

UDK 621.315.592

Effect of thermal history on the properties of efficient thermoelectric alloys $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}^*$

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Received November 20, 2021

Revised November 25, 2021

Accepted November 25, 2021

In this work, we study thermoelectric properties of GeTe-based alloys, doped with bismuth, with partial substitution of lead for germanium: $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$. The aim of the study is to explore the possibility of increasing the thermoelectric efficiency of a compound by combining optimal doping and isovalent substitution to improve the electronic properties with a simultaneous decrease of the lattice thermal conductivity. We studied alloy samples prepared in two different research laboratories using similar, but not completely identical procedures. It is shown that the electronic (thermoelectric power and electrical conductivity) properties of the samples of the two groups are in good agreement with each other. The properties of alloys depend on the thermal history of the samples due to the presence at temperatures of 600–800 K of a phase transition from a low-temperature rhombohedral to a high-temperature cubic structural modification and missibility gap in GeTe-PbTe quasibinary system below 870 K. The thermoelectric figure of merit of alloys reaches a maximum value of 1.5 at a temperature of about 750 K.

Keywords: thermoelectric alloys, thermoelectric power, electrical conductivity, thermal conductivity

DOI: 10.21883/SC.2022.03.53053.34

1. Introduction

Lead, tin and germanium tellurides are used as the basis for the most efficient medium-temperature thermoelectric materials [1]. These materials have been used in thermoelectric generators for ground and space applications. Despite the long history of research and application, extensive study of these materials in order to improve thermoelectric performance and mechanical properties continues, in particular in recent years. According to publications, these efforts were rather successful. Thermoelectric figure of merit $ZT = \frac{S^2\sigma}{\kappa} T$ (here, S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, T is the absolute temperature) [2–4] achieves the values that significantly exceed 2 [5–13]. However, though the publications with high ZT for PbTe- and GeTe-based compounds appeared about 10 years ago [14,15], there have been no information regarding application of these compounds. One of the reasons for this situation is the poor reproducibility of the record results. This circumstance can be associated both with the high sensitivity of the thermoelectric properties of the compounds to the parameters of technological processes during their production, and with subjective factors. In

many cases, high ZT , reported in the literature, are related to very low lattice thermal conductivity in alloys and heavily doped compounds.

Subjective factor may include the absence of any approved standards for thermoelectric properties measurement and resulting significant uncertainty of measurements in various research groups. In particular, this is applicable to thermal conductivity measurements. Thermoelectric materials generally have a very low thermal conductivity and the measurement requires good understanding of and strict adherence to the appropriate procedures. Nowadays, the majority of research groups use non-stationary methods for measuring the thermal diffusivity (α) that is further used to determine the thermal conductivity of material: $\kappa = \alpha C_p d$, where C_p is a heat capacity at a constant pressure, and d is density. To determine the other two transport coefficients (S and σ), which together with κ determine the thermoelectric figure of merit ZT , a separate measuring device and, as a rule, another sample are used. This separation greatly increase the combined uncertainty of ZT .

The other measurement method for ZT is based on the use of a steady-state thermal conductivity measurement procedure that simultaneously allows to measure the Seebeck coefficient and electrical conductivity coefficient and to find ZT using only one sample and one measurement cycle [16,17].

* Report at XXVII Interstate conference „Thermoelectric materials and their applications“ (ISCTA 2021), Saint Petersburg, September 13–16, 2021

In this work, we study the thermoelectric properties of GeTe and PbTe alloys doped with bismuth: $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$. Due to high concentration of equilibrium Ge vacancies, GeTe compound is a *p*-type semiconductor with too high for thermoelectric applications hole concentration [18]. In order to reduce the concentration, doping with elements from Group 5, commonly bismuth or antimony, is used. In addition, it was observed that bismuth doping efficiency increases with partial isovalent substitution of Ge with Pb [19,20]. Moreover, isovalent substitution with lead reduces the lattice thermal conductivity however does not lead to proportional reduction of charge carrier mobility. As a result, in $\text{Ge}_{0.91}\text{Pb}_{0.05}\text{Bi}_{0.04}\text{Te}$ alloys, *ZT* achieves 1.5 at 670–800 K [19]. We study here the possibility to further increase the performance in alloys with increased Pb content. The second goal of the research was to investigate the influence of the thermal history on the thermoelectric properties of alloys. GeTe exists in two modifications: low-temperature rhombohedral (*R3m*) and high-temperature cubic (*Fm $\bar{3}$ m*). In pure GeTe, the transition temperature is 703 K [21], the transition temperature in alloys depends on the composition, level and type of doping [19]. Important feature of the GeTe-PbTe quasibinary alloy phase diagram is that there is unlimited solubility in this system only above about 870 K [22]. Therefore, the properties of GeTe and its alloys with PbTe, at temperature below the miscibility line, depend on the phase composition of the alloy, which, in turn, will depend in a complex way on the thermal history of the sample: annealing temperature, cooling and heating rates, etc. A correct determination of the thermoelectric alloy properties requires clear understanding of the relationship between the structural state and thermal history of the material. And finally, we perform a comparative study of thermoelectric properties of samples with the same composition, but prepared in two different laboratories: in the laboratory for physics of thermoelements of the Ioffe Institute (hereinafter referred to as FTI samples) and Y. Pei laboratory in Tongji University, Shanghai, PRC (hereinafter referred to as Tongji samples). Recently, this group investigated the $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy and obtained a record value of the parameter $ZT = 2.4$ [9]. Our objective is to verify reproducibility of such high efficiency parameters.

2. Samples and experimental procedure

Polycrystalline ingots of the $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy were prepared by direct alloying of the components: Ge (99.999%), Pb (99.99%), Bi (99.99%), Te (99.96%) in evacuated quartz ampoules at $T = 1123$ K. Synthesized ingots were annealed for 120 hours at 773 K for homogenization. Standard X-ray phase analysis confirmed the rhombohedral structure with parameters $a = 4.217 \pm 0.002$ Å, $c = 10.684 \pm 0.006$ Å (in hexagonal representation), in reasonable agreement with the literature data [23–25]. The presence of about 1% of a cubic phase was also found.

The annealed ingots were ground and sieved through a sieve with mesh size of 0.25 mm. Samples for the thermoelectric property measurements were prepared from the powder by hot pressing at 653 K and at pressure of 500 MPa in the form of $9 \times 9 \times 15$ mm parallelepipeds and $9 \times 2 \times 15$ mm plates. The samples were additionally annealed at 770 K for 100 hours and then cooled in furnace.

Samples in Pei group were prepared using a similar technique with some difference in the parameters: homogenizing annealing was carried out at a higher temperature (923 K) during 72 h, and hot pressing was carried out at 873 K and 80 MPa during 40 min. The samples for thermoelectric property measurement were made in the form of $6 \times 6 \times 10$ mm parallelepipeds.

Thermoelectric properties were measured at Ioffe Institute using two original experimental units. Seebeck coefficient, electrical conductivity and thermal conductivity were measured simultaneously in the range of 300–800 K. Classical, steady-state method was used for thermal conductivity measurement [16]. Electrical conductivity was measured using a DC 4-probe method and Seebeck was measured using a differential method. Measurement error for *ZT* when using this measurement system does not exceed 10%. *In situ* measurements of Seebeck coefficient and electrical conductivity during thermal cycling and annealing were carried out using a system that enabled measurements in dynamic temperature regime with temperature variation rate from 0 to 10 K/min [26,27].

3. Experimental results and discussion

The thermoelectric property measurements of $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy samples prepared at Ioffe Institute and at Tongji University ((designated as FTI and Tongji, respectively) are shown in Fig. 1 together with the data from [9]. In general, taking into account the differences in the sample preparation techniques, the results are in quite good agreement with each other. Seebeck coefficient of the FTI sample is greater than that of the Tongji sample, but the latter has a higher electrical conductivity. The most evident differences are observed in thermal conductivity. Despite a slightly lower electrical conductivity, thermal conductivity of the FTI sample is considerably higher than the thermal conductivity of the sample from the Tongji group. However, the thermoelectric figure of merit is practically the same for both samples, and at the same time it is significantly lower of the literature result [9], mainly due to the significantly lower thermal conductivity observed in ref. [9].

Further, more detailed examination has shown that the electronic properties (Seebeck coefficient and electrical conductivity) of the Tongji and FTI samples are almost identical. The differences that can be seen in Fig. 1 are mostly associated with different thermal history of the samples. This is demonstrated in Fig. 2, which shows temperature dependences of Seebeck coefficient

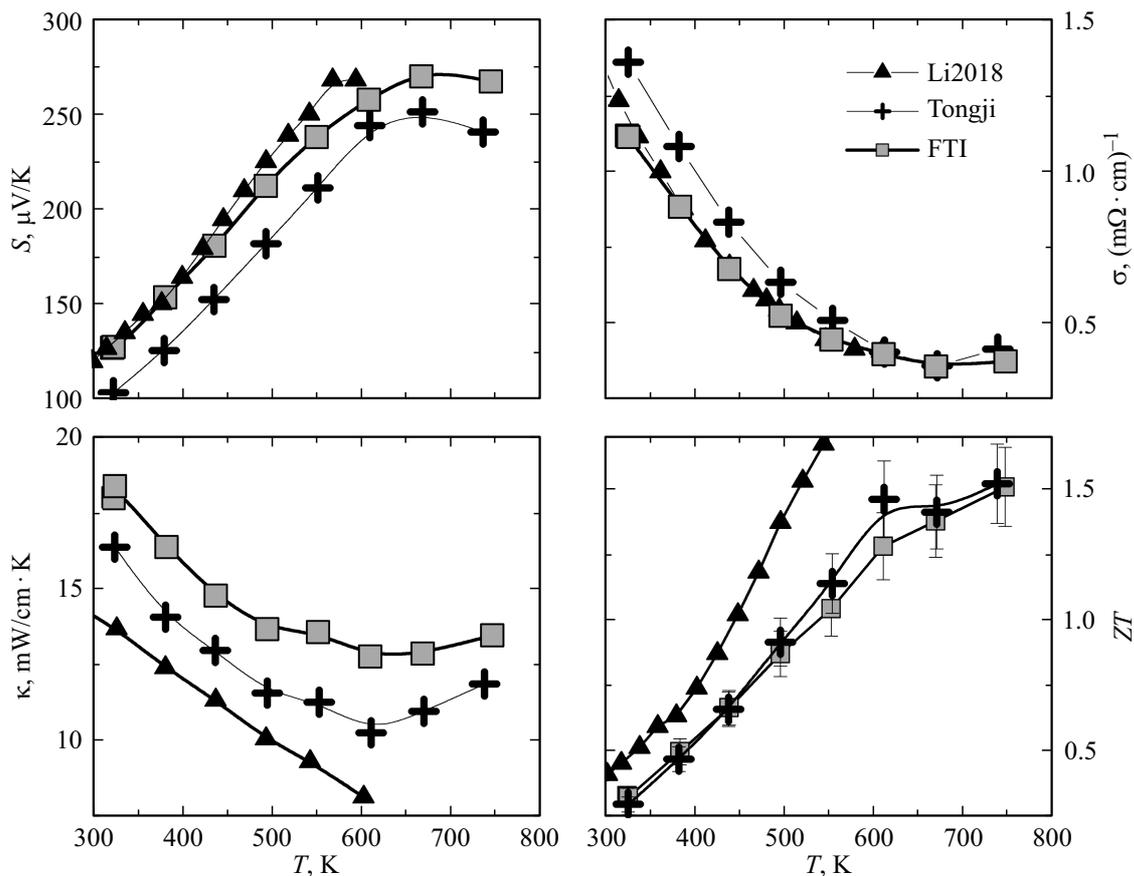


Figure 1. Temperature dependences of Seebeck coefficient, electrical conductivity and dimensionless thermoelectric figure of merit of $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloys. For comparison, the results from [9] (Li2018) are also shown.

and electrical conductivity of the Tongji sample measured with heating up to 800 K and subsequent cooling. These measurements were carried out after the measurements

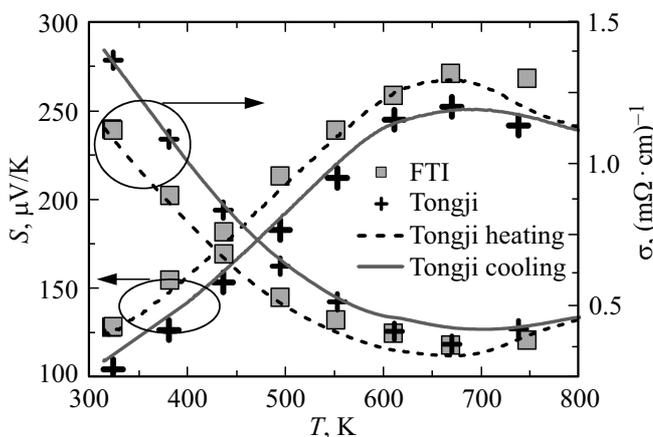


Figure 2. Temperature dependences of the Seebeck coefficient and electrical conductivity of the $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy samples. The symbols represent the results of the measurements under stationary conditions on heating for the FTI and Tongji samples, shown in Fig. 1. The lines are the results of the subsequent measurements of the Tongji sample during heating and cooling at a rate of ~ 5 K/min.

shown in Fig. 1. On the second heating, the temperature dependences of both properties of this sample coincide with the corresponding dependences of the FTI sample measured at the previous step (Fig. 1), whereas the dependences measured during cooling match the dependences for the same sample (Tongji) that were measured at the previous step (Fig. 1). Thus, the electronic properties of the samples from both groups coincide within the measurement accuracy taking into account the thermal history of these samples.

Note, the alloy does not return into the initial low-temperature state upon cooling at a rate of ~ 5 K/min after transition in the high-temperature state on heating the sample above 750 K. For the reverse transition into the low-temperature state to take place, long-term annealing at sufficiently high temperature is required. Before the measurements, shown in Fig. 1, the FTI sample was annealed at 770 K and then slowly (during ~ 24 h) cooled down in a furnace. During this slow cooling, a transition into the low-temperature structural state occurs. Therefore, the measurements on this sample during heating (Fig. 1) characterize the properties of the low-temperature state of $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy. The Tongji sample was quickly cooled after the hot pressing and no transition into the low-temperature state occurred in it. Therefore, the measure-

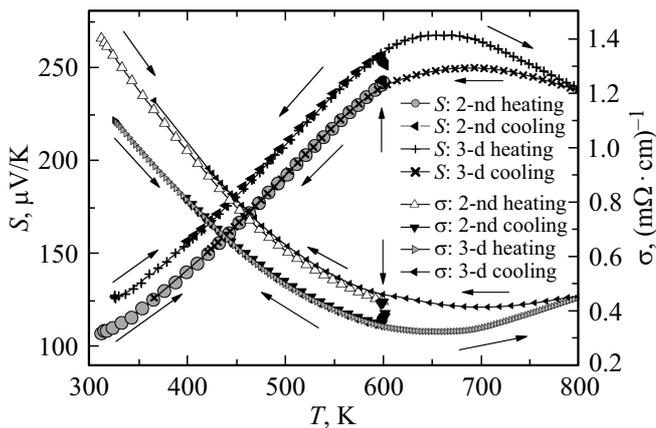


Figure 3. Temperature dependences of the Seebeck coefficient and electrical conductivity of the Tongji $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy sample. The sample was heated from the room temperature up to 600 K and annealed at this temperature *in situ* during 10 hours and then cooled down to the room temperature. Then, the cycle was repeated with heating up to 800 K and cooling down to the room temperature. The arrows show the temperature variation direction.

ments of this samples during the initial heating (Fig. 1) yields the properties of the metastable high-temperature state of the alloy. Further cooling in the steady-state measurement system is carried out slowly, thus the temperature is reduced from 750 K to 500 K in $\sim 3\text{--}4$ hours. During this period, the reverse transition into the low-temperature structural state takes place. Therefore, the measurements during the next heating of the sample (Fig. 2) reflect the properties of the low-temperature state and coincide with that for the FTI sample.

Figure 3 shows the evolutions of the Tongji sample properties for this alloy during heating-cooling and annealing at the temperature lower than the temperature of the phase transition into the high-temperature state. Before this measurement, the sample was in a metastable high-temperature state as a result of the first heating-cooling cycle, shown in Fig. 2. The sample was heated to 600 K and annealed *in situ* at this temperature during 10 hours. As a result of annealing, phase transition into the low-temperature structural state takes place with the Seebeck coefficient (at 600 K) increased by $\sim 8\%$ and electrical conductivity reduced by more than 20%. The alloy properties during thermal cycling are completely reproducible provided that the appropriate heat treatment conditions are selected: during thermal cycling with relatively quick heating and cooling rate ($\sim 1\text{ K/min}$ or higher), the sample heated up to $\sim 800\text{ K}$ will always remain in the high-temperature state; during thermal cycling with intermediate annealing (after heating up to 800 K) at 600–650 K, return into the low-temperature state will take place with corresponding changes in the properties. The characteristic time of transition from the high-temperature state of $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy into the low-temperature state at 600 K is about 5-10

hours. It is evident that this time is strongly dependent on the annealing temperature.

4. Conclusion

The thermoelectric properties of the $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy samples prepared in two different laboratories using similar, but not identical techniques, measured using the equipment from one of the laboratories (FTI) generally coincide. This is indicative of good reproducibility of properties of these alloys and resistance to minor changes in the material synthesis and sample preparation procedures.

The thermoelectric properties of alloys depend on the thermal history of the sample due to the presence of phase transition between two structural modifications and possible phase separation in the range of 600–800 K. The high-temperature state of the alloys upon cooling at a rate of the order of 1 K/min or higher is preserved at low temperatures for a long time. At a temperature of 600 K, the transition from the high-temperature to the low-temperature state is completed upon annealing for a time of about 5 hours.

The parameter of thermoelectric figure of merit ZT of $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloys is close to that of $\text{Ge}_{0.91}\text{Pb}_{0.05}\text{Bi}_{0.04}\text{Te}$ alloys [19]. The maximum ZT of $\text{Ge}_{0.91}\text{Pb}_{0.05}\text{Bi}_{0.04}\text{Te}$ alloy is slightly higher than that of $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy, however, the average values of ZT over 320–740 K coincide and are equal to 0.97. Therefore, $\text{Ge}_{0.86}\text{Pb}_{0.1}\text{Bi}_{0.04}\text{Te}$ alloy may be more preferable in terms of further applications. However, this issue requires additional investigations, in particular, of mechanical properties and thermal stability of the alloys.

In this work, we did not study the influence of thermal history on the thermal conductivity of alloys due to the laboriousness of such studies and the lack of samples of the required size. Such research is clearly necessary and is planned for the near future.

Funding

The research was supported by the Russian Foundation for Basic Research, Grant No. 18-52-80005 (BRICS) and the National Natural Science Foundation of China, Grant 51861145305 (BRICS project).

Conflict of interest

The authors declare that they have no conflict of interest.

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