

## Half-Heusler compounds for thermoelectric energy conversion

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Half-Heusler compounds have a wealth of distinctive characteristics that are promising for use as thermoelectric materials, including excellent electrical properties, mechanical robustness, and good thermal stability. One of the challenges to make efficient half-Heusler thermoelectric devices is the development of high-performance *p*-type and *n*-type half-Heusler compounds with compatible thermal and mechanical properties. In our studies, we focus on the development of the thermoelectric performance of *M*CoSb- and *M*NiSn-based (*M* = Hf, Zr, Ti) half-Heusler compounds. By employing phase separation and the optimization of carrier concentration, we enhanced the thermoelectric performance of *p*-type *M*CoSb-based compounds and obtained a high figure of merit  $zT$  of  $\approx 1.0$ . Furthermore, by considering lanthanide contraction as a design factor to select reasonable alloying atoms, we developed high-performance *n*-type (Zr,Hf)CoSb-based thermoelectric compounds with a high  $zT$  of  $\approx 1.0$ . Herein, we successfully establish *M*CoSb as the first half-Heusler system with matching *p*-type and *n*-type thermoelectric performances. Our results highlight the practical potential of this half-Heusler system for thermoelectric energy conversion.

At present, about 50% of industrial energy is wasted as heat. If a small fraction of this wasted energy is reduced, it will have a huge impact on world energy frontiers. Thermoelectric (TE) materials facilitate this process by converting waste heat into electricity using a temperature gradient. The performance of a TE material is

usually gauged by the dimensionless figure of merit,  $zT = \alpha^2 \sigma T / \kappa$ , where  $\alpha$ ,  $\sigma$ ,  $T$  and  $\kappa$  are the Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Half-Heusler (HH) compounds are ternary inter-metallic compounds with the typical formula XYZ, where X and

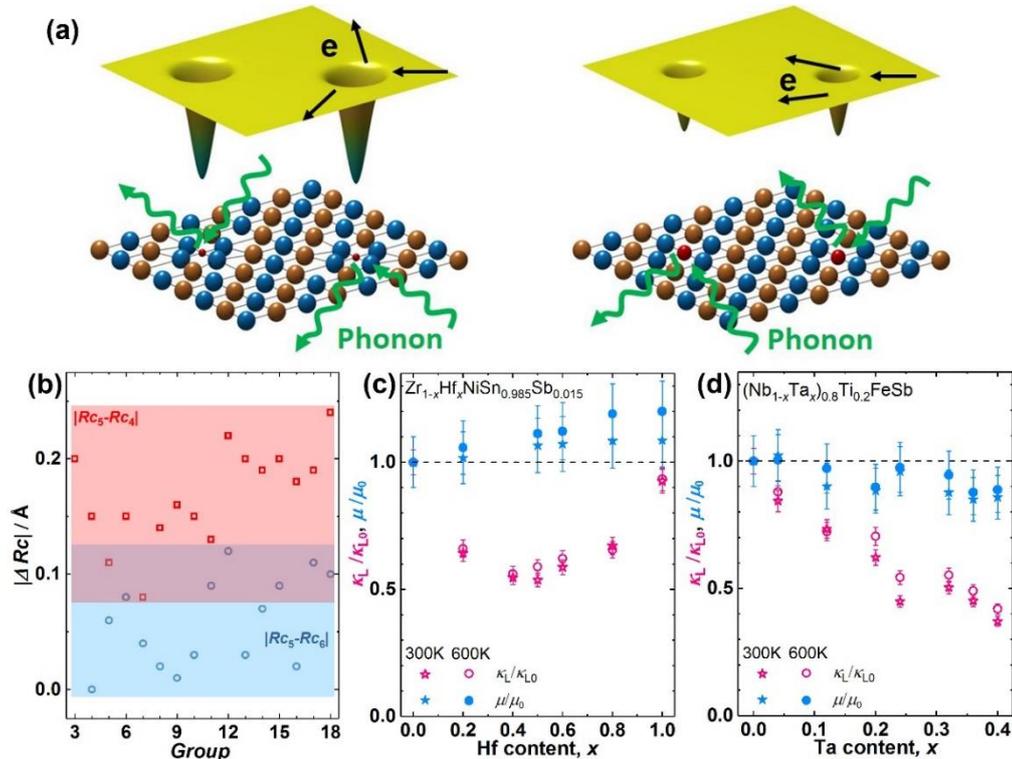


Fig.-1: a) Schematic showing the effect of alloy scattering on the phonon and charge carrier transport. The left panel shows that a larger radius difference between the alloying and host atoms generates stronger perturbation to the periodic potential and thus deteriorates the charge carrier transport. The right panel depicts that a weak effect on charge carrier transport can be realized if the alloying atoms have a similar radius to the host atoms. b) Lanthanide contraction leads to a smaller covalent radius difference between the period-6 elements (post-lanthanides) and their isoelectronic period-5 counterparts. The effects of period-6 elements Hf and Ta on the  $\kappa_L$  and  $\mu$  for c) *n*-type ZrNiSn and d) *p*-type NbFeSb, respectively.

$Y$  are usually transition metals and  $Z$  is a main group element. The adjustable compositions of HH compounds lead to their flexible electronic structure, thus they have various interesting physical properties, such as magnetic, topological insulating, thermoelectric, and superconducting properties. [1] As for TE application, HH compounds have the advantage of good electrical and mechanical properties combined with thermal stability. Further suppression on the lattice thermal conductivity  $\kappa_L$  is the key to increase the  $zT$  and accelerate its application in energy conversion.

Previously, we improved the TE performance of  $p$ -type  $\text{Ti}_{1-x}\text{Hf}_x\text{CoSb}_{0.85}\text{Sn}_{0.15}$  via phase separation and optimization of electrical properties. The presence of an intrinsic microstructure phase separation led to additional boundary scattering at the interfaces and hence to a reduction in the lattice thermal conductivity. [2] We found that fine-tuning the Ti-Hf ratio had a significant impact on  $zT$ . The selection of the optimal electrical properties combined with the lowest thermal conductivity led to a maximum  $zT$  of 1.2 at 710 °C for  $\text{Ti}_{0.25}\text{Hf}_{0.75}\text{CoSb}_{0.85}\text{Sn}_{0.15}$  [3, 4]. For TE applications, thermal stability is an important aspect. We have studied the reliability of the  $\text{Ti}_{1-x}\text{Hf}_x\text{CoSb}_{0.85}\text{Sn}_{0.15}$  compounds under thermal cycling with up to 600 heating and cooling cycles in the temperature range of 100 °C to 700 °C. Micro-structural investigations by SEM and EDX proved that the as-cast sample separated into two HH phases, which were not affected by the consequent annealing process. [4] These results indicated that phase separation is intrinsic and stable, and that it is responsible for the outstanding TE performance.

Based on these previous achievements of  $p$ -type work on  $M\text{CoSb}$ -based HH thermoelectric materials, we are focussed on improving the TE performance of  $n$ -type HH compounds. The results are given below.

### **Lanthanide contraction as a design factor for high performance $n$ -type $M\text{CoSb}$ HH compounds**

Forming solid solutions (*i.e.* alloying), initially proposed to reduce  $\kappa_L$  through enhanced point defect scattering, has been identified as an effective strategy for optimizing the TE performance of a variety of materials, particularly HH compounds. However, the way to reasonably select the alloying elements to maximize the ratio of  $\mu/\kappa_L$ , where  $\mu$  is the charge carrier mobility, remains elusive. A more straightforward question is whether there is an intuitive way to efficiently screen out those reasonable alloying elements to enhance TE performance.

The main problem when forming a solid solution is that the introduced point defects will also scatter the carriers and thus degrade the carrier mobility, which can be represented by the alloy scattering potential  $E_{al}$ . A low  $E_{al}$  indicates weak scattering of carriers and has less effect on carrier mobility. Thus, the question becomes how will a lower  $E_{al}$  be generated when the alloying strategy is used?

According to the electronegativity concept,  $E_{al}$  is positively related to the covalent radius difference between the alloying and host atoms. Therefore, the covalent radius difference, which is more intuitive to some extent, may be viewed as an alternative to  $E_{al}$  in selecting reasonable alloying atoms.

A diagram to show the effect of alloy scattering on electron and phonon transport is illustrated in Fig.-1a. Alloying atoms with a larger mass fluctuation but smaller radius difference with the host atoms is the most reasonable choice when using the alloy scattering strategy to improve TE performance, as the large mass fluctuation could generate strong point defect scattering of phonons, while the small radius differences lead to weak perturbation of the periodic potential.

Lanthanide contraction has an important influence on the post-lanthanides. That is, the radii of the period-6 transition metals are smaller than expected, and are in fact very similar to the radii of the isoelectronic period-5 transition metals (Fig. 1b). Even though the atomic radii are closer between the period-5 elements and the isoelectronic period-6 counterparts, their atomic masses are considerably different. Hence, the basic feature of concurrently having large mass and small radius differences in these two periodic elements provides the possibility of designing optimal compositions to boost TE performance using the alloying strategy. That is, for TE materials containing period-5 elements, selecting the isoelectronic period-6 elements as the alloying atoms could simultaneously induce a strong suppression in  $\kappa_L$  and a small disturbance in  $\mu$ , benefiting from alloy scattering.

HH compounds, with a valence electron count of 18, are typical TE materials containing elements from periods 4-6, which could serve as a model system for studying the effect of lanthanide contraction on the TE properties of solid solutions. Figs. 1c and 1d show that  $\mu$  remains almost unchanged while  $\kappa_L$  displays a significant reduction when alloying the period-6

elements in both  $(\text{Zr}_{1-x}\text{Hf}_x)\text{NiSn}$  and  $(\text{Nb}_{1-x}\text{Ta}_x)\text{FeSb}$  systems, which well justify the unique role of period-6 elements in improving the TE properties of materials containing period-5 elements by largely suppressing the  $\kappa_L$  and maintaining the high carrier mobility  $\mu$ .

ZrCoSb-based HH compounds, which have attracted considerable attention in recent years, are typical  $p$ -type TE materials with a maximum  $zT$  of  $\approx 1.0$ . However, few works are devoted to its  $n$ -type TE properties. The band structure of ZrCoSb shows its lowest conduction band is located at the X point with a band degeneracy of 3, the same as for an  $n$ -type (Zr,Hf) NiSn HH system. This motivated us to study the TE properties HH system. properties of  $n$ -type (Zr,Hf)CoSb by considering lanthanide contraction to design its optimal composition.

A large decrease in the  $\kappa_L$  of ZrCoSb is achieved by alloying Hf while  $\mu$  remains almost unchanged (Fig. 2), as a result of the very close covalent radii of Zr and Hf atoms, and hence a weak alloy scattering of mobility in the alloyed samples. For the Hf/Zr disorder,

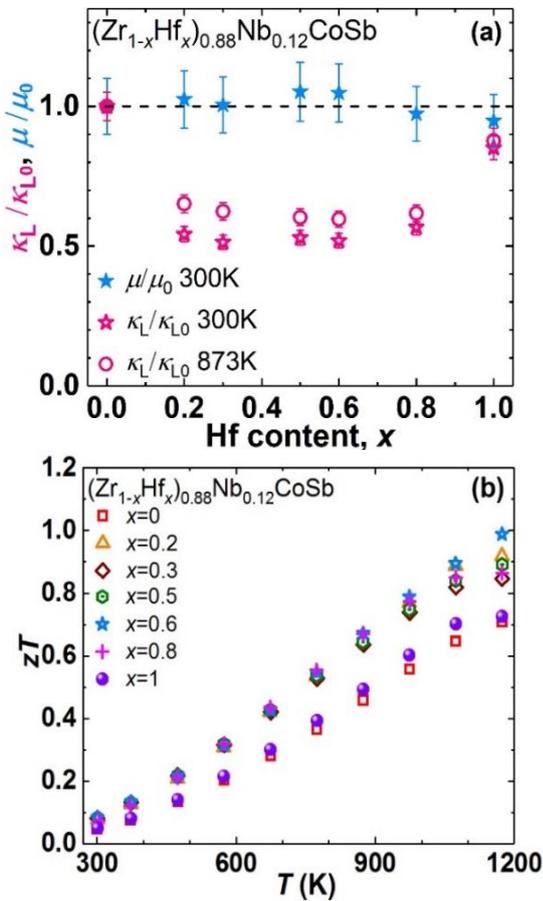


Fig.-2: (a) Effect of Hf alloying on the  $\kappa_L$  and  $\mu$ , and (b) temperature-dependent  $zT$  value for  $n$ -type  $(\text{Zr}_{1-x}\text{Hf}_x)_{0.88}\text{Nb}_{0.12}\text{CoSb}$  system.

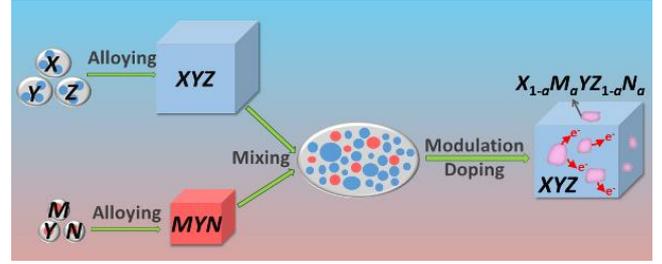


Fig.-3: Schematic of a general process for the realization of modulation doping.

a small  $E_{al}$  is expected according to the electronegativity theory mentioned above. Due to the suppressed  $\kappa_L$  and maintained  $\mu$ , a peak  $zT$  of  $\approx 1.0$  is obtained for  $n$ -type  $(\text{Zr}_{0.4}\text{Hf}_{0.6})_{0.88}\text{Nb}_{0.12}\text{CoSb}$  at 1173 K, about a 40% increase compared with the parent compounds, demonstrating the validity of the proposed strategy. Both  $n$ -type and  $p$ -type TE properties of (Zr,Hf)CoSb-based half-Heusler compounds now render this system very promising for practical applications. [5]

### Enhancing TE performance of $n$ -type TiNiSn via modulation doping and strain field fluctuations

Modulation doping has recently been introduced into the TE field to enhance the electrical conductivity and thus the power factor of TE materials. Fig. 3 presents a general realization of modulation doping in a half-Heusler system. Half-metallic MnNiSb powders dissolve into the TiNiSn matrix and form heavily-doped  $\text{Ti}_{1-x}\text{Mn}_x\text{NiSn}_{1-x}\text{Sb}_x$  phases using a spark plasma sintering process. With an increasing content of MnNiSb, the introduced heavily-doped  $\text{Ti}_{1-x}\text{Mn}_x\text{NiSn}_{1-x}\text{Sb}_x$  phases improved the carrier concentration and maintained the carrier mobility of the system, as can be observed from the Hall effect measurement shown in Fig. 4. Thus, the electrical conductivity and power factor are obviously

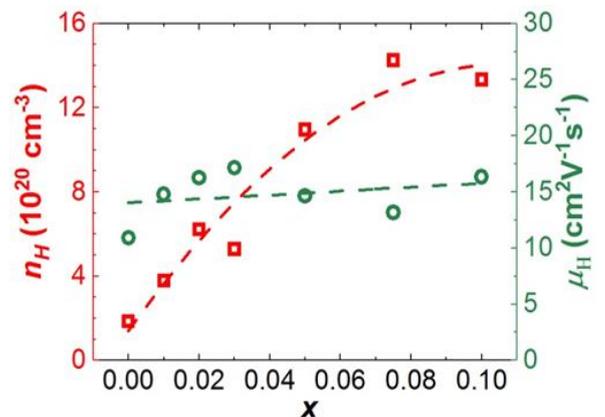


Fig.-4: Carrier concentration and mobility versus  $x$  for the system  $(\text{TiNiSn})_{1-x} + (\text{MnNiSb})_x$ .

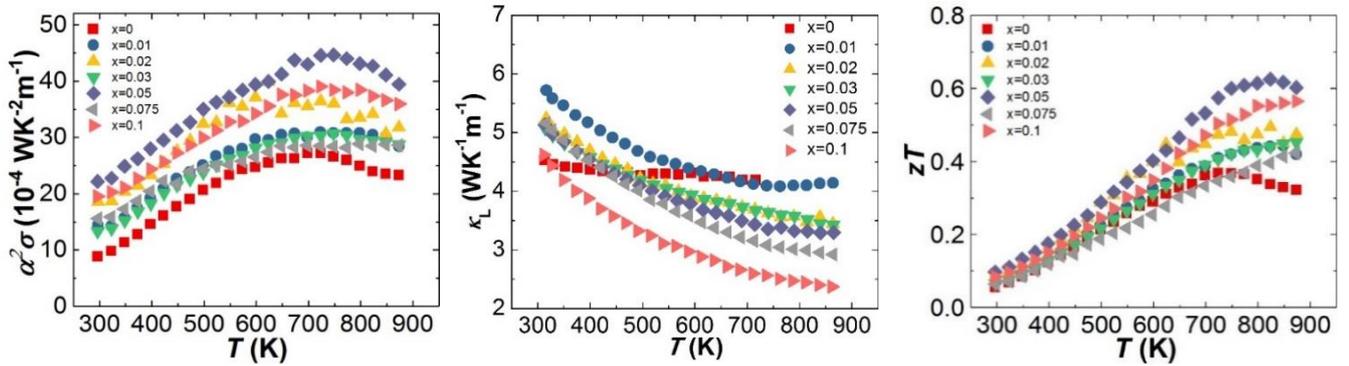


Fig.-5: Power factor, lattice thermal conductivity, and  $zT$  values for the modulation-doped system  $(\text{TiNiSn})_{1-x} + (\text{MnNiSb})_x$ .

enhanced (Fig. 5). Moreover, the modulation-doping phases effectively enhanced the scattering of phonons, leading to reduced lattice thermal conductivity, as shown in Fig. 5. As a result of the simultaneously improved power factor and lattice thermal conductivity, a high  $zT$  of 0.63 is obtained for the system  $(\text{TiNiSn})_{0.95} + (\text{MnNiSb})_{0.05}$  at  $T = 823$  K (Fig. 5). [6]

Point defect scattering, which could induce mass and strain field fluctuations in the host lattice, has been successfully employed in suppressing the lattice thermal conductivity of TE materials. Here, isoelectronic substitutions of Si and Ge on the Sn site were used to reduce the lattice thermal conductivity of TiNiSn. Moreover, we found that Ge substitution has no obvious effect on the electrical properties, whereas Si substitution lowered the power factor. Thus, an improved  $zT$  of 0.48 at 740 K was obtained for the Ge-substituted  $\text{TiNiSn}_{0.975}\text{Ge}_{0.025}$  compound. In order to investigate the dominating fluctuation on the reduction of lattice thermal conductivity in Ge-substituted TiNiSn, we calculated the disorder scattering parameters based on the Klemens and Callaway model. It was found that the strain field fluctuation disorder parameter  $\Gamma_s$  was much larger than the mass fluctuation disorder parameter  $\Gamma_m$ , indicating that the enhanced strain field fluctuation predominantly contributes to the reduced lattice thermal conductivity and consequently improved the TE performance in the Ge-substituted TiNiSn compound. [7]

## Conclusions

High-performance  $\text{MCoSb}$ - and  $\text{MNiSn}$ -based HH thermoelectric materials have been developed via multiple effective strategies. We successfully established  $\text{MCoSb}$  as the first HH system with matching  $p$ -type and  $n$ -type thermoelectric performances. Our results demonstrate a realistic potential of this HH system for thermoelectric energy conversion.

## External Cooperation Partners

B. Balke (Stuttgart University, Germany); G. J. Snyder (Northwestern University, USA); T. Zhu, X. Zhao (Zhejiang University, China)

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