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RAPID COMMUNICATION

Melting and solidification of bismuth antimony telluride under a high magnetic field: A new route to high thermoelectric performance

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Abstract
Imposing an intensity variable high static magnetic field during a traditional melting-solidification (MS) method has been used as a new method to prepare p-type bismuth antimony telluride thermoelectric materials in this work. On this basis, we present a systematic study of the nucleation, crystal orientation, microstructure, electrical and thermal transport properties of the obtained alloy ingots solidified under different magnetic field intensities. A *c*-axis alignment of bismuth antimony telluride in the direction perpendicular to the magnetic field, formation of BST_{II} nanorods, and a simultaneous optimization of the electrical and thermal transport properties have been observed. Consequently, an enhanced $ZT_{max}=1.71$ at 323 K has been achieved in a polycrystalline $Bi_{0.5}Sb_{1.5}Te_3$ sample solidified under a 2 T magnetic field.

Introduction

Thermoelectric (TE) materials, which can directly convert heat to electricity or vice versa, have aroused more and more attention in recent years. The efficiency of a thermoelectric device is known to be determined by the dimensionless figure of merit ZT, which is derived from three interrelated parameters: the Seebeck coefficient *S*, the electrical resistivity ρ, the thermal conductivity κ and the absolute temperature *T*, as $ZT=S^2T/\rho\kappa$ [1,2]. Therefore, high power factor (S^2/ρ) and low thermal conductivity are essential for developing high ZT materials for power generation or refrigeration [3]. Currently, Bi_2Te_3 based alloys [4] are the best materials available for commercial application in TE devices around room temperature due to their excellent TE performance in this temperature range. Commonly, Bi_2Te_3 based ingots are single crystalline or highly aligned polycrystalline

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fabricated by Bridgman, Zone melting and Czochralsky techniques [5], with the preferred crystal orientation and the high ZT along the plane perpendicular to the *c*-axis. However, the poor mechanical properties and the highly energy-consuming and extra time-taking preparation process limit their broader application. Thereby, a great deal of efforts have been made to improve both the mechanical and TE performance of polycrystalline bismuth antimony telluride bulk TE materials in recent years, and some encouraging results have been achieved by means of powder metallurgy (PM) based methods, like MA-PAS, hot forging, and so on [6,7]. However, the multi-step process and complicated equipment demand also somewhat devalue the PM-based methods make them less competitive for large scale industrial production of high performance Bi_2Te_3 based bulk TE materials.

As the most cost-effective technology for large scale production, traditional melting-solidification (MS) method has been widely used to produce metallic engineering materials. However, it has hardly been employed to fabricate thermoelectric materials yet. In our previous work [8], we reported a trial work on preparation of bismuth antimony telluride polycrystalline ingots by this way, high density ingots with good mechanical property were obtained directly in a relatively short duration, which means that this traditional method would be a very promising technology for large scale production of bismuth antimony telluride bulk TE materials if their TE properties can be further enhanced and are comparable to those of bulk single crystal or polycrystalline counterparts.

As is well known, for a given TE material, the thermoelectric and mechanical properties are closely related with its microstructure. When it comes to the MS method, the microstructure of the solidification ingot is specifically related to the thermodynamic and kinetic behavior of the nucleation and growth of the material. As a noncontact extreme physical tool, high magnetic field has long been applied in various areas, like materials science, applied physics, chemical synthesis, biomedicine, and so on [9-11]. At present, the application of high magnetic field in the solidification of metals and alloys has been widely investigated [12], and a significant influence on the liquid metal motion, nucleation, crystallization, microstructure and crystal orientation has been reported in many metallic material systems [13]. Based on this, although high magnetic field has rarely been tried in thermoelectric semiconductor or semimetal materials thermoelectric materials, it offers a possibility of regulating the thermodynamics and kinetics behavior of solidification thus the microstructure of TE materials. Therefore, in this work, a high static magnetic field has been employed during the melting-solidification process of bismuth antimony telluride ($Bi_{0.5}Sb_{1.5}Te_3$), the effect of magnetic field on the nucleation and crystal growth, crystal orientation, as well as the electrical and thermal transport properties of the bismuth antimony telluride alloys has been investigated systematically. By this means, the microstructure has been regulated effectively, and a simultaneous optimization of the electrical and thermal transport properties of bismuth antimony telluride alloys has been achieved, eventually, an improved $ZT_{max}=1.71$ at 323 K was obtained in polycrystalline $Bi_{0.5}Sb_{1.5}Te_3$ solidified under a 2 T magnetic field.

Material and methods

Preparation

A traditional physical metallurgical strategy was employed to prepare the starting materials ($Bi_{0.5}Sb_{1.5}Te_3$ with 3 wt% Te) as illustrated in the supporting information ESI1. During the solidification under magnetic field, the re-melting temperature was set at 1023 K for 30 min, the melt was then cooled to 823 K by furnace cooling and then quenched to room temperature.

Characterization and measurements

Differential thermal analysis (DTA) was performed with a home-made DTA apparatus which can be operated in a magnetic field [14]. Appropriate bismuth antimony telluride powders were loaded in a quartz crucible with alumina powders as the reference. The samples were heated to 1023 K at a rate of 5 K/min, kept for 40 min and then cooled down to room temperature at 5 K/min. The temperature difference between the sample and the reference during the heating and cooling cycles was monitored and measured under a flowing argon atmosphere (50 mL/min). The phase constitution and crystal orientation of the samples were analyzed by X-ray diffraction (XRD) (Philip X'Pert Pro, with Cu Kα radiation, $\lambda=0.15418$ nm). The morphology and composition of the bulk specimens were analyzed with an environmental scanning electron microscope (ESEM), High resolution transmission electron (HRTEM) images and energy dispersive X-ray spectroscopy (EDS) microanalysis were performed by a transmission electron microscope (JEOL JEM-2100) in bright-field mode with an acceleration voltage of 200 kV equipped with an energy-dispersive X-ray spectroscopy (EDS) (FEI Quanta 200). Seebeck coefficient and electrical resistivity were simultaneously measured in a Namicro-II custom designed equipment. Thermal conductivity was calculated in the light of $\kappa=DC_p\lambda$, here the density (D) was determined by Archimedes' method, the specific heat capacity (C_p) was derived by differential scanning calorimeter (PerkinElmer DSC7) and the thermal diffusivity λ was measured using a Netzsch laser flash diffusivity instrument (LFA 457). Hall measurements were accomplished in a Hall effect measurement system (HMS 5500).

Results and discussion

Melting and solidification

The melting and solidifying processes of the samples under various magnetic fields were monitored by DTA instrument and the results are shown in Figure 1. Obviously, the endothermic peak in the melting curves (Figure 1a) is nearly unaffected by the magnetic field, with an extreme at about 883.5 K, and the extrapolated onset temperature (T_M) is about 870.8 K for all the samples, indicating that the solid melting phase transformation can hardly be affected by the given magnetic field. It should mainly be attributed to the low magnetic energy, estimated to be the order of 10^{-4} J/g when considering the maximum magnetic field (6 T) and