$ makes the La-based skutterudites appear as promising thermoelectric materials.

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Thermoelectric materials are of scientific as well as technological interest in particular because of their potential for environment friendly electric power generation. The thermoelectric performance of a material is characterized by the dimensionless figure of merit,

$$ZT = S^2T\sigma/(\kappa_{el} + \kappa_{ph})$$

where $S$ represents the Seebeck coefficient, $\sigma$ the electrical conductivity, and $\kappa_{el}$, $\kappa_{ph}$ are the thermal conductivities attributed to electrons and phonons, respectively. Skutterudites appear as promising thermoelectric materials by combining suitable electronic, vibrational and thermal properties. This is due to their crystal structure which contains large voids formed by framework atoms. Filling the voids by heavier elements may reduce $\kappa_{ph}$ due to the appearance of low-lying optical (so-called rattling) modes \[1\]. Additionally these filler atoms may provide an appropriate number of valence electrons for making $S^2$ large. At present, a $ZT$ at elevated temperatures of about 1.6 is achieved by filled pnictide skutterudites \[1\]. Very recently, values of $ZT = 1.7$ at 800 K were reported for the unfilled skutterudite Fe$_2$S$_x$Co$_{1.2}$Sb$_{12}$ under severe plastic deformation \[2\].

Ge-based skutterudites MPt$_4$Ge$_{12}$ were recently synthesized \[3\] for which the cage framework is formed entirely by Ge atoms. Their Seebeck coefficients are rather low as compared to pnictogen-based skutterudites \[2\].

The aim of the present work is to utilize density functional theory results for understanding the physical properties of Ge-based and Sb-doped filled skutterudites in order to provide a recipe for improving their thermoelectric performance. The quantities provided by DFT are the electronic structure, the Seebeck coefficient, the energy of formation as a function of doping and vibrational properties when searching for rattling modes.

Previously, efforts have been made for investigating the electronic structure in order to optimize the thermoelectric performance. Mahan and Sofo \[10\] proposed that a delta-shaped transport distribution function originating from very narrow electronic density of states (DOS) around the Fermi energy $E_F$ is required to maximize $ZT$, as also recently hinted by experiment \[11\]. For this purpose, doping is essential, as it will be applied also in the present study. On the other hand, the required singularity of the DOS is not accomplishable in many real thermoelectric materials although they possess promising thermoelectric properties \[12\] \[13\]. Based on a tight-binding concept it was argued by Zhou et al. \[16\] that extremely narrow bands are not optimal for maximizing $ZT$ but rather the type of scattering mechanism of the charge carriers is of importance. Here, we propose a scheme of engineering the electronic structure of MPt$_4$Ge$_{12}$ compounds by investigating the substitutionally doped compounds MPt$_4$Ge$_{12-x}$Sb$_x$. In fact, we predict an increase of the Seebeck coefficient by a factor 10 and more upon doping. These findings are corroborated by new experimental results for LaPt$_4$Ge$_{12-x}$Sb$_x$.

According to Boltzmann’s transport theory, the Seebeck tensor is defined as

$$S(T, N) = -\frac{1}{|e|T}K_0^{-1}K_1$$

with the electronic charge $-|e|$. The total number of
electrons $N$ defines the chemical potential $\mu$ by
\[
\int_{-\infty}^{\infty} n(E) f(E, \mu, T) dE = N
\]
when integrating the DOS $n(E)$ weighted by the Fermi–Dirac function $f = 1/(1 + \exp((E - \mu)/kT))$. In the spirit of a rigid band model (i.e. $n(E)$ remains unchanged upon varying $N$) the components of the tensor $S$ become now functions of $N$ and temperature $T$. The tensor $K_n$ is associated with the electronic band structure by
\[
K_n = -\frac{1}{4\pi^3} \sum_{i,k} v_i(k) \otimes v_i(k) \tau_i(k) \times (\varepsilon_i(k) - \mu)^n f'(\varepsilon_i(k))
\]
in which $v_i(k)$ and $v_i(k)$ are the energy eigenvalue and the corresponding band velocity for vector $k$ and for band $i$. The quantity $\tau_i(k)$ represents the corresponding relaxation time comprising all scattering events. The function $f'(E) = \partial f/\partial E$ is the derivative of the Fermi–Dirac distribution. The Seebeck tensor is diagonal with all components equal if the system has cubic symmetry or is symmetrically averaged, which we assume from now on. In fact, skutterudites crystallise in a cubic crystal structure. Within Mott’s approximation derived for low temperatures [17] the Seebeck coefficient is expressed as
\[
S = -\frac{\pi^2 k_B^2 T}{3|e|} \left( \frac{1}{n(E)} \frac{dn(E)}{dE} \right) + \frac{1}{v^2(E)} \frac{dv^2(E)}{dE} + \frac{1}{\tau(E)} \frac{d\tau(E)}{dE} \bigg|_{E=E_F}
\]
relating $S$ to the DOS by the first term on the right side. This term becomes large for a large slope and a small value of $n(E_F)$ which could be the case e.g. for doped semiconductors. Assuming a constant relaxation time $\tau$ (i.e. the third term is zero) and a parabolic behaviour of the valence bands according to $\varepsilon(k) = E_v - \hbar^2 k^2/2m$ and of the conduction bands according to $\varepsilon(k) = \hbar^2 k^2/2m - E_c$ one arrives at the relations
\[
S_n = -|\text{const}| \frac{k_B T}{E_F - E_c}, \quad E_F > E_c
\]
for an n-type semiconductor and
\[
S_p = |\text{const}| \frac{k_B T}{E_v - E_F}, \quad E_F < E_v
\]
for a p-type semiconductor. There, $E_c$ and $E_v$ are the bottom of the conduction band and the top of the valence band, respectively. Actually, a parabolic band behavior is observed for MPt$_4$Ge$_{12}$ (M=Ba,La,Th) skutterudites below the distinctive (pseudo)gaps, as revealed by Figs. 2. Maximizing $|S|$ in the spirit of Mott’s approximation requires that $E_F$ is close to the conduction or valence band edge and that the electron velocities are large according to the second term on the right side of Eq. 5.

For calculating the Seebeck coefficient according to Eqs. 6 and 7 within the constant relaxation time approximation a modified version of the BoltzTrap program [18] is used. Density functional theory (DFT) calculations were carried out by applying the Vienna Ab initio Simulation Package (VASP) [19,20]. The exchange correlation functional is approximated by the generalized gradient approximation as parametrized by Perdew, Burke and Ernzerhof [21], and the pseudopotentials are constructed by Blöchl’s projector augmented wave method [22,23]. In all calculations the structures were fully relaxed utilizing a $5 \times 5 \times 5$ Monkhorst and Pack k-point grid [24] ensuring accurate results. After structural optimization the eigenvalues $\varepsilon_i(k)$ were derived on a very fine $25 \times 25 \times 25$ k-mesh as needed by BoltzTrap.

Substituting Ge by Sb leads to a large homogeneity region in the phase diagram, and because of that it is unfeasible to perform fully relaxed DFT calculations for all possible structures. Therefore, such calculations were only made for the most important structures (i.e. the ones with the highest number of symmetry equivalent atomic configurations), and out of this selection the one with lowest total energy was chosen for finally deriving the thermoelectric properties.

The DFT derived Seebeck coefficients for MPt$_4$Ge$_{12}$ (M=Th,La,Ba) in Fig. 1 are rather small with values less than 10 $\mu$V/K being consistent with experiment [2,3,4]. The left panel of Fig. 1 showing $S$ as a function of electron doping $\Delta N$ at $T = 300$ K; right panel: $S$ as a function of temperature for the undoped compounds (i.e. $\Delta N = 0$). Doping $\Delta N$ is defined with respect to MPt$_4$Ge$_{12}$, and $\Delta N = 4, 5, 6$ places the Fermi energy of MPt$_4$Ge$_{12}$ in the (pseudo)gap. $S$ for $\Delta N \neq 0$ calculated within the rigid band model.

![DFT derived Seebeck coefficients S for MPt$_4$Ge$_{12}$ (M=Th,La,Ba).](image-url)

**FIG. 1:** DFT derived Seebeck coefficients $S$ for MPt$_4$Ge$_{12}$, (M=Th,La,Ba). Left panel: $S$ as a function of electron doping $\Delta N$ at $T = 300$ K; right panel: $S$ as a function of temperature for the undoped compounds (i.e. $\Delta N = 0$). Doping $\Delta N$ is defined with respect to MPt$_4$Ge$_{12}$, and $\Delta N = 4, 5, 6$ places the Fermi energy of MPt$_4$Ge$_{12}$ in the (pseudo)gap. $S$ for $\Delta N \neq 0$ calculated within the rigid band model.
reveals a band with strong dispersion with its maximum in $\Gamma$ (around 1.5 eV for the $\text{MPt}_4\text{Ge}_{12}$ compounds, and at $E_F$ for $\text{LaPt}_4\text{Sb}_5\text{Ge}_7$), which behaves rather linearly along the $\Gamma - H$ direction. These features resemble those of CoSb$_3$, which is a narrow-gap semiconductor. Assuming that substitution of Co and Sb by similar elements such as Pt and Ge does not significantly change the (pseudo)gap formation properties a simple electron counting rule can be constructed. Co$_4$Sb$_{12}$ has 96 valence electrons whereas Pt$_4$Ge$_{12}$, BaPt$_4$Ge$_{12}$, LaPt$_4$Ge$_{12}$ and ThPt$_4$Ge$_{12}$ have only 88, 90, 91 and 92 valence electrons, respectively. For placing now $E_F$ into the (pseudo)gap the Pt-Ge compounds have to be doped by 8, 6, 5 and 4 electrons ("magic" doping), correspondingly.

Figure 2 reveals rather minor influences on the (pseudo)gap when filling the voids of Pt$_4$Ge$_{12}$: it is preserved for Ba- and LaPt$_4$Ge$_{12}$ and becomes a true but small gap for ThPt$_4$Ge$_{12}$ (not shown). For LaPt$_4$Ge$_{12}$ and ThPt$_4$Ge$_{12}$ bands above the conduction band edge are rather flat due to their localized f-like character. Then $\frac{\partial n(E)}{\partial \mu}$ is becoming large and as indicated by Eq. 9 $|S|$ increases accordingly. Apart from changing the sign, this is the reason for the asymmetry of $S$ below and above the (pseudo)gap, with $|S|$ significantly larger for doped $\Delta N > \Delta N_0$. The crucial point is to find appropriate filler atoms which provide the correct number of doping electrons for $E_F$ falling into the (pseudo)gap.

When the filler atom $M$ is chosen for doping, an element which provides 8 valence electrons is needed. Then, the dopant must be a lanthanide or actinide atom with f-states as valence states. However, due to their localized nature the f-states may strongly influence the electronic structure at Fermi energy. For example, a metallic rather than semiconducting behavior is predicted for SmPt$_4$Ge$_{12}$ by previous calculations.

Another way of doping and adding valence electrons could be chosen by substituting the transition element. Noble metal elements such as Cu, Ag, Au are possible candidates providing one more electron than the latest transition elements Ni, Pd, Pt. The question is, how the electronic structure is affected and if the gap feature is preserved. When testing the replacement of Pt by Au by studying MAu$_4$Ge$_{12}$ compounds it turns out that the lowering of the 5d-level of Au in comparison to the Pt 5d-levels destroys the (pseudo)gap feature and hence also the promising thermoelectrical properties.

![FIG. 2: Electronic structure of Pt$_4$Ge$_{12}$ (top left), BaPt$_4$Ge$_{12}$ (top right), LaPt$_4$Ge$_{12}$ (bottom left), and LaPt$_4$Ge$_7$Sb$_5$ (bottom right).](image)

![FIG. 3: DFT derived Seebeck coefficients as a function of doping at T=300K (left panel) and temperature (right panel) for selected MPt$_4$Ge$_{12-x}$Ge$_x$ compounds. The change of sign of $S$ occurs at the "magical" composition, for which the total number of valence electrons is 96.](image)

![FIG. 4: DFT derived (left panel) and experimental Seebeck coefficients (right panel) as a function of temperature for LaPt$_4$Ge$_{12-x}$Sb$_x$ compounds.](image)

A third concept for substitutions is the replacement of Ge by elements such as Sb with a larger number of valence electrons than 4. Filled skutterudites such as BaPt$_4$Sb$_6$Ge$_6$, LaPt$_4$Sb$_5$Ge$_7$ and ThPt$_4$Sb$_5$Ge$_8$ have the "magic" number of valence electrons, namely 96, and what is important for them the desired electronic structure properties are preserved, as shown in Fig. 2 for the La-compounding as an example. Even a small gap opens up, which is not the case for undoped LaPt$_4$Ge$_{12}$. For the calculated thermoelectric properties of LaPt$_4$Sb$_5$Ge$_7$ it turns out that $|S|$ is substantially increased by more than a factor of 10 (Fig. 3) reaching now values even larger than 100 $\mu$V/K for the La-compound and more than 200 $\mu$V/K for the Th-compound. Figure 3(b) depicts temperature dependent Seebeck coefficients of some MPt$_4$Ge$_{12-x}$Sb$_x$ compounds around the critical compo-
tion (i.e. "magic" doping). Values of $|S|$ larger than 100 μV/K are reached in a temperature range of 400-800 K depending on the compound and its composition. From these findings one may speculate that in general large Seebeck coefficients are obtained with a proper doping of Sb for other Ge-based skutterudites.

Figure 4 compares DFT derived and experimental results for LaPt$_4$Ge$_{12-x}$Sb$_x$ compounds. Clearly, the experimental evidence corroborates the theoretical prediction of a very strong increase of $|S|$ upon doping by Sb. This enhancement effect seems to be more pronounced by the DFT results, which predict a maximum of $S(T)$ ranging from 500 to 800 K for p-type materials depending on the amount of substitutions. The DFT data also show the sensitivity upon substitution. Increasing the amount of Sb above the critical value (i.e. crossing the gap) changes its sign and results in comparable (although slightly smaller) values of $|S|$.

For maximizing the figure of merit in Eq. 1 the power factor $S^2\sigma$ should be large. Indeed, from the DFT calculations it was found that for LaPt$_4$Ge$_{7.1}$Sb$_{6.9}$ the power factor reaches a maximum at 600K, at a temperature which is useful also for technological applications. It should be noted that an absolute value of $S^2\sigma$ cannot be obtained from the first-principles calculations, because the relaxation time (assumed to be constant) is not known. For the Seebeck coefficient, however, the constant relaxation time cancels out. Nevertheless, an enhancement of at least two orders of magnitude in the power factor is achieved for each compound within the constant relaxation time approximation. Experimental data for LaPt$_4$Ge$_7$Sb$_5$ at 800 K reveal a power factor of $S^2\rho = 7.3 \times 10^{-5}$ W/K$^2$.

According to Eq. 1 a large figure of merit can also be achieved when the thermal conductivities are small. Concerning $\kappa_{el}$, the electronic contribution, it should be proportional to the DOS at Fermi energy. Inspecting Fig. 2 for LaPt$_4$Ge$_7$Sb$_5$ it is obvious that the DOS is very small just below the gap. Therefore, experimenting with the Sb substitutions close to the critical Sb$_5$ composition might lead to a very small value of $\kappa_{el}$. Concomitantly the electrical conductivity $\sigma$ becomes also small, which counteracts the enhancement effect of $\kappa_{el}$ for the figure of merit.

For synthesizing the material it is important to estimate its thermodynamic stability. Doing this by deriving the DFT enthalpy of formation $\Delta H$ it is found that about 1 kJ/mole is gained per substituting Sb atom with the minimum of $\Delta H$ (i.e. strongest bonding) for the doped compound MPt$_4$Ge$_2$Sb$_5$. Further increasing the amount of Sb reduces the bonding and hence the energy of formation is becoming less negative. This behavior reflects the filling of bonding valence states upon doping until the gap is reached for 5 Sb atoms (Fig. 2 right bottom panel). Adding more Sb adds non- or antibonding conduction band states to the total energy of the compound and hence $\Delta H$ is getting less negative.

On the basis of DFT calculations we predict new and promising thermoelectric materials, when in MPt$_4$Ge$_{12}$ skutterudites Ge is suitably replaced by Sb. In particular, LaPt$_4$Ge$_{7-x}$Sb$_{5-x}$ is studied which reveals strongly enhanced values of the Seebeck coefficient up to about 200 μV/K at 600 K. The "magic" composition of 7 Ge and 5 Sb atoms can be understood in terms of band engineering revealing the importance of electronic bands with large dispersions below a (pseudo)gap, very similar to CoSb$_3$. Samples of LaPt$_4$Ge$_{7-x}$Sb$_{5-x}$ were experimentally synthesized. Measurements of the Seebeck coefficient strongly supports the DFT predictions. In addition, from the DFT derived vibrational properties of LaPt$_4$Ge$_7$Sb$_5$, which reveal rattling modes, it can be concluded that the phonon thermal conductivity is expected to be small, which—in addition to the large Seebeck coefficient—would enhance the figure of merit.

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