

Thermoelectric Properties Study of ZrCoSb-Based Medium- and High-Entropy Half-Heusler Alloys

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ABSTRACT: As a novel design concept, the design idea of medium- and high-entropy alloy has been successfully applied in various TE systems, which provides a new path for the further development of TE materials. However, it is absent of systematic research on the design and TE performance regulation of medium- and high-entropy HH alloy. Moreover, the research on the TE transport mechanism is relatively shallow, and the mapping relationships between configuration entropy and key TE parameters such as electrical conductivity, Seebeck coefficient, power factor, lattice thermal conductivity, thermal conductivity, and peak ZT are fuzzy. Therefore, based on the iterative design concept among configurational entropy, chemical composition, microstructure, and transport properties, three N-type ZrCoSb-based medium- and high-entropy HH alloys were designed and prepared via multi-site alloying, Zr-site high configurational entropy, and analogous triple crystal structure design strategies. The effects of configurational entropy, V, Nb, Ta, and Ni donor-doping elements on the electrical transport mechanism are elucidated by band structure theory calculation and single parabolic band model. The corresponding phonon transport mechanism is revealed by combining in situ Raman spectroscopy, spherical aberration-corrected transmission electron microscope, with sound velocity, Grüneisen parameter, and other intrinsic physical parameters.

Keywords: Entropy engineering; Triple half-Heusler alloys; Low thermal conductivity

1 Introduction

Thermoelectric performance is directly related to the figure of merit (ZT), $ZT = S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature. A lower κ or higher power factor ($PF = S^2\sigma$) enhances ZT . However, high κ prevents further improvement of ZT in n-type ZrCoSb-based HHs. Consequently, phonon engineering and entropy engineering have focused on reducing κ to improve ZT . First, phonon engineering regulates the multiscale microstructure for reducing lattice thermal conductivity (κ_L) by scattering phonons of different frequencies. For instance, owing to differences in the mass and atomic radius between Zr and Hf, the room temperature κ of n-type ZrCo_{0.9}Ni_{0.1}Sb half-

Heusler (HH) compound was $\sim 12 \text{ W m}^{-1}\text{K}^{-1}$, whereas that of Zr_{0.5}Hf_{0.5}Co_{0.9}Ni_{0.1}Sb HH compound was only $\sim 5.5 \text{ W m}^{-1}\text{K}^{-1}$ [1]. In p-type Zr_{1-x}Hf_xCoSb_{0.9}Sn_{0.1} HH compound, Hf substitution considerably reduced phonon mean free path compared to the average crystallite size, affording a very low thermal conductivity of $\sim 2.2 \text{ W m}^{-1}\text{K}^{-1}$ at 873 K [2]. Besides, the decrease in κ was attributed to the Hf-Ti dual-doping in the FeVSb HH compound by El-Khouly et al. [3]. Second, entropy engineering usually comprises five or more elements with nearly equimolar ratios of 5%–35%. The high mixing entropy, chemical complexity, and large differences in atomic sizes cause severe lattice distortion and high-temperature stability for medium- and high-entropy HHs. Previously, Yan et al. realized a κ_L of $\sim 2.5 \text{ W m}^{-1}\text{K}^{-1}$ at 873 K for Nb_{1-x}M_xFeSb (M = Hf, Zr, Mo, V, and Ti, equimolar) HHs developed via the entropy engineering [4], which shows an excellent potential of the entropy engineering in reducing the κ_L . Finally, it includes double HHs except for the 17 and -19-electron systems in the newly developed HH systems. Anand et al. reported that the Ti₂FeNiSb₂ double HH compound comprising TiNiSb and TiFeSb shows a considerably lower κ_L than the TiCoSb HH compound [5]. Notably, there is an intrinsic low κ_L in double HHs and high-entropy alloys, substantially inspiring our work. We tried to manipulate the Zr-site composition in the n-type ZrCoSb HH compound to develop low thermal conductivity triple HHs via entropy engineering.

In this study, n-type M_{0.8}N_{0.2}CoSb (M = Ti, Zr, Hf; N = V, Ta, equimolar) triple HHs with a low κ_L of $\sim 3.3 \text{ W m}^{-1}\text{K}^{-1}$ at 323 K and $\sim 3.0 \text{ W m}^{-1}\text{K}^{-1}$ at 923 K is prepared to trisect the TiCoSb-, ZrCoSb-, and HfCoSb-based HHs. The study focuses on the successful application of the Zr-site entropy engineering strategy in triple HHs with a low κ_L to optimize ZT .

2 Experimental procedure

High-purity Zr (99.5%), Hf (99.95%), Ti (99.99%), V (99.95%), Ta (99.99%), Co (99.95%), and Sb (99.99%) elements are measured according to the nominal stoichiometric ratios of M_{1-x}N_xCoSb (M = Ti, Zr, Hf; N = V, Ta, equimolar). Ingots of M_{1-x}N_xCoSb triple HHs ($x = 0.05, 0.1, 0.15, \text{ and } 0.2$) are prepared via levitation melting using a levitation melting furnace (LMF, FM-40, Kejing, China), and the broken ingots are ball milled in a planetary

ball mill machine (Pulverisette 4, Fritsch, Germany). 5% excess Sb is added to avoid the loss of Sb during the levitation melting process. The ball-milled powders are sintered at 1173 K for 2 min at 50 MPa using an SPS furnace (SPS, SPS-30, Chen Hua, China).

3 Result and discussion

Fig. 1 shows the temperature-dependent thermal performance of medium-entropy triple HHs. As shown in Fig. 1(a), the thermal diffusivity decreases approximately linearly with the increasing temperature. The entropy engineering indicates a sharp decrease in the thermal diffusion coefficient at 323 K from 4.95 mm² S⁻¹ for the ZrCoSb HH compound to 1.49 mm² S⁻¹ for the M_{0.8}N_{0.2}CoSb triple HH compound. C_p first increases and becomes stable with the increasing temperature in Fig. 1(b). The overall trend of C_p is downward with the increasing doping content, which may be attributed to the increasing average atomic mass of M_{1-x}N_xCoSb triple HHs. Fig. 1(c) demonstrates the decrease in κ for the ZrCoSb HH compound with the increasing temperature. The κ of the ZrCoSb HH compound is higher than that of triple HHs over the studied temperature range. Fig. 1(d) shows that the κ_L is determined by subtracting the electronic contribution ($\kappa_e=L\sigma T$) from κ , where the Lorentz factor (L) is derived from the single parabolic band model. Furthermore, the increasing doping content decreases the κ_L gradually. For instance, the κ_L of the ZrCoSb HH compound decreases from 12.6 Wm⁻¹K⁻¹ at 323 K to 7.5 Wm⁻¹K⁻¹ at 923 K and the κ_L of M_{0.95}N_{0.05}CoSb triple HH compound decreases from 4.0 Wm⁻¹K⁻¹ at 323 K to 3.6 Wm⁻¹K⁻¹ at 923 K. The obtained results are attributed to entropy engineering, i.e., the strong lattice distortion is beneficial to enhance the scattering of phonons. Moreover, the difference in atomic radius and relative atomic mass causes the local mass and stress field fluctuations, further enhancing the alloy scattering for phonons [6]. Although the κ_e increases with the increasing carrier concentration, the decrease in κ_L caused by lattice distortion offsets the increase in κ_e caused by carrier concentration. Therefore, the κ of M_{0.8}N_{0.2}CoSb triple HH compound decreases by 71.4% at 323 K and 50.7% at 923 K.

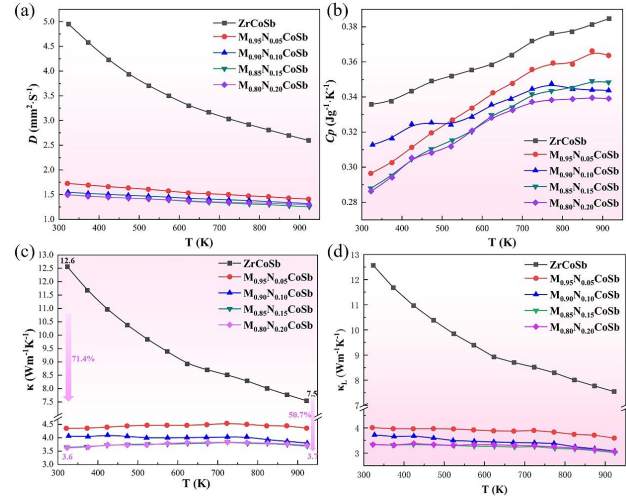


Fig. 1. Temperature-dependent thermal performance of medium-entropy triple HHs: (a) Thermal diffusion coefficient, (b) C_p, (c) κ , (d) κ_L .

4 Conclusion

In summary, this study proposes a new concept (triple HHs) for designing high-performance HHs. Compared with the ZrCoSb HH compound, the κ of the M_{0.9}N_{0.1}CoSb triple HH compound decreases by 67.5% at 323 K and 49.3% at 923 K. The results obtained from this study demonstrate that Zr-site entropy engineering holds great promise for lowering κ_L .

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