Synthesis and Thermoelectric Properties of Sn-doped ZrCoBi-based Half-Heusler Compounds (Postprint)

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Abstract

To investigate the effects of Sn doping on the structure and thermoelectric properties of ZrCoBi compounds, a series of ZrCoBi1-xSnx (x=0, 0.05, 0.10, 0.15, 0.20, 0.25) samples with different doping concentrations were prepared by induction melting combined with spark plasma sintering, and their phase structure and thermoelectric properties were tested and analyzed. Experimental results demonstrate that the synthesized ZrCoBi-based compounds all exhibit a standard Half-Heusler phase, with the maximum solid solubility of Sn in the ZrCoBi matrix being 20%. At a given temperature, as the Sn doping concentration at the Bi site increases, the electrical conductivity increases, the Seebeck coefficient first increases and then decreases, and the ZT value continuously increases. Through Sn/Bi substitution, the thermal conductivity of ZrCoBi1-xSnx is significantly reduced; near 730 K, the ZrCoBi0.80Sn0.20 sample attains a minimum thermal conductivity value of 2.56 W · cm-1 · K-1. Due to the increased power factor and decreased thermal conductivity, near 730 K, the ZT value increases from 0.39 for the undoped ZrCoBi sample to a maximum of 1.02 for the ZrCoBi0.20Sn0.80 sample. Sn doping introduces acceptor impurities, optimizing the carrier concentration and enhancing both electrical conductivity and power factor. Simultaneously, due to the size and mass differences between Sn and Bi atoms, point defect scattering is enhanced, further reducing the thermal conductivity, thereby overall increasing the ZT value and improving the thermoelectric performance.

Full Text

Abstract

This study investigates the synthesis and thermoelectric properties of Sn-doped ZrCoBi Half-Heusler compounds. $ZrCoBi_1$ Sn samples (x = 0, 0.05, 0.10, 0.15,

0.20, 0.25) were prepared by induction melting combined with spark plasma sintering. Phase structure and thermoelectric properties were systematically characterized. All synthesized compounds exhibited a standard Half-Heusler structure. Sn doping introduced acceptor impurities, optimizing carrier concentration and enhancing electrical conductivity and power factor. The increased atomic size and mass differences between Sn and Bi atoms strengthened point defect scattering, significantly reducing thermal conductivity. The $ZrCoBi_{0\cdot80}Sn_{0\cdot20}$ sample achieved the lowest thermal conductivity, and its ZT value increased from 0.02 for the undoped sample to a maximum of 1.02, representing a substantial improvement in thermoelectric performance.

Introduction

The large-scale utilization of fossil fuels has precipitated a global energy crisis and environmental challenges, necessitating the development of renewable energy technologies for sustainable economic growth. Thermoelectric materials, which enable direct conversion between electrical and thermal energy, show tremendous potential for applications in solid-state cooling and waste heat recovery. The efficiency of thermoelectric materials is quantified by the dimensionless figure of merit ZT = $S^2\sigma T/$, where S is the Seebeck coefficient, σ is electrical conductivity, T is absolute temperature, and is total thermal conductivity (comprising electronic and lattice components). Enhancing ZT requires either increasing the power factor ($S^2\sigma$) or reducing thermal conductivity.

Half-Heusler compounds have attracted considerable attention due to their excellent thermoelectric performance, high mechanical strength, and good thermal stability. However, their relatively high intrinsic thermal conductivity limits ZT values compared to other thermoelectric materials. Among Half-Heusler systems, ZrCoBi exhibits a high power factor due to its high band degeneracy and low lattice thermal conductivity. To overcome the thermal conductivity limitation, researchers have employed strategies including nanocompositing, band engineering, and alloying to enhance phonon scattering across multiple length scales. In this work, we adopt a Sn-doping approach to simultaneously optimize carrier concentration and introduce point defect scattering, thereby improving the overall thermoelectric performance of ZrCoBi.

Experimental Methods

Sample Preparation

$ZrCoBi_1$ Sn compounds (x = 0, 0.05, 0.10, 0.15, 0.20, 0.25) were synthesized using vacuum induction melting, planetary ball milling, and spark plasma sintering. High-purity elemental powders of Zr (99.95%), Co (99.95%), Bi (99.99%), and Sn (99.999%) were weighed according to stoichiometric ratios. The raw materials were loaded into quartz tubes and induction-melted under an inert atmosphere, with the ingot remelted three times to ensure compositional homogeneity. Considering the high vapor pressure of Bi, excess Bi was added to

compensate for melting losses. The resulting ingots were coarse-ground using an agate mortar, then ball-milled in stainless steel jars using a planetary ball mill (QM-3B). The milled powders were consolidated by spark plasma sintering into bulk samples with a diameter of [FIGURE:N] mm and thickness of [FIGURE:N] mm under optimized conditions (sintering temperature: [MATH_0]°C, holding time: [MATH_1] min, heating/cooling rate: [MATH_2]°C/min). The sintered pellets were subsequently annealed in a box furnace at [MATH_3]°C for [MATH_4] hours.

Characterization

Phase structure was analyzed by X-ray diffraction (XRD, Empyrean PIXcel) and field-emission scanning electron microscopy (FE-SEM, Quanta). Electrical transport properties, including electrical conductivity and Seebeck coefficient, were measured using a commercial system (ZEM-3, ULVAC-RIKO) under helium atmosphere. Thermal diffusivity (D) was measured by laser flash analysis (LFA-467HT Hyperflash) under argon atmosphere. Specific heat capacity was determined by differential scanning calorimetry (DSC404, Netzsch). Total thermal conductivity was calculated via = D • C • d, where C is specific heat and d is density measured by the Archimedes method. Hall coefficient measurements were performed at room temperature under magnetic fields from -0.5 T to 0.5 T to determine carrier concentration (n) and Hall mobility ( ).

Results and Discussion

Structural Analysis

XRD patterns of polished $ZrCoBi_1$ Sn samples are shown in [FIGURE:N]. All samples can be indexed to the standard Half-Heusler structure (PDF#51-1225) without detectable secondary phases within the resolution limit, confirming the maximum solid solubility of Sn in the ZrCoBi matrix. The calculated lattice constants gradually decrease with increasing Sn content ([TABLE:N]), consistent with the smaller atomic radius of Sn (0.140 nm) compared to Bi (0.155 nm). This substitution induces lattice distortion in the ZrCoBi host, which enhances alloy scattering. The relative densities of all samples exceed 95%, except for $ZrCoBi_{0·75}Sn_{0·25}$ which shows a slightly lower value, indicating that spark plasma sintering produces highly dense bulk materials.

Electrical Properties

The temperature dependence of electrical conductivity for $ZrCoBi_1$ Sn samples is presented in [FIGURE:N]. The undoped ZrCoBi exhibits intrinsic semiconductor behavior with conductivity increasing slightly with temperature. In contrast, all doped samples show decreasing conductivity with rising temperature, typical of degenerate semiconductors. The conductivity increases monotonically with doping concentration, reaching 0.83$×10^{5}$ S/m for $ZrCoBi_{0·80}Sn_{0·20}$

at room temperature, compared to 0.68$×10^{5}$ S/m for the undoped sample. This enhancement primarily stems from increased carrier concentration via acceptor doping.

[FIGURE:N] displays the Seebeck coefficient as a function of temperature. All samples exhibit positive Seebeck coefficients that increase monotonically with temperature, indicating p-type transport characteristics. Sn doping successfully converts the intrinsic ZrCoBi to p-type conduction. The Seebeck coefficient peaks near [MATH_5]°C for the $ZrCoBi_{0·95}Sn_{0·05}$ sample, then decreases with further doping due to the inverse relationship between Seebeck coefficient and carrier concentration.

The power factor ($S^2\sigma$) versus temperature is plotted in [FIGURE:N]. The undoped ZrCoBi shows a low power factor with a maximum of only [MATH_6] $W \cdot cm^{-1} \cdot K^{-2}$ across the temperature range. Doped samples exhibit significantly enhanced power factors that increase with temperature, peaking around [MATH_7]°C. The power factor improves continuously with doping concentration, reaching a maximum of [MATH_8] $W \cdot cm^{-1} \cdot K^{-2}$ for $ZrCoBi_{0·80}Sn_{0·20}$, reflecting the combined optimization of electrical conductivity and Seebeck coefficient.

Thermal Properties

Thermal diffusivity measurements ([FIGURE:N]) show that all samples exhibit decreasing thermal diffusivity with increasing temperature. The undoped ZrCoBi possesses the highest thermal diffusivity, while Sn-doped samples show progressively lower values. Specifically, $ZrCoBi_{0·80}Sn_{0·20}$ demonstrates the lowest thermal diffusivity, reduced by [MATH_9]% compared to the pristine sample.

Specific heat capacity ([FIGURE:N]) increases with temperature for all compositions due to enhanced lattice vibrations. The heat capacity gradually decreases with Sn doping concentration, consistent with the lighter mass of Sn compared to Bi.

The total thermal conductivity ([FIGURE:N]) decreases with temperature for all samples, mirroring the trend in thermal diffusivity. Sn doping effectively suppresses thermal conductivity through enhanced point defect and alloy scattering. The $ZrCoBi_{0·80}Sn_{0·20}$ sample achieves the lowest thermal conductivity of [MATH_{10}] $W \cdot m^{-1} \cdot K^{-1}$ at [MATH_{11}]°C, representing a 36.9% reduction compared to the undoped sample. This substantial decrease arises from the combined effects of mass and strain field fluctuations introduced by Sn substitution.

Thermoelectric Figure of Merit

The temperature-dependent ZT values are shown in [FIGURE:N]. All samples exhibit increasing ZT with temperature, with Sn-doped samples showing supe-

rior performance. The $ZrCoBi_{0\cdot80}Sn_{0\cdot20}$ sample reaches a maximum ZT of 1.02 at [MATH_{12}]°C, a 162% improvement over the undoped material (ZT = 0.39). This enhancement originates from the synergistic optimization of power factor and thermal conductivity. The results demonstrate that Sn doping is an effective strategy for improving the thermoelectric performance of ZrCoBi Half-Heusler compounds.

Conclusion

Through systematic investigation of Sn-doped ZrCoBi Half-Heusler compounds prepared by induction melting and spark plasma sintering, we have demonstrated that Sn substitution simultaneously optimizes electronic and thermal transport properties. The introduction of acceptor impurities enhances carrier concentration and electrical conductivity, while the atomic size and mass mismatch between Sn and Bi strengthens phonon scattering, significantly reducing lattice thermal conductivity. The $ZrCoBi_{0\cdot80}Sn_{0\cdot20}$ composition achieves a peak ZT of 1.02, representing a substantial improvement over the pristine material. This work provides valuable insights for the design of high-performance Half-Heusler thermoelectric materials through elemental doping strategies.

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Note: Figure translations are in progress. See original paper for figures.