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Impact of Sm alloying and thermal annealing on the structural and thermoelectric properties of $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys

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ABSTRACT

Besides the energy-conversion efficiency and production cost, the thermal stability is also a key parameter for the wide-spread use of a thermoelectric material in device-level. The rare-earth-element Sm content is introduced into the $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys to tune the thermal stability and structural properties of these alloys, especially the spinodal decomposition. The Sm content shows suppression effect on the generation of secondary-phase PbTe-rich domains, and it also tend to stabilize the thermodynamically balanced state with stabilized microstructures and thermoelectric performance. The reduction of the lattice thermal conductivity by Sm alloying is mainly ascribed to the grain refining and the designing of all-scale hierarchical architectures for full-spectrum phonon scattering. By thermal annealing, the ZT values can increase by 25% and 76% for the $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys with $x = 0.2$ and $x = 0.28$ respectively. The synergetic strategy of rare-earth element doping and thermal annealing in this study opens up a potential pathway to enhance the thermoelectric performance and thermal stability.

1. Introduction

Thermoelectric (TE) materials are able of generating electricity from waste heat based on Seebeck effect [1], which are attractive for sustainable energy management. The economic viability of TE materials greatly rely on developing new strategies to minimize the production cost and to improve the efficiency of energy conversion [2]. Good TE materials must have high TE power factor PF ($=S^2/\rho$, where S is the Seebeck coefficient and ρ is the electrical resistivity) and low thermal conductivity κ. Those two parts give a dimensionless figure of merit ZT, defined as $ZT = (S^2/\rho)(1/\kappa)T$, where T is the absolute temperature [1]. The κ usually can be summed by two parts, the lattice thermal conductivity κ_{lat} and the electrical thermal conductivity κ_e, where $\kappa_e = LT/\rho$ based on the Wiedemann-Franz law (L is the Lorenz number). Many nanostructuring approaches [3,4] and all-scale hierarchical architectures designing [5,6] have been proposed to enhance the ZT values by reducing the κ_{lat} without compromising the PF much.

Some spark plasma sintering method for rapid consolidation have been reported retain most of the nanoscale feathers [7,8]. However, one of the challenge while dealing with nano- and micro-structuring approaches for the enhancement of ZT lies in retaining those nano- and micro-structures under high-temperature working conditions, especially for high-temperature thermoelectric materials. Usually, one has to study the thermal stability of TE materials under thermal treatment in order to determine their usefulness for device-level power-generation application, such as the routine thermal stability test in commercialized TAGS (GeTe-$AgSbTe_2$) TE materials [9,10]. Grain coarsening and thermodynamically driven phase separation often happen under thermal annealing [11], which are supposed to affect the microstructures and TE performance. On the other hand, some phase separation by spinodal decomposition under thermal annealing also has positive effect on TE performance, which has been reported to enhance the ZT values in many materials systems such as PbTe-PbS [12], PbTe-Ag_2Te [13], GeTe-PbTe [11,14,15], GeTe-GeSe-GeS [16] and half-Heuslers [17,18]. Alloying with foreign elements is a widely-used method to adjust the carrier density and band structure for high PF and to introduce point defects and nanostructures for low κ_{lat}, which then enhances the ZT values of alloys [1,19,20]. Improving the solubility of substituted atoms in a solid-solution alloy can be a big challenge in some material system, such as filled skutterudites [21]. Forming single solid-solution phase with a high solubility of substitution elements and achieving phase-separation phases are

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two competition strategies for optimizing the TE performance, and appropriate compromise strategy to balance the solid-solution solubility and phase separation is another efficient method for the enhancement of TE performance [11,16]. Group-IV tellurides PbTe and GeTe are promising TE materials for mid-temperature (500–900 K) power generation [9,22,23], and their pseudo-binary alloys have the spinodal decomposition (miscibility gap) below 860 K [11], which make the GeTe-PbTe alloys perfect material systems to study the control of solid solution and phase separation for enhancing the TE performance and thermal stability. The alloying strategy has also been applied in the GeTe-based alloys to control the solid solution, nano- and micro-structures for enhancing their TE performance [14–16,24–36], and the corresponding mechanism is mainly ascribed to the enhanced phonon scattering for κ_{lat} [16,25,29], as well as the optimized carrier density [26,28] and band structure [24] for high *PF*. What's more, the strategy of alloying with other elements and compounds has also been introduced to control the solid-solution solubility and phase-separated features of the GeTe-PbTe alloys [11,14–16,27,31,35], showing great promise for enhancing the TE performance and thermal stability. Rare-earth element with larger atomic size doped in GeTe based alloys can be used to tune the lattice distortion and electronic transport for better thermoelectric performance [37].

In this study, rare-earth Sm element is introduced into the GeTe-PbTe system to form $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys with x from 0 to 0.28, and the impact of thermal annealing and Sm content on the structural and TE properties of the alloys is systemically studied. The adding of Sm content tend to depress the spinodal decomposition of $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys in the spark plasma sintering process, and also to expedite and stabilize the formation of thermodynamically balanced state with stabilized microstructures and TE performance. By thermal annealing, the ZT values can increase by 25% and 76% for the $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys with $x = 0.2$ and $x = 0.28$ respectively. The maximum ZT values can be enhanced to ~0.96 at 673 K for $x = 0.2$ after annealing treatment. What's more, the $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys after annealing also have good thermal stability, making the strategy of rare-earth element doping and phase separation quite attractive for improving the thermal stability and further enhancing the TE performance.

2. Experimental details

2.1. Synthesis process

The starting pure elementals Pb (99.99%), Ge (99.99%), Sm (99.9%) and Te (99.99%) for synthesis of $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ ($x = 0$, 0.04, 0.08, 0.12, 0.16, 0.20, 0.24 and 0.28) were weighted stoichiometrically and sealed in the evacuated quartz tube (6×10^{-3} Pa). These starting materials were heated at 1050 °C for 20 h to be completely mixed in liquid phase and then were slowly cooled to 600 °C in 4 h. After held at 600 °C for 10 h, these samples were quenched in liquid nitrogen. The quenched alloys were grinded into powders using an agate mortar and pestle, and then the powders were consolidated into bulk pellets by spark plasma sintering (SPS) at 500 °C for 5 min under and axial pressure of 50 MPa (peak impulse value of 675 A). The bar specimens with dimensions of 15.0 mm × 5.0 mm × 5.0 mm were prepared for the electrical properties measurement and the disk specimens with diameter of 10.0 mm and thickness of ~2.0 mm for the thermal conductivity measurement. To study the impact of thermal annealing on the TE properties of those alloys, the sintered bulk samples with composition $x = 0.2$ and 0.28 were annealed at 420 °C in sealed quartz tubes (6×10^{-3} Pa) for different time (from 0 h to 168 h).

2.2. Characterization methods

Scanning electron microscopy (SEM, Hitachi SU-70) equipped with energy dispersive spectrometer (EDS) was performed for morphology and elemental analysis, and the powder X-ray diffraction (XRD) spectra were taken using a Bruker D8 advance SS/18 kW diffractometer with Cu K_α radiation ($\lambda = 0.15404$ nm; 40 kV, 200 mA) for structure and phase analysis. Transmission electron microscopy (TEM) investigation was performed using a JEOL 2100 F (JEOL, Tokyo, Japan) microscope operating at 200 kV. The temperature-dependence Seebeck coefficient (S) and the electrical resistivity (ρ) were measured using a ZEM-2 apparatus (Ulvac-Riko) under helium atmosphere. The thermal conductivity (κ, $\kappa = \lambda d C_p$) was determined by the measurement of thermal diffusivity λ, density d and specific heat capacity C_p. The λ was measured by a laser flash technique (TC-9000, Ulvac-Riko), and the d of a sample was calculated from the sample's mass and geometry, which was also checked by the Archimedes method, as shown in supporting information Table S1. Like previous report of the GeTe-related materials system [25,28,32], our C_p was also determined using the Dulong-Petit law $C_P = 3k_B$ per atom, where k_B is the Boltzmann constant. The C_p was also measured by differential scanning calorimeter (DSC 404 F3, Netzsch) as a reference to check the availability of the Dulong-Petit law that applied in our $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys, as shown in the supporting information.

3. Results and discussion

3.1. Structural properties

The pseudo binary phase diagram of GeTe-PbTe shows unlimited mutual solubility above 600 °C [11], and our $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys that are obtained by solid-solution alloying process followed with liquid-nitrogen quenching process also shows mutual soluble single-phase alloys as revealed by the XRD patterns (Fig. S1). As demonstrated in the XRD patterns of SPS-processed $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys (Fig. 1a), the $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ can decompose into GeTe-rich and PbTe-rich phase during the SPS process, which can be ascribed to the spinodal decomposition of GeTe-PbTe solid solution below 600 °C (our SPS temperature is 500 °C). Tiny Ge phase nearly appears in every $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ samples before and after the SPS process, as well as before and after annealing process (Fig. 1 and Fig. S1). The Ge vacancy in the lattice of GeTe-based alloys is formed when Ge impurity is extruded from the matrix, which usually gives rise to p-type carrier concentration [14,38,39]. Besides the main GeTe-based rhombohedral and PbTe-based rock-salt phases, some tiny $SmTe_{1.8}$-based phase also become evident in $(GeTe)_{0.85}(Pb_{1-x}Sm_xTe)_{0.15}$ alloys when the composition Sm x increases to 0.2 and larger (Fig. 1a and Fig. S2), which indicates that the solubility limit of Sm in the GeTe-PbTe based alloys is around 0.16–0.20. All the XRD patterns in Fig. 1 are normalized by setting the intensity of the strongest GeTe-related peak (202) to 1, which can be used as references to compare the relative intensity of each peak. Comparing the relative intensity of PbTe-based peaks ((202) and (220)) as shown in Fig. 1a, the ratio of PbTe-related phase to GeTe-based phase is found to decrease as the composition Sm x increases, indicating the suppression effect of Sm element on the spinodal decomposition of GeTe-PbTe solid solution in the SPS process.

Compared with the standard PDF card of GeTe (PDF#47-1079, hexagonal, $R3m$ structure with cell parameters $a = 0.83428$ nm and $c = 1.0668$ nm), each corresponding peaks of GeTe-based phase in Fig. 1 shows smaller 2θ degrees, which can be explained by the formation of GeTe-rich Ge-Pb-Sm-Te solid solution with larger atomic-size Pb, Sm atoms in the GeTe matrix, which expand the