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Significant *ZT* enhancement in p-type Ti(Co,Fe)Sb–InSb nanocomposites via a synergistic high-mobility electron injection, energy-filtering and boundary-scattering approach

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Abstract

It has been demonstrated that InSb nanoinclusions, which are formed in situ, can simultaneously improve all three individual thermoelectric properties of the n-type half-Heusler compound (Ti,Zr,Hf)(Co,Ni)Sb (Xie WJ, He J, Zhu S, Su XL, Wang SY, Holgate T, et al. Acta Mater 2010;58:4795). In the present work, the same approach is adopted to the p-type half-Heusler compound Ti(Co,Fe)Sb. The results of resistivity, Seebeck coefficient, thermal conductivity and Hall coefficient measurements indicate that the combined high-mobility electron injection, low energy electron filtering and boundary scattering, again, lead to a simultaneous improvement in all three individual thermoelectric properties: enhanced Seebeck coefficient and electrical conductivity as well as reduced lattice thermal conductivity. A figure of merit of $ZT \approx 0.33$ was attained at 900 K for the sample containing 1.0 at.% InSb nanoinclusions, a ~450% improvement over the nanoinclusion-free sample. This represents a rare case that the same nanostructuring approach works successfully for both p-type and n-type thermoelectric materials of the same class, hence pointing to a promising materials design route for higher-performance half-Heusler materials in the future and hopefully will realize similar improvement in thermoelectric devices based on such half-Heusler alloys.

Keywords: Thermoelectric; Half-Heusler; Nanocomposites

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1. Introduction

Thermoelectricity is the simplest technology applicable to the direct conversion of waste heat into electricity in an environmentally friendly way. A practical thermoelectric (TE) device consists of legs each made of high dimensionless figure of merit (ZT) n-type or p-type material, where $ZT = \alpha^2 \sigma T/\kappa$, α is the Seebeck coefficient, σ the electrical conductivity, κ the thermal conductivity, and T the absolute temperature. The thermal conductivity is composed of two parts: one due to the charge carriers (κ_e) and one due to the lattice (κ_L); $\kappa = \kappa_e + \kappa_L$. Though there is no known upper limit for ZT theoretically, the state-of-the-art TE materials have a $ZT \approx 1$–2 because of the interdependence of α, σ and κ. A ZT value of ~1 has been regarded as the benchmark for practical TE materials. Among the wide variety of TE materials, half-Heusler (HH) compounds have attracted considerable interest because of their promising ZT values between 600 K and 1000 K, which happens to also be the temperature range

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of most industrial waste heat sources, and therefore they are quite suitable for TE energy harvest in this temperature range [1–4]. HH compounds crystallize in the cubic MgAgAs-type structure featured by four interpenetrating face-centered-cubic (fcc) sublattices, allowing for doping on each of the three occupied fcc sublattices in order to manipulate each of the individual TE properties [5–9]. In n-type MNiSn (M = Ti, Zr and Hf) based HH compounds, for example, the carrier concentration can be tuned via doping the Sn site, while the lattice thermal conductivity can be reduced via doping the M and/or Ni sites, thereby doping induced point defects, mass fluctuations and strain field fluctuations in order to effectively scatter short- and mid-wavelength heat-carrying phonons. *ZT* values of ~1.0 at 725 K, ~0.81 at 1025 K, and ~1.0 at 1000 K have been reported for n-type $(Ti_{0.37}Zr_{0.37}Hf_{0.26})NiSn$ [10], $(Hf_{0.75}Zr_{0.25})Ni(Sn_{0.975}Sb_{0.025})$ [11] and $(Hf_{0.6}Zr_{0.4})Ni(Sn_{0.98}Sb_{0.02})$ [12], respectively.

A practical HH compound-based TE device requires not only high *ZT* n-type and p-type materials, but also that the n-type and p-type materials have similar compositions and thus similar thermal expansion and mechanical properties. However, the *ZT* values of p-type HH compounds have previously been inferior to those of n-type counterparts because doping can only optimize the TE properties to a fairly limited degree. For example, p-type MCoSb HH compounds can be prepared via doping the Co and/or Sb site, e.g. $TiCo_{0.85}Fe_{0.15}Sb$ [13], $Zr_{0.5}Hf_{0.5}CoSb_{0.8}Sn_{0.2}$ [14] and $Zr_{0.5}Hf_{0.5}Co_{0.3}Ir_{0.7}Sb_{0.99}Sn_{0.1}$ [15]. The highest *ZT* of ~0.5 at 973 K was reported for p-type $Zr_{0.5}Hf_{0.5}CoSb_{0.8}Sn_{0.2}$ [14].

Further improvement of the TE properties of p-type HH compounds is thus dependent upon new materials design approaches other than simple substitutional doping. To this end, the nanostructuring process is a promising approach, since nanostructuring has become a new paradigm approach to improving the *ZT* of bulk TE materials over the past several years. In a nanostructured bulk TE material (i.e. nanocomposite), the lattice thermal conductivity can be depressed by phonon scattering due to the numerous interfaces, whereas the Seebeck coefficient can be increased without significantly sacrificing the electrical conductivity, by an energy-filtering process on the interfaces [16–18]. Implementation of the nanostructuring process in HH compounds has indeed led to enhancement of the *ZT* in many cases, which has been predominantly due to a significant reduction in the lattice thermal conductivity [19–22]. Until recently, Xie et al. [23] and Makongo et al. [24] reported that the nanostructuring process simultaneously enhanced the Seebeck coefficient and electrical conductivity, and depressed the thermal conductivity in n-type (Ti,Zr,Hf)(Co,Ni)Sb–InSb and $Zr_{0.25}Hf_{0.75}NiSn$–$Zr_{0.25}Hf_{0.75}Ni_2Sn$ nanocomposites, respectively. An immediate question arises as to whether one can apply the same nanostructuring process in p-type HH compounds, and whether a positive outcome can be realized.

Reported herein is an inductive-melting-spark-plasma-sintering synthesis process of p-type Ti(CoFe)Sb-based nanocomposites in which InSb nanoinclusions were formed in situ during the synthesis process. It was confirmed experimentally that this process results in in situ formed InSb nanoinclusions, which in effect simultaneously enhanced the Seebeck coefficient and electrical conductivity while reducing the lattice thermal conductivity. These changes are attributed to the combined nanoinclusion-induced high-mobility electron injection, energy filtering and boundary scattering. In view of previous work on the n-type HH compounds [23], the current study sheds new light on employing the nanostructuring process in order to enhance the electrical properties of HH compounds and other classes of TE materials.

2. Experimental procedures

Ingots of $TiCo_{0.85}Fe_{0.15}Sb$ alloys with nominal ratio $x = 0$, 0.7, 1, 1.5 and 3 at.% of InSb nanoinclusions that formed in situ were prepared by inductively melting appropriate amounts of single elements in an argon atmosphere. To compensate for the evaporation of Sb, a 5 at.% excess of Sb powders was added to the starting materials. All the ingots were melted three times, and then annealed at 1173 K for a week to ensure sample homogeneity. The ingots were then pulverized and sintered using a spark plasma sintering (SPS) technique at 1373 K for 8 min under a pressure of 45 MPa in order to obtain highly densified bulk samples.

The density (*d*) of SPSed bulk samples was determined by the Archimedes method and found to be at least 97% of the theoretical density. The phase structure, chemical composition and micro-morphology of the bulk samples were analyzed by means of X-ray diffraction (XRD) (PANalytical X'Pert Pro® X-ray diffractometer), electron probe microanalysis (JXA-8230®), and field emission scanning electron microscopy (SEM; Hitachi S-4800®) with energy-dispersive X-ray spectroscopy (EDS). The bulk samples were cut into rectangular bars with dimensions $\sim 2 \times 2 \times 10\ mm^3$ for electrical conductivity and Seebeck coefficient measurements on a ZEM-3 system (Ulvac Riko Inc.) under an inert gas (He) atmosphere from 300 to 900 K. The thermal diffusivity was measured by the laser flash method on a Netzsch LFA457® system. Specific heat was measured by differential scanning calorimetry on a Netzsch DSC-404C® calorimeter. The thermal conductivity κ was then calculated from the thermal diffusivity D, specific heat per unit volume C_p and density d, from the relationship $\kappa = DC_pd$. The electrical conductivity, Seebeck coefficient and thermal conductivity measurements on the same samples were also conducted on custom-designed low-temperature apparatus from 15 to 310 K [25,26]. The low-temperature specific heat data were taken on a Quantum Design® Physical Properties Measurement System (PPMS) from 1.8 K to 300 K. Hall coefficients R_H were measured on a PPMS using a five-probe configuration by sweeping the magnetic field between ±1.5 T from 5 K to 400 K. The effective carrier concentration n and Hall