Thermoelectric performance of \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) fabricated by high pressure sintering method

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Abstract

\((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) is one of good middle temperature thermoelectric materials. Here, the effects of \(x\) values and heat treatment \((673 \text{ K } 24 \text{ h})\) on the thermoelectric property of \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) \((x = 0, 0.02, 0.04, 0.06)\) prepared by solid-state synthesis \((873 \text{ K})\) and high pressure sintering \((6 \text{ GPa})\) method were studied, the composition, microstructure, and the thermoelectric properties in temperature range of \(300–731 \text{ K}\) were investigated. The results indicate that high pressure sintering (HPS) is beneficial to the dissolution of \(\text{Sb}_2\text{Te}_3\) in \(\text{GeTe}\) and the acquisition of nanocrystalline \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\). Soluble \(\text{Sb}_2\text{Te}_3\) can greatly change the crystal structure of \(\text{GeTe}\), and results in the high pressure phase and different thermoelectric property in \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) \((x = 0)\). Heat treatment does not change the high pressure phase of \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) \((x = 0)\), meanwhile it increases the crystal grain size of \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) \((x = 0)\). Samples of \(x = 0.04\) and \(x = 0.06\) show the maximum Seebeck coefficient value at \(724 \text{ K}\), and \((\text{GeTe})_{0.94}(\text{Sb}_2\text{Te}_3)_{0.06}\) shows the highest power factor \((\text{PF} = 3.70 \mu\text{W/mmK}^2\) at \(724 \text{ K}\)). The largest value of \(ZT = 0.56\) at \(724 \text{ K}\) is obtained for \((\text{GeTe})_{0.94}(\text{Sb}_2\text{Te}_3)_{0.06}\).

1. Introduction

Thermoelectric (TE) materials can convert heat into electrical energy, which in turn makes them the most challenging materials to be studied in the past decade so as to secure continuous future energy supply [1]. A dimensionless figure of merit \(ZT = S^2\sigma T/\kappa\), where \(S, \sigma, \kappa\), and \(T\) are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, is applied to evaluate the performance of a TE material. TE materials with high conductivity, high Seebeck coefficient and low thermal conductivity are required to increase the power factor \(S^2\sigma\) and decrease the total thermal conductivity \(\kappa\) of TE materials at the same time in order to get the best performance [2]. Given that there is a close connection among the Seebeck coefficient, electrical conductivity, and thermal conductivity, it is difficult to enhance the \(ZT\) [3–9]. To get high power factor \(S^2\sigma\), strategies have been applied, including minority carrier blocking, resonant state doping, reversible phase transition, charge carrier scattering modification and band engineering [10–16]. Some other strategies, namely nanostructuring [17, 18], intrinsic anharmonicity, the development of a matrix with nanoprecipitates and hierarchical architetecture, are also deployed to make the TE material have low thermal conductivity \(\kappa_{\text{int}}\). In the case of thin film superlattices or ‘quantum well’ materials with feature sizes of several to tens of nanometers, the \(ZT\) can be greater than 2 [19]. GeTe is considered to be a base for high-performance multicomponent TE materials in the intermediate temperature range. Because of the considerable Ge deficiency, pristine GeTe, a highly degenerated p-type semiconductor with room-temperature carrier concentration \(n\) as high as \(\approx 10^{21} \text{ cm}^{-3}\), gives rise to a large \(\kappa_{\text{e}}\) [20–24], and the reduction of power factor due to low Seebeck coefficient. Element doping will increase or decrease the carrier concentration of GeTe. Too high carrier concentration will cause the reduction of power factor. Because a large carrier concentration causes a decrease in the Seebeck coefficient. Too little carrier concentration will lead to a decrease in conductivity. The carrier concentration of GeTe needs to be adjusted to an appropriate value. Germanium–antimony–tellurium (Ge-Sb-Te or GST), as an excellent potential material in TE applications, exists in various compositions and crystal structures. The structural phase transformation of GST material, of which the physical properties can exert impact on their functions, is from high
under high pressure. The room temperature XRD patterns for synthetic Sb$_2$Te$_3$ at room temperature, presents tetradymite-like Sb$_2$Te$_3$ blocks which are enlarged by the insertion of GeTe layers [25]. Fahnrbauer et al. have shown a high ZT of 1.9 at 723 K for the composition of Ge-Sb-Te with nanoprecipitates of Co$_3$Ge$_2$ [26]. Therefore, there have been an increasing number of researchers focusing on the study of GeTe-based materials. Under the circumstance of the alloy of GeTe with PbTe, the ZT has significantly increased from 0.6 for pristine GeTe to 2 [27]. Researchers like Christakoudi did a systematic study on the TE properties of GeTe alloys with varying Bi$_2$Te$_3$ content and later an explanation of temperature and composition dependence by electronic band structures [28]. In the past few years, a lot of efforts and attempts have been made by researchers. As a result, there are a number of effective approaches, such as optimizing carrier concentration through doping [24, 29, 30], valence band convergence [31, 32] and nano/microstructure modulations [33, 34], which have been functioning normally.

An effective way to modulate energy band structure is high pressure sintering (HPS), which also can improve the mechanical property of a semiconductor [34–38]. Compared with other existing fabrication methods, HPS has a series of advantages, such as high efficiency, low cost, more suitable for large-scale production, more homogeneous, nanocrystalline grain and restraining nanometer grain from coarsening during sintering process that can decrease lattice thermal conductivity, etc [39]. HPS can be completed in a few minutes, so it can effectively inhibit the volatilization of elements such as Te in the process of calcination. The pressure-induced stress, on the one hand, can effectively decrease the electrical resistivity caused by the induced antisite defects and vacancies. On the other hand, it might increase the Seebeck coefficient to a certain extent [40]. It is expected that the power factor (PF = $S^2\sigma$) of the materials fabricated by HPS will be increased. Therefore, in this study, (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$, ($x = 0, 0.02, 0.04, 0.06$) was synthesized by vacuum melt synthesis, sintered by HPS method, and annealed in vacuum for 24 h at 673 K. The effect of Sb$_2$Te$_3$ content and heat treatment on TE properties of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ were studied.

2. Experimental procedure

The starting materials use pure GeTe and Sb$_2$Te$_3$ powders. They were weighed out in appropriate atomic ratios, mixed in an agate mortar for 2 h, sealed in quartz tubes, and then synthesized for 8 h in a vacuum atmosphere (10$^{-3}$ torr) at 873 K.

The synthetic materials were crushed into powder, pressed into a square anvil by cold pressure, sintered under high pressure (6.0 GPa) at 773 K for 3 min under cubic pressure with the sintering size of $\Phi$16 $\times$ 10 mm, and then were annealed for 24 h in vacuum at 673 K. The electric conductivity ($\sigma$) was measured by the standard four-probe method in the temperature range from 303 to 773 K. When the temperature difference (3 K) was applied at both ends of the sample, the Seebeck coefficient ($S$) was measured at the same time. The power factor (PF) is calculated by the formula: $PF = S^2\sigma$. Laser flash method (NETZSCH, Germany, LFA427) was used to measure thermal diffusivity ($\lambda$) in the temperature range of 300 K to 730 K, specific heat ($C_p$) was measured by thermal analyzer (Dupont 1090B, America), and density ($d$) was measured by Archimedes method. The thermal conductivity ($κ$) was calculated by formula $κ = \lambda/d$. The data of $S$, $\sigma$, $\lambda$ and $\kappa$ at a given temperature were substituted into the formula: $ZT = S^2\sigma T/κ$, and the optimal value ZT of the sample was calculated. The phase structure was determined by powder x-ray diffraction method (XRD, Rigaku D/MAX-2550PF diffractometer, Cu Kα ($\lambda = 0.154056$ nm)). The field-emission scanning electron microscopy (FE-SEM, FEI, Quanta FEG 450, America) was used to observe the microstructures of the samples. DTG/DSC analysis were carried out by simultaneous thermal analyzer NETZSCH STA 449F3.

3. Results and discussion

The room temperature XRD patterns for synthetic (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$, with $x = 0, 0.02, 0.04$ and 0.06 are shown in figure 1(a). All materials are crystallized in the low-temperature rhombohedral structure of GeTe (PDF#47–1079). There are also several peaks corresponding to the Sb$_2$Te$_3$ phase, as impurities when $x \geq 0.02$. As the Sb$_2$Te$_3$ content increases, the diffraction peak intensity of Sb$_2$Te$_3$ phase increases. After high pressure sintering, the XRD powder diffraction patterns depend on x values as shown in figure 1(b). Firstly, the peaks corresponding to Sb$_2$Te$_3$ have decreased, which indicates HPS is beneficial to increase the solubility of Sb$_2$Te$_3$ in GeTe. Secondly, the distance between peaks at 41.08 and 44.02 degree is larger than that before HPS, that indicates the crystal structure of GeTe doped with Sb$_2$Te$_3$ after HPS is different from that of pure GeTe greatly, which is called high-pressure phase. The reason is that HPS (6 GPa $\times$ 773 K $\times$ 3 min) would introduce huge stress, cause deformation of the crystal lattice of the material, and lead to the increase of the distance between the peaks of 41.08° and 44.02° of XRD. The ion radius of Sb$^{3+}$ is larger than that of Ge$^{2+}$, resulting in lattice distortion. The lattice distortion is more severe under high pressure, and even Sb$^{3+}$ will enter the position of Te$^{2-}$ after high pressure. As the results, the TE property for samples doped with Sb$_2$Te$_3$ will be different greatly with that of GeTe fabricated by HPS. Thirdly, the main peaks shift towards large angles versus x value. The grain sizes of HPS (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ are calculated to be tens of nanometers.
Figure 1 shows the change of diffraction peak around 29.5° versus x value. It can be seen that after Sb$_2$Te$_3$ doping, the diffraction peak of the samples shifts to the right, indicating that the interplanar crystal spacing is reduced. Besides, Sb$_2$Te$_3$ doping induces the widening of the diffraction peaks of GeTe. Therefore, Sb$_2$Te$_3$ doping will be conducive to obtaining nanocrystal GeTe. Figure 1(c) shows the powder xrd pattern of the samples after heat treatment. It can be seen that the high pressure phase still exists after heat treatment. But the peaks corresponding Sb$_2$Te$_3$ phase are enhanced. And an excess of Te peaks appears near 31° according to figure 1(c), showing Sb$_2$Te$_3$ and Te separate out from the solid solution. In addition, the XRD peaks of 4 samples become sharp. Therefore, the grain sizes are increased by heat treatment. Table 1 shows the variation of lattice parameters of samples versus doping amount of Sb$_2$Te$_3$ after heat treatment, and table 2 shows the size of ion radius of the three elements. As can be seen from table 1, the lattice parameters of the sample gradually decrease with the increase of doping amount. And because the ion radius of Sb$^{3+}$ is larger than Ge$^{2+}$, but smaller than Te$^{2-}$, it is speculated that a considerable number of Sb$^{3+}$ occupy the bit of Te$^{2-}$ and constitute an antisite defect, leading to the reduction of lattice parameters. With the increase of Sb content, the more antisite defects of Sb$^{3+}$ occupying Te$^{2-}$ bit, the smaller the lattice parameters. In the case of lattice deformation caused by HPS and crystal defects caused by inversion doping, it is beneficial to enhance phonon scattering and reduce lattice thermal conductivity.
Figure 1 shows the temperature dependences of GeTe ($x = 0$) heat flux (blue line) and mass loss rate (red line) from 320 K to 770 K. Interestingly, according to the temperature dependences of the heat flux (blue line) and the mass loss rate (red line), the GeTe sintered by HPS has 3 phase transitions at 390 K, 640 K and 730 K because both of the temperature dependences of the heat flux and the mass loss rate have 3 inflection points at 3 temperature above respectively. Generally, GeTe will change from rhombohedral phase to cubic phase at 640 K. Three phase transition temperatures occurred in this experiment should be related to the HPS processing. The mechanism of these three phase transitions need to be further studied with advanced equipment in the future.

The microstructure and elemental mapping of the HPS (GeTe)$_{0.98}$Sb$_2$Te$_5$_{0.02} studied by FE-SEM and EDXS (energy-dispersive x-ray spectroscopy) are shown in figures 2(a)–(e). As shown in figure 2(a), GeTe has many

| Sample                  | Lattice constant $a$/Å | Lattice constant $c$/Å |
|-------------------------|------------------------|------------------------|
| GeTe                    | 8.355                  | 10.734                 |
| (GeTe)$_{0.98}$Sb$_2$Te$_5$_{0.02} | 8.349                  | 10.724                 |
| (GeTe)$_{0.96}$Sb$_2$Te$_5$_{0.04} | 8.344                  | 10.720                 |
| (GeTe)$_{0.94}$Sb$_2$Te$_5$_{0.06} | 8.343                  | 10.692                 |

Figure 1(e) shows the temperature dependences of GeTe ($x = 0$) heat flux (blue line) and mass loss rate (red line) from 320 K to 770 K. Interestingly, according to the temperature dependences of the heat flux (blue line) and the mass loss rate (red line), the GeTe sintered by HPS has 3 phase transition at 390 K, 640 K and 730 K because both of the temperature dependences of the heat flux and the mass loss rate have 3 inflection points at 3 temperature above respectively. Generally, GeTe will change from rhombohedral phase to cubic phase at 640 K. Three phase transition temperatures occurred in this experiment should be related to the HPS processing. The mechanism of these three phase transitions need to be further studied with advanced equipment in the future.
small grains of about 100 nanometers, which are easily agglomerated into large particles. This is consistent with xrd analysis results. It shows that in some micro-region Ge content is a little higher than that of other parts, so the composition of GeTe is not completely uniform (the black area on figure 2(b)). The SEM images of other samples are similar to this sample.

Figures 3(a) and (b) show the temperature dependence of Seebeck coefficients $S$ for the samples (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x = 0$–0.06) before and after heat treatment respectively. The positive values of the Seebeck coefficient for (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x = 0$–0.06) in temperature range from 300 K to 725 K suggests that the main charge carriers in all samples are holes. It is seen that the samples studied here show a degenerated semiconducting behavior, meaning an increase in Seebeck coefficient with increasing temperature. The Seebeck coefficients $S$ for 4 samples increased steadily with the rise of temperature, regardless of heat treatment. After heat treatment, the Seebeck coefficient of the samples is higher than the original. Therefore, heat treatment is beneficial to improve the Seebeck coefficient of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$. It can be attributed to the decrease of the crystal defect and the carrier content caused by heat treatment. Due to the large internal stress in the samples prepared by high pressure, the bandgap width was reduced. This caused carrier concentration to increase and conductivity to increase. After heat treatment, the internal stress was greatly reduced, and the bandgap width was increased, so the carrier concentration was also reduced, thereby reducing the conductivity and improving the Seebeck

![Figure 3](image-url)
When the material has a large number of nanocrystals, due to more grain boundaries and incomplete crystals at the interface, more carriers are generated. After heat treatment, the integrity of the crystals increases, the carriers at the interface decrease, and the electrical conductivity decreases. Onodera et al. also reported a decrease in GeTe resistivity at high pressures below 6 GPa. Besides, dopant Sb$_2$Te$_3$ can improve the Seebeck coefficient of GeTe only in temperature higher than 473 K or 623 K before or after heat treatment. A special result is that in low temperature the GeTe has higher Seebeck coefficient than that of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x \neq 0$), but in high temperature it is reverse, regardless of heat treatment. The reason is that in low temperature, the sample doped with Sb$_2$Te$_3$ retains higher residual internal stress and more crystal defects due to HPS than in high temperature, which reduces the bandgap, increases carrier concentration, and leads to low Seebeck coefficient. With the increase of temperature, the residual internal stress and crystal defects decrease, the carrier concentration decreases, the Seebeck coefficient increases. In high temperature, as more Sb$_2$Te$_3$ precipitates from of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x \neq 0$), the carrier contents of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x \neq 0$) decrease more quickly than GeTe, until the Seebeck coefficients of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x \neq 0$) are higher than that of GeTe.

As shown in figure 4, the electrical conductivities $\sigma$ of the samples (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x = 0 – 0.06$) before and after heat treatment decrease in accordance with temperature, showing metal-like behavior because of negative temperature coefficient. It is also found that the samples doped with Sb$_2$Te$_3$ have higher electrical conductivity than that of GeTe in whole temperature range. The samples with $x = 0.02$ and 0.04 have the highest electrical conductivity before heat treatment. The reason is GeTe doped with Sb$_2$Te$_3$ is of different crystal structure with pure GeTe, or is of high-pressure phase, as shown in figure 1(b), that might contain high carrier concentration by Sb anti-site defects formed by Sb atoms occupy Te sites in addition to Ge vacancy. After heat treatment, the electrical conductivities for all samples are lower than the original. Besides, for the samples doped with Sb$_2$Te$_3$, the electrical conductivities decease versus $x$ value. The reason is crystal defect and the solubility of Sb$_2$Te$_3$ decrease, as shown in figure 1(e). And precipitated Sb$_2$Te$_3$ decreases the electrical conductivity of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x = 0$). These results indicate that suitable amount of dopant Sb$_2$Te$_3$ can increase high temperature Seebeck coefficient and electrical conductivity of GeTe at same time by high-pressure phase of (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x = 0$).

In order to examine the temperature behavior of the electric conductivity of the samples, the logarithm of $\sigma T$ as a function of the reciprocal of temperature is plotted as shown in figures 4(c) and (d), it can be seen that the

![Figure 4](image-url)
linear behavior in some temperature range follows,

$$\ln (\sigma AT) = - \frac{E_a}{k_B T}$$  \hspace{1cm} (1)

where $A$ is a constant, $k_B$ is the Boltzmann constant, and $E_a$ is the apparent activation energy. Before heat treatment, the sample doped with Sb$_2$Te$_3$ are small polaron scattering at 570–670 K, and the sample undoped are small polaron scattering at 470–670 K. After heat treatment, samples doped with Sb$_2$Te$_3$ are small polaron scattering over 600 K at high temperature, while samples undoped are small polaron scattering at 525–675 K and below 427 K. In other temperature ranges, multiple phase transitions due to high pressure synthesis or other reasons may cause the electrical conduction mechanism of the four samples to be not obvious. Small polaron scattering at high temperature can increase both conductivity and Seebeck coefficient.

Figure 5(a) and (b) show the temperature dependence of power factor $PF$ for the samples (GeTe)$_{1-x}$(Sb$_2$Te$_3$)$_x$ ($x = 0–0.06$) before (a) and after heat treatment (b).

$\kappa_{\text{total}}$ is the sum of the electronic ($\kappa_{\text{elec}}$) and lattice ($\kappa_{\text{latt}}$) thermal conductivities. It can be seen that the lattice thermal conductivity decreases as the temperature and dopant amount of Sb$_2$Te$_3$ increase. Due to the difference of mass, size, and electric charge between Sb$^{3+}$ and Ge$^{2+}$, alloy defects produce both mass and strain fluctuations to enhance the phonon scattering in doped GeTe, which leads to the decrease of lattice thermal conductivity [42]. Therefore, dopant Sb$_2$Te$_3$ can decrease the lattice thermal conductivity of GeTe. Besides, because of high electrical conductivity, the total thermal conductivity of
sample with \( x = 0.02 \) is higher than that of GeTe in whole temperature range. But the total thermal conductivity decreases as the dopant amount and temperature increase. The figures of merit ZT values for the \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) with \( x = 0, 0.02, 0.04 \) and 0.06.

**4. Conclusion**

The \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) \((x = 0, 0.02, 0.04, 0.06)\) were fabricated by solid state synthesis, high pressure (6 GPa) sintering (773 K) (HPS) method and heat treatment. The composition and microstructure were analyzed. The TE properties were studied in the temperature range of 297–731 K. Experimental results show that the HPS is beneficial to the dissolution of \(\text{Sb}_2\text{Te}_3\) in GeTe, obtaining nanocrystalline \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\), and producing complex phase transitions. Three phase transition temperatures appeared in the GeTe sample synthesized by HPS. Under the condition of high pressure synthesis, the crystal structure of GeTe samples dissolved with \(\text{Sb}_2\text{Te}_3\) is changed, resulting in \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) \((x = 0)\) shows high pressure phase and fully different thermoelectric property comparing with GeTe or \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) fabricated by hot pressure sintering or SPS. FE-SEM and EDXS show that the HPS method can enable \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) to obtain nanocrystalline, and the composition of \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) is not homogeneous. After heat treatment, the Seebeck coefficient of \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) increased slightly, but the electrical conductivity decreased. HPS sample with \( x = 0.02 \) shows the highest power factor, PF = 3.70 \(\mu\)W/mmK\(^2\) at 724 K. The value of ZT increases gradually with the increase of temperature. The sample with \( x = 0.06 \) gets ZT\(_\text{max}\) of 0.56 at 724 K. Heat treatment can improve the TE properties of HPS \((\text{GeTe})_{1-x}(\text{Sb}_2\text{Te}_3)_x\) \((x = 0–0.06)\), because the stress produced by high pressure can be released, and the crystal defects can be decreased.
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