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Thermoelectric Properties of Ternary Ge-added $In_{10}Sb_{10}Ge$ Alloy

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【Abstract】 It was reported that InSb single crystal has an excellent thermoelectric power factor due to its extremely high carrier mobility. In the present work we prepared Ge-added ternary In-Sb-Ge alloy using a mild solidification technique and evaluated its thermoelectric properties in the temperature range from 320 K to 708 K. Observations reveal that the microstructure is composed of the InSb phase with Ge-containing phase embedded, which is in agreement with the X-ray analysis. Measurements show that the lattice thermal conductivities are very low over the entire temperature range, especially at low temperatures, while the electronic component reduces from 6.3 to 2.4 ($W \cdot m^{-1} \cdot K^{-1}$) with increasing temperature, and plays a dominant role in carrying heat. The highest thermoelectric figure of merit ZT of 0.18 can be achieved for $In_{10}Sb_{10}Ge$ at 708 K.

【Key words】 thermoelectric properties; ternary $In_{10}Sb_{10}Ge$ alloy; spark plasma sintering

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添加 Ge 的 $In_{10}Sb_{10}Ge$ 三元合金热电性能

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【摘 要】 InSb 单晶材料具有相当高的载流子迁移率，因而有良好的电学性能。本文采用缓慢凝固技术制备出 In-Sb-Ge 三元合金，并在 320 K 到 706 K 的温度范围内测量其热电性能。显微结构观察表明，In-Sb-Ge 三元合金的微观组织由嵌入含锗相的锑化铟相组成，这一结果与 X 射线衍射分析的结果相符。性能测试表明，其晶格热导率在整个温度范围内都非常低，尤其在低温下更低，而载流子热导率随温度的升高，从 6.3 ($W \cdot m^{-1} \cdot K^{-1}$)降低到 2.4($W \cdot m^{-1} \cdot K^{-1}$)，在热传输过程中起主要作用。在 708 K 时 $In_{10}Sb_{10}Ge$ 合金的最高 ZT 值为 0.18。

【关键词】 热电性能；$In_{10}Sb_{10}Ge$ 三元合金；放电等离子烧结

1 Introduction

InSb has the highest electron mobility among all binary III V compound semiconductors[1], and has a narrow band gap of 0.18 eV at room temperature[2], therefore, it has many applications in the electronic fields. Currently, many electronic devices have been scaled down, and accordingly, the electric power necessary for their operations has become lower. At

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this point, InSb is the most appropriate material because the device operation voltage using InSb is expected to be very small. The thermal conductivity of single crystal bulk InSb is large, and has been reported in the range from 11 to 18 W m^{-1} K^{-1}[3], but it is the lowest one among four III V compounds InSb, InAs, GaAs, and InP[4]. For the commercial application point of view, we still need some decrease of the thermal conductivity in order to obtain high thermoelectric (TE) figure of merit (ZT).

In recent years, many works have been done in order to improve TE performance of InSb. Yamaguchi studied the TE properties of a Te doped InSb bulk single crystal, and obtained the maximum TE figure of merit of 0.6 at 673 K[5]. Mingo reported that InSb is a promising candidate for which nanowire around 10 nm thick might suffice to obtain a reasonably high ZT value[6], possibly due to the reduction of nanowire thickness that yields strong boundary scattering of the mid frequency phonons.

InSb alloy exhibits a p-type semiconductor behavior probably because of the vacancy at In sites. For the Te doped InSb bulk single crystal, negative Seebeck coefficients can be obtained[5], and the element Te may provide extra electrons, so that it plays a donor action in the bulk InSb. A similar achievement can also be expected if element Ge with four-valence is doped. Besides, the larger the mass difference in the alloy, the larger the reduction of the lattice thermal conductivity[7]. The atomic mass difference between the guest and host plays a key role on the reduction in the lattice thermal conductivity[8,9], the maximal phonon scattering by mass fluctuation between Ge and In (Sb) should therefore be expected in a defected crystal structure because the maximum atomic mass difference can be achieved on one or more lattice sites.

In the present work, a Ge-added ternary $In_{10}Sb_{10}Ge$ alloy was prepared using spark plasma sintering, and its TE properties were evaluated in the temperature range from 320 K to 708 K.

2 Experimental

The mixture, composed of the three elements In, Sb and Ge with a purity of higher than 99.999%, according to the formula $In_{10}Sb_{10}Ge$, was loaded into the silica tube under vacuum and then melted at 1273 K for 24 h, during which 30 s rocking every 1 h was conducted to ensure that the composition was homogenous without segregation. After cooling to 833 K in the furnace for the molten mixture, a subsequent cooling in the air was conducted. The ingot was pulverized and then ball milled in a stainless steel bowl at a rotation rate of 350 rpm for 5 h. Subsequently, the dried powder was quickly sintered at 723 K using a spark plasma sintering apparatus (SPS-1030) with designed sintering program at a pressure of 40 MPa. The densities of the sintered samples were measured using an Archimedes method, and each sample was cut into 3 mm slices measuring 2.5×15 mm^2 from the sintered block with the size of $\phi 20 \times 2.5$ mm^2 for property measurements.

The electrical properties involving the Seebeck coefficients and electrical conductivities as a function of temperature were measured using an apparatus (ULVAC ZEM-2) in a helium atmosphere. The thermal diffusivities were measured by a laser flash method using Netzsch LFA 457 apparatus, and the thermal conductivities were calculated from the densities, specific heats and thermal diffusivities. The structural analysis of powders for the alloys was made by a powder X-ray diffractometer (XRD-98) using Cu K radiation ($\lambda = 0.154\ 06$ nm), using a scan rate of 4° min^{-1} to record the patterns in the range of $10° \leqslant 2\theta \leqslant 90°$. The microstructures of the bulk sample were observed using Field Emission Scanning Electron Microscopy (FESEM) (JSM 6700F), and the chemical compositions in different phases in the sample were observed by an Electron Probe Micro analyzer (EPMA) (JXA-8100) with an analyzing accuracy of higher than 97%.

3 Results and discussion

The XRD patterns of the alloys $In_{10}Sb_{10}Ge$ and InSb were presented in Fig. 1, where we observed a two phase structure, one phase corresponding to the bulk phase InSb, and another to the single element

Ge that is insoluble. After a close observation, we find that there is a very small decrease for all the interplanar distances (d) and shift for all the diffraction peaks toward large angles after Ge-addition, implying that the lattice constants of the ternary alloy decrease, and some Ge atoms are incorporated into the InSb matrix. Although InSb has vacancies at in sites, which is capable of taking foreign elements to a some degree, there is still a limited solubility for element Ge. An observation of the microstructure of the Ge-added sample reveals that some black Ge-containing chunks were embedded in the InSb matrix, with the size varying from several dozen nanometers to several hundred micrometers, as shown in Fig. 2 (a, b). The image with a higher magnification indicates some black Ge-containing chunks with the size of about 100 nm in the matrix (Fig. b), these chunks might include the insoluble Ge, which was identified using XRD analyzer. Since the chunks are too small, the surrounding elements such as In and Sb are therefore identified at the same time, and also because the Ge atoms that were incorporated into the matrix are too limited to be identified by EPMA.

Fig. 3 shows the Seebeck coefficients (α) of the

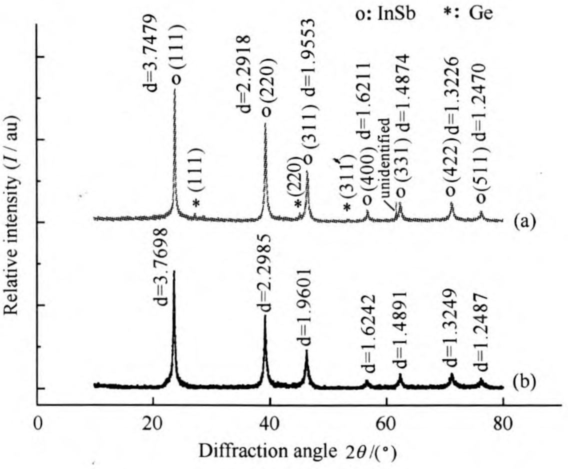

Fig. 1　XRD patterns of the powders for $In_{10}Sb_{10}Ge$ and InSb. (a) $In_{10}Sb_{10}Ge$; (b) InSb.

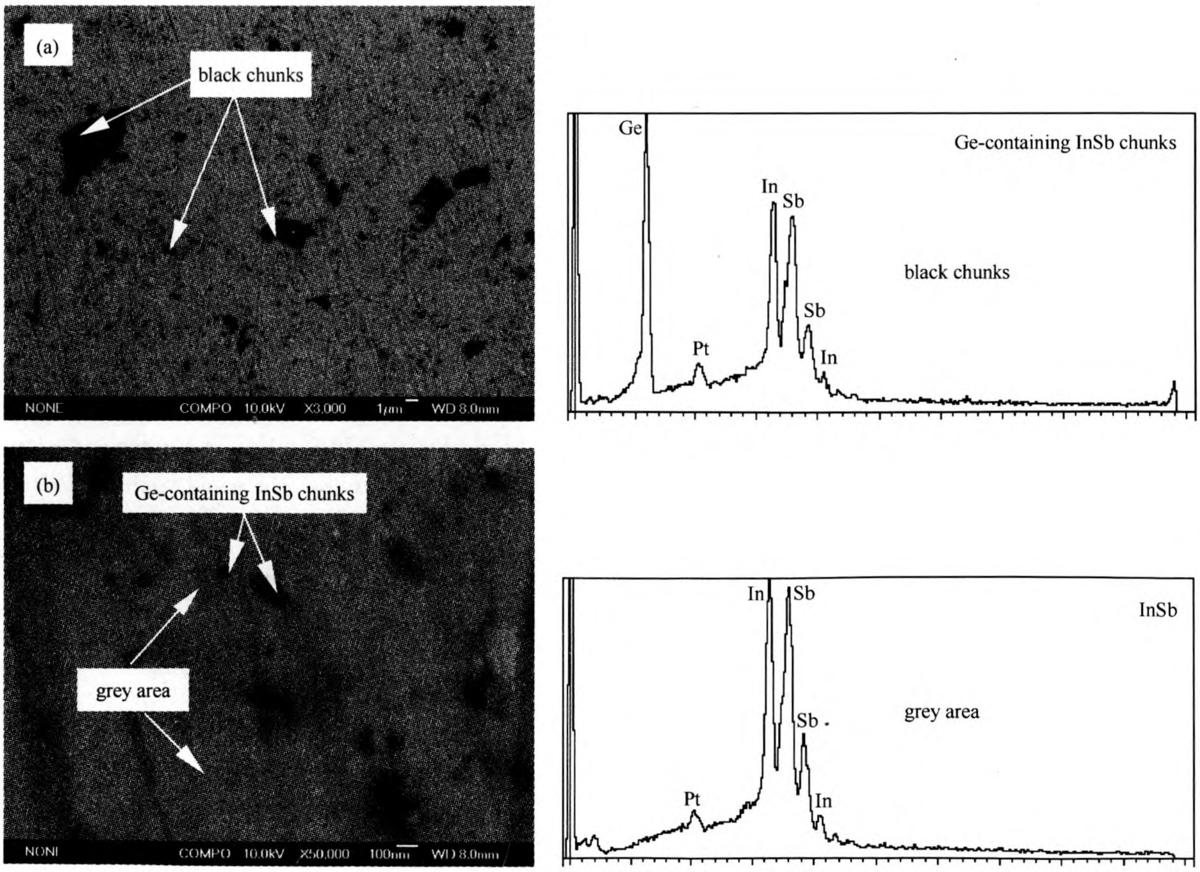

Fig. 2　(a, b). Back scattered electron images (left side) and EPMA results (right side) of the bulk samples. (a): Microstructure of $In_{10}Sb_{10}Ge$, some Ge rich black chunks randomly embedded in the InSb matrix, and the remaining grey area represents InSb; (b): Image with high magnification of the bulk sample.

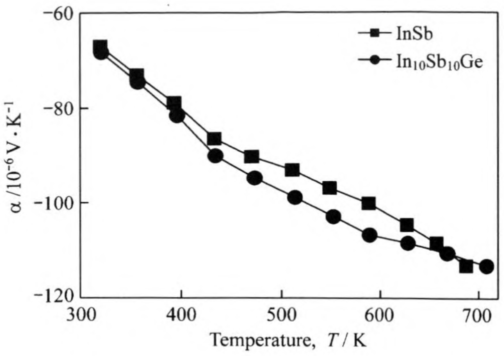

Fig. 3 Seebeck coefficients as a function of temperature for the alloys $In_{10}Sb_{10}Ge$ and InSb prepared by spark plasma sintering

alloys as a function of temperature. The values are negative for both InSb and Ge-added InSb samples, indicating n-type conducting behavior. Similar behaviors were reported by Biefeld *et al.*, who found that Sn is a donor in InSb grown by MOVPE[10]. But Ehsani, *et al.* reported that Si is a well behaved p-type dopant in GaSb and $Ga_{0.8}In_{0.2}Sb$ compounds[11]. The values for the two samples are almost the same, suggesting that there is a similar basic conducting mechanism upon adding Ge. The values of the electrical conductivities (σ) as a function of reciprocal temperature are shown in Fig. 4, about a decrease by a factor of 1.3 to 1.5 was observed after adding Ge, possibly because of the decrease of the carrier mobility, according to the expression $\sigma = ne\mu$, where n is a free carrier (electron) concentration, μ is the mobility.

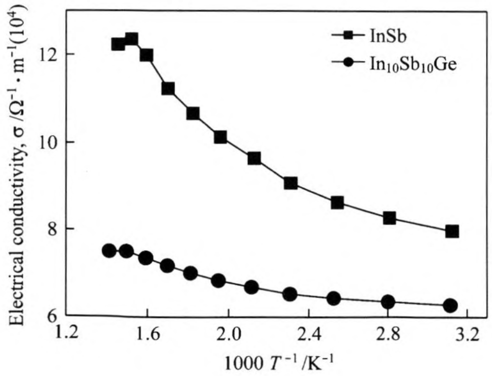

Fig. 4 Electrical conductivities as a function of reciprocal temperature for the alloys $In_{10}Sb_{10}Ge$ and InSb prepared by spark plasma sintering

The total thermal conductivity (κ), is the sum of the electronic contribution, κ_e, and lattice component, κ_L, and their values as a function of temperature are presented in Fig. 5. The $In_{10}Sb_{10}Ge$ alloy exhibits the total thermal conductivity from 6.7 (W · m^{-1} · K^{-1}) at 320 K to 3.7 (W · m^{-1} · K^{-1}) at 708 K, higher than those of Bi_2Te_3, ZnSb and PbTe based alloys[12-14], but much lower than those of undoped InSb, which ranges from 11 to 18 (W · m^{-1} · K^{-1})[3]. The electronic component, κ_e, which is estimated using the Wiedemann Franz law, $\kappa_e = L\sigma T$, where L is the Lorenz constant ($L = 2.45 \times 10^{-8}$ V^2K^{-2})[15], ranges from 2.4 to 6.3 (W · m^{-1} · K^{-1}), and plays a dominant role in carrying heat. Although a decrease in the electrical conductivity after Ge addition yields low electronic contribution to the total thermal conductivity, the lattice contribution, κ_L, takes only a small part in the total κ over the entire temperature range, suggesting that in the Ge added InSb there are two phonon scattering mechanisms prevailed, one is carrier phonon scattering caused by the electrons, and the another is the grain boundary scattering to the mid frequency phonons caused by the Ge-containing chunks.

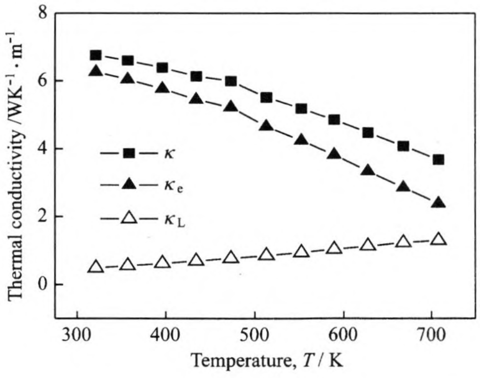

Fig. 5 Thermal conductivities as a function of temperature for the alloy $In_{10}Sb_{10}Ge$ prepared by spark plasma sintering

The TE figure of merit (ZT) for $In_{10}Sb_{10}Ge$ is plotted against temperature in Fig. 6. The ZT value enhances with increasing temperature, and reaches the highest at 0.18 at 708 K. Although the value is not comparable to those reported in our previously work for the ternary Sb-Te-Ge (Ga) alloys[16,17], if we were able to be assisted by the thermal conductivities of 11～18 W · m^{-1} · K^{-1} reported in *ref.* [3] and calculated the ZT values of InSb, we could estimate that the maximum ZT value of InSb is less than 0.1 at the corresponding temperature, hence the $In_{10}Sb_{10}Ge$ already outperforms the TE performance of Ge-free InSb. If we would optimize the chemical compositions to the current $In_{10}Sb_{10}Ge$ based alloys, in order to further increase the Seebeck coefficient without sacrificing the electrical conductivities, a significant improvement of the TE property of this ternary alloy can be expected.

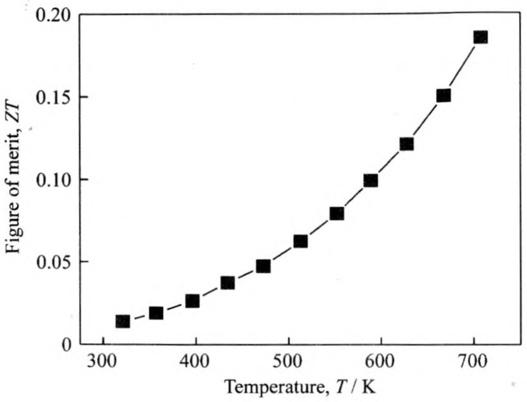

Fig. 6 Relationship between temperature and the thermoelectric figure of merit (ZT) in 320-708 K for the alloy $In_{10}Sb_{10}Ge$ prepared by spark plasma sintering

4 Conclusions

A Ge-added ternary alloy $In_{10}Sb_{10}Ge$ was prepared using spark plasma sintering and its TE properties were evaluated in the temperature range from 320 K to 708 K. An analysis reveals that the microstructure is composed of two phases, with one phase being insoluble Ge that is embedded in the matrix, and another being InSb. The Seebeck coefficients are almost the same as those of Ge free InSb, but the lattice thermal conductivities are very low and the highest ZT value of 0.18 is obtained at 708 K. A big improvement of TE property can be expected if an optimization of the chemical compositions to the current $In_{10}Sb_{10}Ge$ based alloys would be made.

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