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Full Length Article

## A nanocomposite approach for enhancement of thermoelectric performance in Hafnium-free Half-Heuslers

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## ABSTRACT

The interest in developing highly efficient Hf-free Half-Heusler (HH) thermoelectric (TE) materials is rejuvenated by the growing concerns on their cost and scalability. Despite being the most expensive element among other HH constituents, Hf has remained an essential ingredient for reducing the intrinsically high lattice thermal conductivity normally observed in HH alloys. This work demonstrates a nanocomposite approach as an effective paradigm for enhancing the thermoelectric figure-of-merit (ZT) in Hf-free HH alloys, which otherwise presently is far below unity. The optimized *n*-type (ZrNiSn)<sub>1-x</sub>(ZnO)<sub>x</sub> HH compositions exhibit a state-of-the-art ZT ~ 1.0 at 873 K. The synthesised HH nanocomposites, comprising of uniformly-dispersed semiconducting ZnO nano-inclusions and in-situ formed insulating ZrO<sub>2</sub> precipitates within the ZrNiSn HH matrix were studied for temperature dependent TE properties. These multi-dimensional secondary phases in the HH matrix act as additional scattering centres for heat-carrying phonons and energy barriers for energy filtering of low-energy and low-mobility carriers, thus simultaneously reducing the thermal conductivity and elevating the power factor. The synergistic scattering of phonons and energy filtering of electrons results in a ZT ~ 1.0 at 873 K for optimised (ZrNiSn)<sub>1-x</sub>(ZnO)<sub>x</sub> HH nanocomposite, which corresponds to ~70% enhancement over its pristine *n*-type ZrNiSn HH counterpart. The present work demonstrates exciting possibilities for similar HH systems that feature enhanced thermoelectric performance via. the nano-composite approach.

## 1. Introduction

Half-Heusler (HH) materials are of great interest for thermoelectric (TE) applications in mid-temperature regime owing to their environmentally-benign and earth-abundant compositions, with excellent mechanical strength and high-temperature stability [1–3]. Despite such interest, the inherently high lattice thermal conductivity observed in HH limits their TE figure-of-merit (ZT), which still remains significantly lower in comparison to the state-of-the-art TE materials [4–8]. Among *n*-type HH TE materials, MNiSn (M = Ti, Zr, Hf), with 18 valence electron count per unit cell and a narrow energy band gap has been widely studied and were found to exhibit unique and tunable electrical transport [9,10]. In recent years, high ZT ~ 1.0 has been realized for *n*-type HH, mainly by grain size reduction and extensive incorporation of Hf [11–15]. The ineffectiveness of other substituents in reducing the inherently high thermal conductivity of HH, as well as high prices and toxicity associated with use of Hf, are all major bottlenecks for commercial usability of HH in thermoelectric applications. Efforts aimed at

Hf reduction have achieved only minor success, and ZT still remains far below unity in Hf-free HH alloys [16,17].

Scalable methodology for synthesizing high performance HH based TE material in large quantities at low cost is a necessity for practical applicability of HH in TE devices. Several strategies have been investigated to introduce additional scattering mechanism that can significantly lower the thermal conductivity in HH without affecting the electrical transport properties. Such strategies include fabrication of substituted HH [14,18–20], intrinsically phase separated HH [21–23], nanostructured HH [13,15,24] and inclusion-dispersed HH nano-composites [25–29]. Among these strategies, nanostructuring, inculcated in various forms, remains the most effective route for thermal conductivity reduction. However, by nanostructuring induced grain boundary scattering, phonons with short range mean free paths (MFPs) is mostly scattered, while phonons with long MFPs, still remain largely unaffected. In this context, inclusion-dispersed HH composites enable significant enhancement in the phonon scattering strength, but the electrical transport is also affected, depending on whether the inclusion is conductive or

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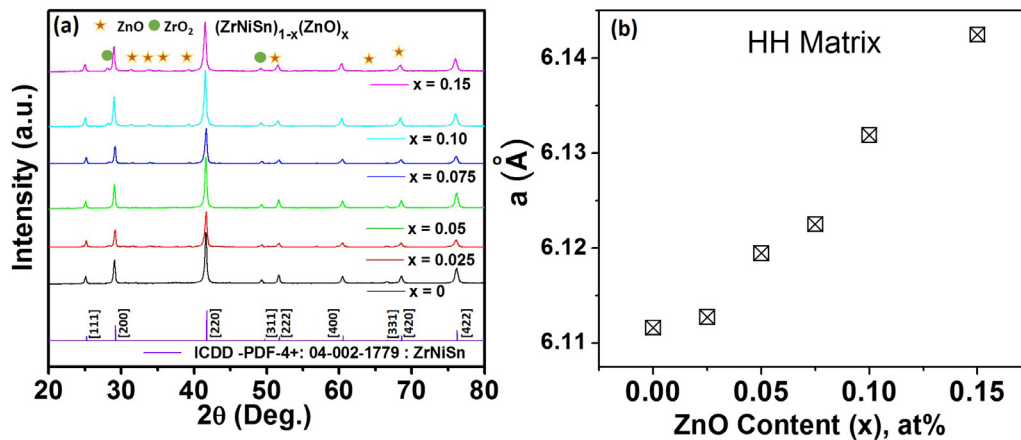


Fig. 1. (a) X-ray powder diffraction patterns and (b) the unit cell lattice parameters of the HH matrix with increasing ZnO content ( $x$ ); of  $\text{ZrNiSn}_{1-x}\text{ZnO}_x$  ( $x = 0-0.15$ ).

insulating. For improved thermoelectric performance, incorporation of insulation or conducting nanoparticles has been well documented as an efficient top-down approach for modulating the electrical and thermal transport properties. Such nanoparticles included  $\text{ZrO}_2$  [25,29,30],  $\text{NiO}$  [26],  $\text{InSb}$  [27] and more recently  $\text{HfO}_2$  [28]. With the aim of improving the TE performance by synergistically tuning the electrical and thermal transport in HH materials, the addition of a semiconducting secondary phase seemed a worthy proposition. Such semiconducting inclusions could bring remarkable phonon scattering and could simultaneously improve the charge carrier transport.

In the current study, Half-Heusler based  $(\text{ZrNiSn})_{1-x}(\text{ZnO})_x$  ( $x = 0-0.15$ ) compositions were fabricated by uniform dispersion of semiconducting ZnO nano-inclusions in arc-melted  $\text{ZrNiSn}$  HH matrix followed by rapid consolidation employing spark plasma sintering (SPS), in an attempt to improve the ZT. During high temperature sintering, growth of in-situ  $\text{ZrO}_2$  precipitates of meso-scale sizes at oxygen defect sites of ZnO was observed. This contributes additionally to increasing the phonon scattering strength. The synthesized HH nanocomposites were found to favourably tune the TE transport, resulting in maximum  $\text{ZT} \sim 1.0$  at 873 K for an optimised composition of  $x = 0.05-0.075$  in  $(\text{ZrNiSn})_{1-x}(\text{ZnO})_x$  nano-composite, which is significantly higher when compared to Hf-free HH alloys [16,17]. In addition, high stability of the optimised nanocomposites at higher temperature and low cost of ZnO and other constituents indicates the wider possibility of Hf elimination and cost-effective scale up.

## 2. Experimental details

The ingots (~5 g) with nominal composition  $\text{ZrNiSn}$  were synthesized by arc melting the stoichiometric amount of Zr (Foil, 99.97%), Ni (powder, 99.97%) and Sn (shots, 99.98%) under an argon atmosphere. The ingots were re-melted several times to ensure sample homogeneity and subsequently pulverized using a mortar and pestle. Commercially available ZnO powder (200 nm), was pre-milled using high energy mechanical ball milling (HEBM, Fritsch, Pulverisette-4) carried out in argon atmosphere at 250 rpm for 20 h with ball-to-powder weight ratio of 20:1. The arc-melted HH alloy was then blended with pre-milled ZnO nano-powder (~30 nm) using HEBM at 300 rpm for 5 min for homogeneous mixing with ball-to-powder weight ratio of 20:1. For both pre-milling process of ZnO and blending process between ZnO and arc-melted HH alloys, the grinding jars (250 ml) and balls (diameter – 5 mm) of the HEBM were used which are made of hardened stainless steel. The blended powder was then loaded into the graphite die (inner diameter 12.7 mm) and high temperature sintered by spark plasma sintering (Dr. Sinter; SPS Syntex, 725) at 1473 K, under 50 MPa in a vacuum (2–4 Pa) to obtained bulk dense pellets. The surface of the sintered sam-

ples was polished to remove contamination. The phase purity and the microstructure were characterized by XRD (XRD; Rigaku), Field Emission Scanning electron microscopy (FESEM; Zeiss, Supra 40VP), and High resolution transmission electron microscopy (HRTEM model: Tecnai G2F30 STWIN operated at the electron accelerating voltage of 300 kV).

The density, as determined by the Archimedes principle, was found to be  $\sim 98 \pm 1\%$  of the theoretical density for all the synthesized HH alloys. The Seebeck coefficient and the electrical resistivity measurements were made employing commercial equipment (ULVAC; ZEM3). The thermal conductivity was obtained from the product of the measured density, the thermal diffusivity from laser flash technique (Laser Flash Analyzer; Lineseis, LFA 1000) and the specific heat from differential scanning calorimeter (Netzsch; DSC 404 F3). Density ( $\rho$ ) was obtained using an Archimedes method (Mettler Toledo; 822e). The carrier concentration and mobility were determined using Hall Effect Measurement System (HEMS, Nano-magnetics), under a magnetic field of 0.5T. The accuracies in transport measurement are:  $\pm 6\%$  for thermal diffusivity,  $\pm 7\%$  for electrical conductivity,  $\pm 7\%$  for Seebeck coefficient,  $\pm 5\%$  for specific heat and  $\pm 0.5\%$  for density.

## 3. Results and discussions

### 3.1. Phase, morphology, structure and elemental composition

Fig. 1(a) shows the XRD patterns of the synthesised pristine  $\text{ZrNiSn}$  and  $(\text{ZrNiSn})_{1-x}(\text{ZnO})_x$  ( $x = 0.025-0.15$ ) HH nanocomposites samples with varying concentration of ZnO nanoparticles. The XRD clearly suggests  $\text{ZrNiSn}$  as the major phase along with peaks corresponding to the ZnO as the minor phase. However, the XRD also shows the presence of an additional  $\text{ZrO}_2$  phase, especially at higher ZnO concentrations. The origin of this phase, which is formed in-situ during the high temperature sintering, is due to the inherent oxygen defects in ZnO [31] which cause the oxidation of Zr into  $\text{ZrO}_2$  during SPS at high temperature. The preference of Zr over other available Ni and Sn for oxide formation can be understood in terms of the electro-positivity of Zr in comparison to Ni and Sn [10,28]. The formation mechanism may be explained by the intrinsically semiconducting nature of ZnO and the existence of defects i.e. vacancies, interstitials, and anti-sites of Zn and O. These native point defects in ZnO exist in donor and acceptor form. The Zn interstitial ( $\text{Zn}_i$ ), O vacancy ( $\text{O}_v$ ) and Zn anti-site are donor-type defects leading to  $n$ -type doping. Whereas, the Zn vacancy ( $\text{Zn}_v$ ), O interstitial ( $\text{O}_i$ ), and O anti-site are acceptor-type defects which leads to  $p$ -type doping. In  $n$ -type ZnO,  $\text{Zn}_i$  under thermal equilibrium are in abundance owing to their relatively low formation enthalpy, while Zn anti-site can be regarded as a complex of an  $\text{O}_v$  and a  $\text{Zn}_i$ . Among acceptor-type defects,  $\text{Zn}_v$  is associated with high formation enthalpy and usually do not appear.

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