Materials Today Physics 6 (2018) 1–8

Contents lists available at ScienceDirect

Materials Today Physics

journal homepage: https://www.journals.elsevier.com/materials-today-physics

Processing high efficiency functional gradient thermoelectric materials

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ARTICLE INFO

Article history:
Received 25 May 2018
Received in revised form
24 June 2018
Accepted 24 June 2018

Keywords:
Thermoelectrics
Semiconductors
N-type doped PbTe
Directional solidification

ABSTRACT

The converting efficiency of thermoelectric material is rated by its figure of merit, *zT*, which varies with temperature and usually goes through a maximum at a temperature T_M. To have a better utilization on their temperature ranges of high *zT*, cascaded components have been designed by stacking up different material layers that have their T_M at different temperature ranges. There are shortcomings in this arrangement mainly because of the monolithic properties of each layer and the thermal gaps between them. To improve its efficiency, thermoelectric properties need to vary continuously along its length, the so-called functional gradient (FG) thermoelectric materials, such that the value of T_M of each individual thin layer matches the actual temperature along its thermal gradient. Here, we show that such a high efficiency FG thermoelectric material with continuously monotonic variation of T_M can be accomplished by melt growth using the directional solidification technique and have demonstrated it in the n-type doped PbTe system.

1. Introduction

Thermoelectric materials convert thermal energy, i.e. heat, into electric energy. When one end of the materials is exposed to a heat source, thus creates a thermal gradient inside, the sample generates a thermoelectric voltage across its two ends. The converting efficiency is rated by the values of figure of merit, $zT = \alpha^2\sigma T/\kappa$, which is determined by three material properties: Seebeck coefficient α, electrical conductivity σ, and thermal conductivity κ. The measured value of *zT* varies with temperature and usually goes through a maximum, zT_M, at a temperature T_M. To improve the converting efficiency of thermoelectric material, most of efforts have been focused on increasing the value of zT_M. However, the thermoelectric materials are usually processed by hot-press or quench-annealing methods and, consequently, have uniform properties throughout the sample. When positioned in a thermal gradient, only a small section of the material is operating in the temperature range near its T_M with the *zT* values close to zT_M, which contributes to most of the converting efficiency, whereas the rest of the sample operates at lower levels of efficiency. To have better utilization of the materials in their temperature ranges of high *zT*, cascade configuration has been proposed and designed [1] which stacks up different systems of thermoelectric material layers that have zT_M at different temperature ranges along the thermal gradient. There are shortcomings in this arrangement: (1) with uniform thermoelectric properties, each layer still only operates near its maximum efficiency within a narrow temperature range, (2) with thermal gaps created at the boundaries between different layers, additional thermal interfaces, such as high temperature grease or solder, are needed, and (3) differences in thermal expansion coefficients of the various layers create physical stress. The design improves but does not maximize the converting efficiency and causes more potential hardware problems such as multiple harvesting electric circuits. The improvement of the cascade design has also been reported by physically joining segments of PbTe discs with different doping levels. This included the jointing of two-segments of I-doped PbTe by (1) plasma-activated sintering [2] and (2) liquid state diffusion bonding by hot-press [3]. This idea of joining segments of same material system still shares some of the shortcomings described above for the cascaded thermoelectrics.

To maximize the efficiency and eliminate the gaps between each layer in the cascade/segment arrangement, a real functional gradient (FG) thermoelectrics need to take the form of infinite number of thin layers in the cascaded concept by processing a material with its thermoelectric properties that vary continuously along its length such that the value of T_M of each thin layer matches the actual temperature along its thermal gradient during the

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https://doi.org/10.1016/j.mtphys.2018.06.001
2542-5293/

operation. As the example shown in top of Fig. 1, the FG thermoelectric material is situated in a thermal gradient with temperatures T_H (650°C) and T_C (250°C) at its hot and cold end, respectively. The schematic figure of merit for six thin layers along the axial direction is shown as functions of temperature in the bottom of Fig. 1. Because each layer is operating in a temperature range near its value of T_M, the whole sample can be visualized to exhibit a constant value of zT_M with a rectangular function of temperature from 250°C to 650°C (shown as red line).

The value of zT, defined as $\alpha^2\sigma T/\kappa$, is a complicated quantity that involved the values of the three material properties as functions of temperature. It has been found [1] decades ago that different doping levels produce zT_M at different temperatures with more heavily n-type I-doped PbTe results in higher temperature of T_M. To confirm this dependence of T_M on the doped PbTe system, we have examined the experimental results of 19 n-type doped-PbTe ingots grown by directional solidification, with the starting composition $(PbTe)_{1-x}D_x$ ($x < 0.10$) and donor, D, as Ag, Sb, or Bi [4]. The thermoelectric properties of 46 discs sliced at different axial locations of these ingots were measured. After plotting the measured T_M as a function of electrical conductivity,σ, at 38°C, shown in Fig. 2, it was found that for σ below around 2500S cm^{-1}, the data scattered with no apparent correlation, presumably because of the masking of residual impurities over the doping level. However, when σ goes up from 2500 to 5000S cm^{-1}, the dependence shows that the higher the measured electrical conductivity, the higher the value of T_M, as T_M increases from 420 to about 650°C.

Since electrical conductivity is proportional to carrier concentration, the finding is consistent with the early report [1]. It was also recognized that melt growth by directional solidification will be able to produce continuously monotonic variation in dopant concentration along the length of the grown crystal. Fig. 3(a) shows the schematic phase diagram of a dopant B near the melting point of a semiconductor A with the existing regions of liquid (L), solid (S) and liquid + solid ($L + S$) separated by the liquidus and a typical solubility curve of B. During vertical directional solidification from a melt, either Bridgman or gradient freeze technique, a homogenized sample with nominal doping composition of element B, X_N, is sealed inside a fused-silica ampoule under vacuum. The ampoule is initially completely melted at the top, hot section of the thermal

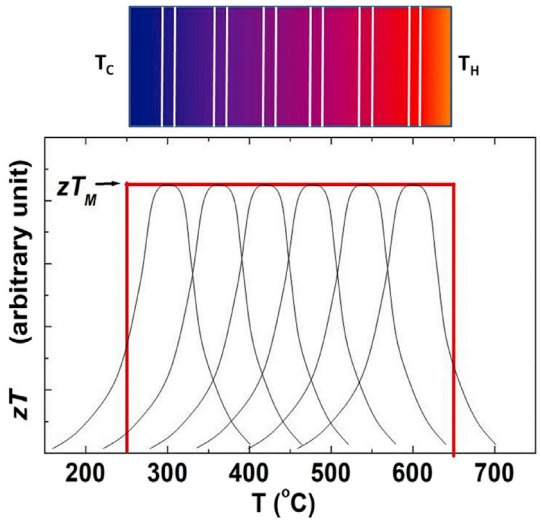

Fig. 1. The schematics of functional gradient thermoelectric material. Top section shows the sample is positioned between the hot and cold temperatures, T_H and T_C, respectively. Bottom section shows the figure of merit, zT, for six individual layers along the length of the ingot.

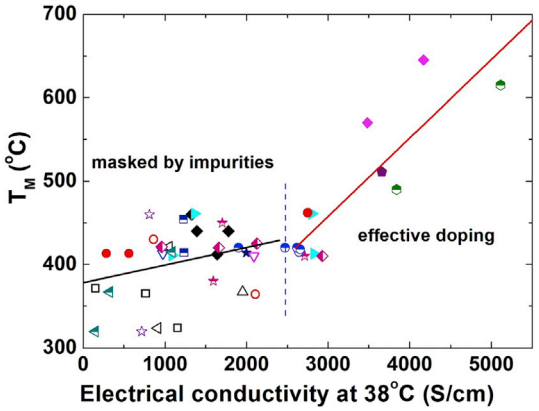

Fig. 2. From the thermoelectric properties measured on 45 n-type PbTe samples, the temperature of the zT maximum, T_M, is plotted against the measured electrical conductivity at 38°C for each sample.

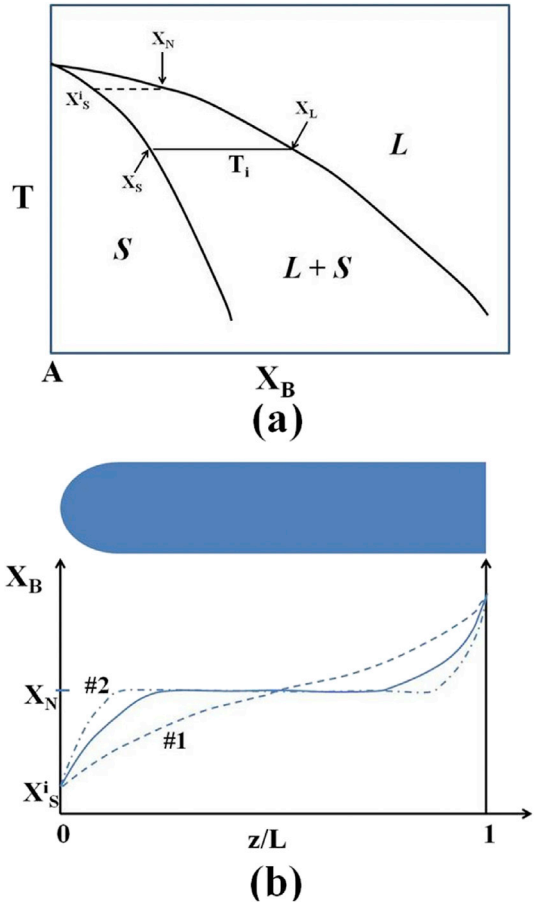

Fig. 3. (a) A schematic phase diagram of a dopant B near the melting point of a semiconductor A. (b) The resultant dopant composition vs. normalized length along the ingot after growth by directional solidification (from left to right) with three different growth rates.

profile, which extends into a cold bottom section, provided by the multizone growth furnace. As the thermal profile moves upward relative to the ampoule, the first freeze solid will have composition X^i_S, as given by the phase diagram shown in Fig. 3(a). Since X^i_S is smaller than X_N, the melt adjacent to the solid-liquid interface will have composition higher than X_N because of the rejection of B element from the frozen solid and form a boundary layer of melt