Postprint: Thermoelectric Properties of Nb-doped Lead Telluride Alloys

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Abstract

Bulk Nb-doped Pb1.1Te alloys were prepared via mechanical alloying (MA) and spark plasma sintering (SPS). The electrical resistivity, Seebeck coefficient, and thermal diffusivity were measured in the temperature range of 323-673 K, and the thermoelectric figure of merit was calculated. The results indicate that Nb doping in Pb1.1Te effectively enhances the carrier concentration and optimizes the electrical properties, yielding a power factor for Pb1.03Nb0.07Te that exceeds 20 $\mathrm{mW \cdot cm^{-1} \cdot K^{-2}}$ in the 523-673 K temperature range. Concurrently, the introduction of Nb strengthens phonon scattering and reduces lattice thermal conductivity, resulting in a higher thermoelectric figure of merit. The sample b1.03Nb0.07Te achieves a maximum ZT value of 1.27 at 673 K, which is double that of the matrix material Pb1.1Te.

Full Text

Preamble

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Thermoelectric Properties of Nb-doped Lead Telluride Alloys

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Abstract

Bulk Nb-doped $Pb_{1\cdot1}Te$ alloys were prepared by a combined process of mechanical alloying (MA) and spark plasma sintering (SPS). The electrical resistivity, Seebeck coefficient, and thermal diffusion coefficient were measured in the temperature range of 323-673 K, and the thermoelectric figure of merit was calculated. The results demonstrate that Nb doping in $Pb_{1\cdot1}Te$ effectively increases the carrier concentration and optimizes electrical performance, with $Pb_{1\cdot03}Nb_{0\cdot07}Te$ achieving power factors exceeding 20 mW/(cm · K^2) in the 523-673 K temperature range. Simultaneously, the introduction of Nb enhances phonon scattering and reduces the lattice thermal conductivity, leading to a higher thermoelectric figure of merit. The sample $Pb_{1\cdot03}Nb_{0\cdot07}Te$ exhibits a maximum ZT value of 1.27 at 673 K, which is twice that of the pristine $Pb_{1\cdot1}Te$ matrix.

Keywords: metallic materials, Seebeck coefficient, lattice thermal conductivity, n-type PbTe alloys

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Introduction

Thermoelectric materials are functional materials that enable direct conversion between thermal energy and electrical energy through the motion of charge carriers within solids. With growing concerns over energy shortages and environmental pollution, thermoelectric materials have attracted significant attention as a novel class of energy conversion materials. The theoretical foundation of thermoelectric materials rests on the Seebeck and Peltier effects in semiconductors, with primary applications including thermoelectric power generation and refrigeration, such as radioisotope thermoelectric generators and portable coolers.

The performance of thermoelectric materials is characterized by the dimensionless figure of merit ZT = $S^2T/(\ +\ )$, where S, T, , , and represent the Seebeck coefficient, absolute temperature, electrical resistivity, electronic thermal conductivity, and lattice thermal conductivity, respectively. Higher ZT values indicate superior thermoelectric performance. Enhancing thermoelectric performance primarily involves increasing the Seebeck coefficient while reducing electrical resistivity and thermal conductivity. However, these three parameters are interrelated, as they all depend on the electronic structure and charge carrier transport characteristics. Consequently, tuning the carrier concentration represents one of the most important approaches for optimizing thermoelectric performance.

PbTe is among the earliest studied and practically applied mid-temperature range (300-800 K) thermoelectric materials. It crystallizes in a NaCl-type face-centered cubic structure with a high melting point (1095 K), wide bandgap (~0.3 eV), and stable chemical properties. High-performance PbTe thermoelectric materials have been achieved through various strategies including resonant state introduction, nanostructuring, and band structure engineering. For instance, Tl-doped PbTe alloys have demonstrated a maximum ZT value of 1.5 at 773 K by introducing resonant states near the Fermi level. N-type bulk AgPb SbTe $_2$ (LAST) nanostructured materials have shown significantly enhanced ZT values (reaching 2.2 at 800 K), primarily attributed to quantum nanodots of Ag-Sb in the PbTe matrix. In the PbTe-PbS system, the emergence of PbS nanostructures has led to a ZT value of 1.8 at 800 K. Heavy doping of PbTe:Na has yielded a ZT value of 1.4 at 750 K due to its multi-valley valence band structure, and composition tuning of $PbTe_1$ Se has achieved a ZT value of 1.8 at 850 K. These experimental results demonstrate that elemental doping can effectively optimize the thermoelectric properties of PbTe-based alloys. Therefore, identifying suitable dopants and adjusting their composition ratios represents a crucial pathway to obtaining high-performance thermoelectric materials.

In n-type PbTe, incorporating excess Pb can improve mechanical properties, compensate for Pb loss during material processing, and ensure reproducible resistivity measurements. This study investigates Nb-doped $Pb_{1\cdot1}Te$ materials to examine the influence of Nb on the thermoelectric performance of the matrix material.

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1 Experimental Methods

High-purity Pb powder (99.999%), Te powder (99.999%), and Nb powder (99.99%) were weighed in a glove box according to the stoichiometric ratios of $Pb_{1\cdot1}$ Nb Te (x = 0, 0.02, 0.04, 0.06, 0.07, 0.08). The mixed powders were sealed in stainless steel ball-milling jars with a ball-to-powder weight ratio of 20:1 and milled for 10 h at 350 rpm using a planetary ball mill (QM-WX4). The milled powders were then loaded into graphite dies and consolidated by spark plasma sintering (SPS) under a vacuum of 0.1 Pa at 623 K for 5 min under an applied pressure of 50 MPa.

The phase composition of the bulk samples was analyzed using a BRUKER D8-Discover X-ray diffractometer (XRD). Fracture surface morphology was examined using an S-4800 scanning electron microscope (SEM). The electrical resistivity, Seebeck coefficient, and thermal diffusion coefficient were measured in the temperature range of 323–673 K, and the Hall coefficient was measured at 300 K. Electrical resistivity and Seebeck coefficient were measured under static helium atmosphere using an LSR-3 (Linseis) system. The Hall coefficient was measured using the van der Pauw method. The thermal diffusion coefficient was measured under flowing high-purity argon (50 mL/min) using a Netzsch LFA 457 laser flash analyzer. The specific heat Cp (in KB per atom) was calculated using the relation Cp = 3.07 + 4.7$\times10^{-4}\times$(T/K - 300) from literature, and the density was measured by the Archimedes method. The thermal conductivity was calculated as = DC d, where D is the thermal diffusion coefficient, C is the specific heat, and d is the density.

2.1 Phase Analysis and Microstructure

[Figure 1: see original paper] shows the XRD patterns of the bulk samples Pb$_{1\cdot1}$ Nb Te (x = 0, 0.02, 0.04, 0.06, 0.07, 0.08). The main diffraction peaks correspond to the face-centered cubic structure of PbTe alloy. The presence of minor Pb diffraction peaks indicates that the excess Pb did not fully incorporate into the PbTe sublattice. No Nb diffraction peaks were observed in the XRD patterns due to the low Nb content.

[Figure 2: see original paper] presents SEM images of the fracture surfaces for Pb$_{1\cdot1}$Te and Pb$_{1\cdot03}$Nb$_{0\cdot07}$Te. The grain sizes of the samples range from 200 to 400 nm, a benefit derived from mechanical alloying that reduces grain size. The reduced grain size enhances phonon scattering at grain boundaries, thereby lowering the lattice thermal conductivity.

2.2 Electrical Transport Properties

[Figure 3: see original paper] illustrates the temperature dependence of electrical resistivity, Seebeck coefficient, and power factor for Pb$_{1\cdot1}$ Nb Te samples with various Nb contents. As shown in [Figure 3: see original paper]a and b, both resistivity and the absolute Seebeck coefficient increase with temperature, exhibiting degenerate semiconductor behavior. The resistivity of Pb$_{1\cdot1}$Te at 323 K is 3.55 mΩ • cm, which is lower than that of pure PbTe reported previously. According to literature, partial Pb in PbTe creates Te vacancies in the crystal lattice, causing the material to shift toward n-type conduction. The resistivity decreases continuously with increasing Nb content, reaching a minimum of 0.95 mΩ • cm at 323 K for Pb$_{1\cdot02}$Nb$_{0\cdot08}$Te, which is one-quarter of the resistivity of the pristine Pb$_{1\cdot1}$Te at this temperature. Based on the relation 1/ = ne and considering that carrier scattering reduces mobility, the decreased resistivity originates from increased carrier concentration. The room-temperature mobility of Pb$_{1\cdot1}$Te is only 571 cm^2/(V • s), smaller than that of PbTe, because excess Pb creates lattice distortion that scatters phonons and reduces carrier mobility. The absolute Seebeck coefficient of Pb$_{1\cdot1}$Te is higher than that of pure PbTe, possibly due to increased relaxation time from excess Pb. Both the Seebeck coefficient and Hall coefficient are negative, confirming n-type conduction in Nb-doped lead telluride.

The absolute Seebeck coefficient decreases monotonically with carrier concentration, which can be explained by the theoretical relation. As carrier concentration increases, carrier scattering intensifies, reducing carrier mobility. Additionally, Nb substitution for Pb in the lattice introduces strain fields due to differences in atomic mass and radius between Nb and Pb, which also scatter carriers. Consequently, as Nb content increases, these combined effects lead to continuously decreasing mobility with increasing carrier concentration.

The power factor (S^2/) comprehensively describes the influence of Nb on the electrical transport properties of PbTe. As shown in [Figure 3: see original paper]c, Pb$_{1\cdot 03}$Nb$_{0\cdot 07}$Te achieves power factor values exceeding 20 mW/(cm · K^2) over a broad temperature range (523-673 K), which is higher than previously reported values for PbTe-based materials. This indicates that Nb doping effectively enhances the electrical performance of Pb$_{1\cdot 1}$Te.

2.3 Thermal Transport Properties

[Figure 5: see original paper] shows the temperature dependence of total thermal conductivity (= +) and lattice thermal conductivity ( ) for Pb$_{1\cdot 1}$ Nb Te. The electronic thermal conductivity ( ) follows the Wiedemann-Franz law: = LT/ , where L is the Lorenz factor (L = 2.45$\times10^{-8}$ V^2/K^2 for free electrons). The thermal conductivity of Nb-doped Pb$_{1\cdot 1}$ Nb Te decreases with increasing temperature, primarily due to enhanced phonon scattering. The lattice thermal conductivity decreases continuously with increasing Nb content, reaching only 0.51 W/(K · m) at 673 K for Pb$_{1\cdot 02}$Nb$_{0\cdot 08}$Te, which represents a 41% reduction compared to the matrix material at this temperature. The reduction in lattice thermal conductivity arises from two mechanisms: first, decreased grain size and increased grain boundary density—when bulk material grain sizes fall below 500 nm, lattice thermal conductivity decreases rapidly; second, Nb substitution creates lattice defects that scatter phonons, and the mass difference between Pb and Nb atoms induces strain field fluctuations that also produce phonon scattering.

2.4 ZT Values

[Figure 6: see original paper] presents the temperature dependence of ZT values for Pb$_{1\cdot 1}$ Nb Te (x = 0, 0.02, 0.04, 0.06, 0.07, 0.08). The ZT values increase continuously with temperature, primarily due to the combined effects of increasing power factor and decreasing thermal conductivity. The sample Pb$_{1\cdot 03}$Nb$_{0\cdot 07}$Te achieves a maximum ZT value of 1.27 at 673 K, which is twice that of the pristine Pb$_{1\cdot 1}$Te matrix.

3 Conclusions

Nb-doped n-type Pb$_{1\cdot 1}$Te samples were successfully prepared by mechanical alloying and spark plasma sintering. Nb doping increased the carrier concentration of the matrix material from 0.4$\times10^{19}$ to 1.63$\times10^{19}$ cm^{-3} at room temperature. At 673 K, $Pb_{1\cdot03}Nb_{0\cdot07}Te$ achieved a maximum power factor of 22.5 mW/(cm • K^2), more than double that of $Pb_{1\cdot1}Te$, and the ZT value improved from 0.64 to 1.27, demonstrating significant optimization of electrical performance.

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