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A BRIEF REVIEW ON THERMOELECTRIC PERFORMANCE OF HALF HEUSLER ALLOYS

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Abstract

In this article we briefly review on the thermoelectric (TE) performance of the Half–Heusler(HH) alloys. In the recent years HH alloy based TE materials have greatly attracted the research community and shown great improvement in waste heat recovery. They are widely used because of their high TE performance, environmental friendliness, highstability, moderate cost and good mechanical properties.It is well known that TE materials can be made up of either n-type or p-type. Here in we report about the performance of both the materials. Overall it has been noticed that thep-type HH alloys have shown poor thermoelectric performance. In addition, different physical parameters were reviewed.

Introduction

Thermoelectric (TE) materialsis the ability of directly converting heat into electricity and vice versa, which can harvest waste heat and have been gaining intensive attentions for its potential applications in energy conversion technologies. The performance of a thermoelectric material is determined by the dimensionless figure of merit (ZT), defined as $ZT = (S^2\sigma/\kappa)\ T$, where S, σ, κ, and T are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature,respectively. To achieve high conversion efficiency, largeZT value is required, that means high Seebeck coefficient, high electrical conductivity, and lowthermal conductivity are favorable. Recent improvements to increase the TE efficiency is made by reducing the size and dimensionality of TE materials in nanoscale and nanostructured materials due to quantum confinement and nanostructure effect. Enhanced ZT valueshave already been achieved in materials

such as Bi2Te3 based materials which are used for applications near room temperature, lead chalcogenides and skutterudites for middle temperature power generation, and SiGe for high temperatures. Among these materials half-Heusler compounds stand out for its high thermal stability, good mechanical strength, low toxicity, etc.

Half-Heusler materials with the general formula *XYZ* (for example, TiNiSn, ZrCoSb, LiSiAl, etc.) constitute a widely investigated class of semiconductors and intermetallic compoundswhere X and Y are transition metals and Z is a main group element.A series of doped samples were synthesized and studiedby arc-melting the elements to first form ingots, then ball-milling the ingots to obtain finepowders, and finally hot-pressing the fine powder to form bulk samples.HH is used in solar cell applications, transparent conductor applications, piezoelectric applications, spintronic applications, and its topological band-structure properties due to there mid-to-high range from 500 °C to 800 °C temperature power generation applications. The big advantage in the optimisation of thermoelectric properties of HH compounds is the opportunity to dope each of the four sub-lattices individually.

TE performance of n-type HH alloys

For p-as well as n-type materials, peak ZT values in the range of ZT~1 or in case of n-type material even ZT > 1. HHs are complex compounds: MCoSb and MNiSn, where M can be Ti, Zr, Hf, or a combination of two or three of these elements. The compounds form in a cubic crystal structure with an *F4/3m* space group. These phases are semiconductors with an 18 valence electron count (VEC) per unit cell and a narrow energy gap, and the Fermi level is slightly above the top of the valence band. Different approaches have also been adopted to improve the thermoelectric performance of the MNiSn based n-type half-Heuslers. carrier concentrations can be optimized by doping with the adjacent elements such as Sb forSn, Ta for M, and so on . Ternary alloying of M by Hf, Zr, and Ti can reduce the lattice thermal conductivity by introducing point defects scatteringNb has one more valence electron than Hf/Zr so it can increase the carrier concentration for this n-type half-Heusler compound. In fact, Hiroaki Muta*et al.* did Nb doping in ZrNiSn and TiNiSn before and the maximum ZT value of 0.6 was obtainedfor Zr0.98Nb0.02NiSn at 800 K . Most recently, Julia Krez*et al.* reported Nb doping in thephase separated n-type Ti0.3Zr0.35Hf0.35NiSn compound and peak ZT value around 0.7 at 900 K. It is interesting to note that some full-Heusler nanoinclusions are found within the half-Heusler matrix by SEM and TEM analysis, which could also play a positive role in the improvement of the thermoelectric properties.

TE performance of p-type HH alloys

HH Alloys of P-type materials, NbFeSb is a promising TE material which exhibits a high power factor of up to 10 mW m^{-1} K^{-2} at room temperature and *ZT* of 1 at 1000 K by experimental and theoretical studies . The thermoelectric figure of merit (ZT) is given by the equation ZT=S2σT/κ and several theoretical and experimental studies which aim to optimise the thermal conductivity (κ) as well as the Seebeck coefficient (S) and electrical conductivity (σ) ,have been conducted in the past couple of years have a larger potential for band-engineering to improve the thermoelectric properties, as degenerate band extremer allow for an increase in the density of states effective mass. The main research focus was on developing p-type materials based on XIVCoSb. This involved developing strategies for alloying and carrier doping and resulted in zT 1and zT 0.7 at 773 K for the n-types and p-types respectively. Recent advances include the rise of p-type compositions XVFeSb (XV = V, Nb and Ta) and ZrCoBi, each with zT 4-1 at 773 K. It also includes the widespread use of single parabolic band (SPB) and Callaway modelling, coupled to first principles calculations, which have placed understanding of the HH alloy. However, the typical p-type HH compounds, (Zr,Hf)CoSb, have the reproducible highest zT of only ~0.5. Therefore, developing high performance p-type HH compounds is imperative to achieve high efficiency high temperature TE devices based on HH compound.

Discussion *n-type HH alloys*

Half-Heusler ingot was synthesized by arc-melting instoichiometry. To ensure the homogeneity, the ingot was arc-melted under Ar protection at least three times and flipped over every time. Then the alloyed ingot was directly put into a stainless steel jar with grinding balls and ball-milled for 5-9 hours(SPEX 8000M Mixer/Mill).to make them nanopowders. Finally the nanopowders were hot pressed in a graphite die to form bulk samples. The disks of 12.7 mm in diameter and around 2mm in thickness were obtained for measurements. On the other hand, another ingot sample was made by annealing the arc-meltedingot at 700 °C for 60 hours for comparison with the ball-milled nanostructured samples. The volumetric densities of the samples were measured by Archimede's method. The thermal diffusivities of the disks were measured on a laser flash equipment (LFA457, Netzsch). Samples were also cut into about 2 x 2 x 12 mm bars for electrical conductivity and Seebeck coefficientmeasurements on a commercial equipment (ZEM3, Ulvac).

Hall measurements were performed on a Physical Property Measurement System (Quantum design) to get the carrier concentrations of these samples at room temperature.

The Hall mobility μH is calculated by the equation μH = σ / (nHe), where σ, nH, and $e$are electrical conductivity, Hall carrier concentration, and elementary charge, respectively. The samples were also characterized by XRD (X'pertPROPANalyticaldiffractometer with a Cu Ka radiation source), SEM (LEO

1525), and TEM (JEOL 2100F) to study their crystallinity and grain size. The measurement errors were estimated to be 3% for electrical conductivity, 5% for Seebeck coefficient, 3% for thermal diffusivity, and 3% for specific heat capacity, which results in an uncertainty of 11% for ZT. For better readability, all the figures are plotted without error bars.[For example:VCoSb was synthesized by arc-melting method using vanadium pieces (99.7%, Alfa Aesar), cobalt pieces (99.9+%, Alfa Aesar), and antimony rod (99.8%, Alfa Aesar)]

Discussion of p-*type HH alloys:*

We start following the procedure of using BoltzTraP to obtain the electronic properties of the material and then solve the phonon BTE using ShengBTE. The higher atomic mass of (compared to Nb) increases the scattering strength is doped , which reduces the lattice thermal conductivity of the compound. At the same time, p-type charge carries exhibit higher mobility and relaxation time, which increases the power factor. Here we calculate κlatt by solving the Boltzmann transport equation andsubsequently including the contributions of grain boundaries, point defects and electron–phonon interaction. A detailed study of the carrier concentration and temperature dependance of the Seebeck coefficient (S), Power factor, lattice and electronic thermal conductivity and hence the figure of merit (ZT) is carried out. The chemical stability, electronic structure, mechanical stability and TE properties for the compounds simulations are performed by using density functional theory (DFT) implemented within Vienna simulation package (VASP) with a projected augmented-wave basis.We used the Generalized Gradient Approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) scheme for the electronic exchange-correlation functional. Tetrahedron method with Blochl corrections were used to calculate the Density of states (DOS). This uses Maximally Localised Wannier Function (MLWF) basis set by interpolating first principle plane wave results to determine the Seebeck coeffcient (S), electrical conductivity and the electronic part of the thermal conductivity using semi classical Boltzmann transport theory .To calculate the lattice contribution to the thermal conductivity we use Boltzmann transport theory for phonons as implemented.It is expected that Sn&Sb will lead to an increase in the electrical conductivity of the samples due to the increase in hole concentration (p) and/or mobility (μ). Such high grain boundary density is expected to increase phonon scattering leading to a large reduction in the lattice thermal conductivity of the compositions.). To check the purity of the synthesized materials, powder X-ray diffraction (PXRD) patterns were measured using a PANalytical X'pert Pro X-ray diffraction system equipped with a curved graphite crystal monochromator.

Conclusions

In conclusion, half-Heusler compounds with VEC of 19 are successfully synthesized by arc-melting, ball-milling and hot-pressing. Despite the high carrier concentration due to the VEC
of 19, the electrical conductivity is not very high since the mobility is low. By the nanostructuring approach, the thermal conductivity can be reduced and the power factor can be improved simultaneously compared to the ingot. Lower hot-pressingtemperature results in some porosity. A peak power factor of 25 μW cm-1 K-2 and ZT of about 0.5 are achieved at 700 °C for all the nanostructured samples. A cost-effective ball-milling and hot-pressing technique has been applied to n-type HHs to improve the *ZT* value. This enhancement in *ZT* mainly results from reduction in thermal conductivity dueto the increased phonon scattering at the grain boundariesof nanostructures, and optimization of carrier contributionleading to lower electronic thermal conductivity. Further *ZT* improvement would be possible if the grains were less than100 nm in size.In the p-types, there is more diversity and more opportunity for bandstructure engineering. Alloying has been widely explored to reduce thelattice thermal conductivity but can also lead to substantially different bandstructures. The electronic structures of the half-Heusler alloys are unique because of the very low effective masses of the p type carriers.The latter compound is probably at the edge of a transitionbetween the indirect and direct band gap, which probably could be tuned by application of strain.Most importantly, ScPtSb exhibits particularly good thermoelectric performance with the power factor reaching 4–6 mWK−2m−1 at high temperatures. For all the ScMSb phases studied, the thermoelectric characteristics can be tuned by intentional doping of charge carriers in arange from 1019 to 1021 cm−3.The results obtained in this work indicate that using the deformation potential approximation for the carrier relaxation time is necessary for adequate discussion of the ab initio calculated transport properties of half-Heusler alloys.

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