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Thermoelectric properties of $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composites prepared by mechanical blending and in-situ polymerization ①

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[Abstract] $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composites were prepared by mechanical blending and in-situ polymerization, and their transport properties were measured. It was found that for the composites with 1%, 3%, 5% and 7% polyaniline (mass fraction) respectively, which were prepared by mechanical blending, the power factors decrease by about 30%, 50%, 55% and 65% compared with the $Bi_{0.5}Sb_{1.5}Te_3$ samples, which is mainly due to the remarkable decreases of the electrical conductivity. The electrical conductivity and power factor of the composites samples with 7% polyaniline prepared by in-situ polymerization are higher by about 65% and 60%, respectively, than that of the corresponding samples prepared by mechanical blending.

[Key words] thermoelectric property; $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composite; mechanical blending; in-situ polymerization
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1 INTRODUCTION

Thermoelectric materials are used to convert thermal energy directly to electric energy or in reverse[1~4]. The performance of the thermoelectric materials is determined by the Seebeck coefficient α, the electric conductivity σ, and the thermal conductivity κ, or by their combination called the figure of merit of the material: $Z = \alpha^2\sigma/\kappa$. The larger the Z, the higher the conversion efficiency of thermoelectric generator. So ways of improving the thermoelectric materials performance include increasing the power factor $\alpha^2\sigma$ or decreasing the thermal conductivity κ. The power factor $\alpha^2\sigma$ mainly depends on the materials character, which is typically optimized as a function of the carrier concentration through doping in order to give the largest Z. The thermal conductivity results mainly from the scattering of phonons, it can be decreased through the adjusting of crystal structure and the microcosmic morphology. There are many researches have been done in recent years to develop novel materials with a low thermal conductivity and therefore to improve the thermoelectric performances. The most interesting new developed materials are filled skutterudites[5,6], clathrate structured compounds[7] and quasicrystal materials[8]. The thermal conductivities of these materials are largely reduced because the phonons are strongly scattered by the inharmonic vibration of the loose bonded foreign atoms or by the asymmetric crystal lattices. However, these novel materials have the lower Seebeck coefficients than the traditional thermoelectric materials such as Bi_2Te_3 and $FeSi_2$ based alloys.

Other possible ways to reduce the thermal conductivity include using fine grain sizes[9] or multiphase structures to enhance the phonon scattering by grain boundaries or phase boundaries. Considering the fact that some conducting polymers such as polyaniline have relatively high ratio of electric conductivity to thermal conductivity σ/κ[10,11], $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composites have been prepared by mechanical blending[12] and in-situ polymerization, and have been studied in the present work.

2 EXPERIMENTAL

Elemental bismuth, antimony and tellurium (99.999%, mass fraction) granules were weighted in a stoichiometric mole ratio of 0.5∶1.5∶3.0 and sealed in a vacuum quartz tube (10^{-3} Pa, d 30 mm × 120 mm). The tube was heated up to 750 ℃ then held for about 8 h with irregular shake to ensure the homogeneity of the molten. The $Bi_{0.5}Sb_{1.5}Te_3$ green alloy was further ball milled for 4 h in ligroin with the milling rotation rate being 150 r/min, and the mass ratio of stainless balls to alloy powders being 15∶1.

$HClO_4$ doped polyaniline were synthesized by electrochemical method. The dark green polyaniline were washed several times with distilled water and dried in vacuum at 60 ℃ for 60 h. Then the polyaniline powders with the mass ratio of 1%, 3%, 5% and 7% were blended into the $Bi_{0.5}Sb_{1.5}Te_3$ alloy powders by grinding them together in an agate mortar. The hybrid powders were pressed into pellet shaped samples with a gauge of d 10 mm × 5 mm presunder sure of about 1 GPa. To characterized the

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properties of the polyaniline, a cylinder sample (*d* 6 mm × 10 mm) was pressed from the polyaniline powders with about 800 MPa at room temperature. Compared with the samples prepared by mechanical blending, the other samples were also prepared by in-situ polymerization. The certain $Bi_{0.5}Sb_{1.5}Te_3$ powders dipped into aqueous solution of aniline and $HClO_4$ (1.0 M) for about 1.5 h, and then which were added in drops by the $(NH_4)_2S_2O_8$ aqueous solution, the solution have been changing gradually into dark green, and the polymerization is completed. Before the polymerization, the suitable reagent dosage were used according the 100% polyaniline production rate in order to provide the composites with the 7% polyanline; after the polymerization, the mass analyses also show that the obtained composites contain about 7% polyaniline (mass fraction).

The Seebeck coefficients were measured from 300 to 388 K in vacuum using a 10 K temperature difference between two ends of the sample. The electric conductivities were measured by four-probes method under vacuum in the same temperature range of Seebeck coefficient measurements.

3 RESULTS AND DISSCUSSION

Fig. 1 shows that the polyaniline sample is a P-type semiconducting polymer with a maximum Seebeck coefficient of about 6 μVK^{-1} at 360 K. The electric conductivity of the polyaniline sample is about 2 000 $\Omega^{-1}m^{-1}$ at 300 K and 2 600 $\Omega^{-1}m^{-1}$ at 370 K. Both Seebeck coefficient and electric conductivity are much lower than that of Bi_2Te_3 based thermoelectric alloys. However, considering the low thermal conductivity of polyaniline, about one-third or even smaller than that of Bi_2Te_3 based thermoelectric alloys, polyaniline additives would still helpful to improve the thermoelectric properties of the alloys.

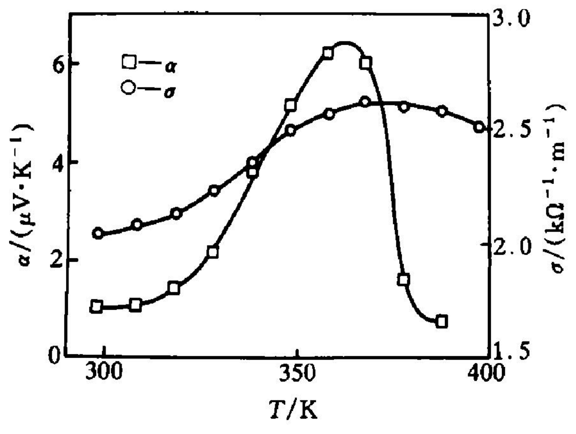

Fig. 1 Transport properties of polyaniline as function of temperature

Fig. 2 shows that the transport properties of $Bi_{0.5}Sb_{1.5}Te_3$ and the $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline samples with different contents of polyaniline additives. It can be seen that the average Seebeck coefficients of the composites samples with 1% polyaniline decrease about 9% compared with the $Bi_{0.5}Sb_{1.5}Te_3$ sample in the measuring temperature range. However, the further increases of polymer content in the composite materials do not lead to the remarkable decreases of the Seebeck coefficients. This means that although the polymer component will decreases the Seebeck coefficients of the composites since the polymer has a much smaller α value than the alloy, the dispersed polymer powders would enhance the scattering of carries and thus would increase the α values of the composite materials to a certain extent on the other hand.

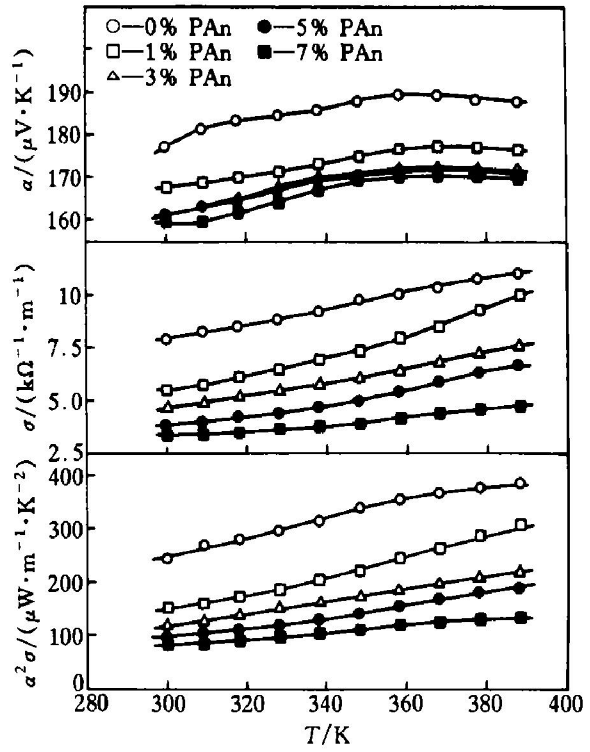

Fig. 2 Transport properties of $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composites prepared by mechanical blending

With the increase of the polyaniline content in the composite materials, the electrical conductivities decrease more significantly than the Seebeck coefficients, as shown in Fig. 2. The remarkable decrease of the electrical conductivities is the major origin of the decrease on the power factor $\alpha^2\sigma$ for the composites samples. From Fig. 2, it can be seen that compared with the $Bi_{0.5}Sb_{1.5}Te_3$ sample, the power factors decrease about 30%, 50%, 55% and 65% for the composites samples with 1%, 3%, 5% and 7% polyaniline, respectively, which is mainly due to the remarkable decreases of the electrical conductivities of the composites samples.

Transport properties of the $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composites prepared by mechanical blending and in-situ polymerization, respectively, are shown in Fig. 3.

Compared with that of the mechanical blending

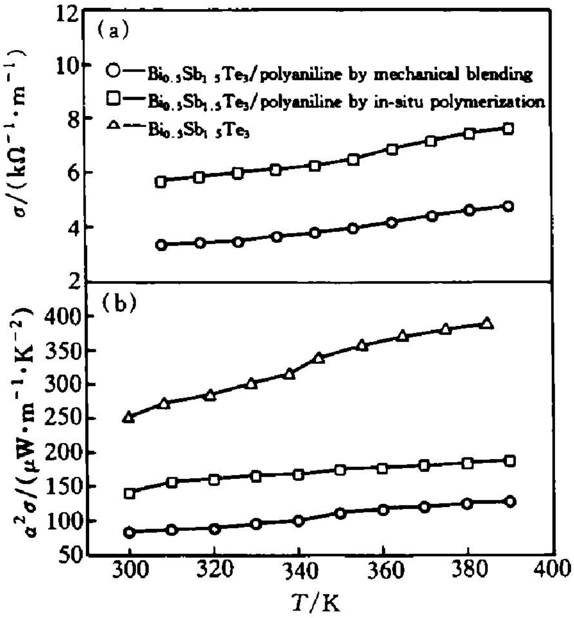

Fig. 3 Transport properties of $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline prepared by mechanical blending and in-situ polymerization

samples, the average electrical conductivity of the in-situ samples increases about 65%, which results in the increase of the power factor. The power factor of the in-situ samples increases about 60% compared with that of the mechanical blending samples and only decreases about 45% compared with that of the $Bi_{0.5}Sb_{1.5}Te_3$ alloy samples. The in-situ samples reduce the contact resistance between $Bi_{0.5}Sb_{1.5}Te_3$ inorganic phases and the polyaniline organic phases, and eventually obtain the improved power factor.

3 CONCLUSIONS

The $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composites have been prepared by mechanical blending and in-situ polymerization, and their transport properties show that for the $Bi_{0.5}Sb_{1.5}Te_3$/polyaniline composites prepared by mechanical blending, the power factors of composites with polyaniline (mass fraction) 1%, 3%, 5%, 7% decrease respectively about 30%, 50%, 55% and 65% compared with those of the $Bi_{0.5}Sb_{1.5}Te_3$ alloy samples, which results from the remarkable decrease of the electrical conductivity. For the composites with 7% polyaniline, the electrical conductivity and the power factor of the in-situ samples increase about 65% and 60%, respectively, than those of the mechanical blending samples, which suggests that the in-situ samples reduce the contact resistance between multiphase and improve the power factor of the composites.

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