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High performance functionally graded and segmented Bi_2Te_3-based materials for thermoelectric power generation

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Bi_2Te_3-based materials possess a figure of merit maximum over a narrow temperature range. When used in a generating mode over a large temperature difference the material operates at a substantially lower overall figure of merit than its maximum value. The conversion efficiency of a thermoelectric generator for low temperature waste heat recovery can be increased by employing functionally graded or segmented materials. In this work functionally graded *p*-type Bi_2Te_3-based thermoelectric materials have been prepared from melt by the Bridgman method using double doping technique. Segmented *n*-type thermoelement has been fabricated by joining two Bi_2Te_3-based materials with figure of merit maximum at 270 K and 380 K. The thermoelectric properties of the materials and a thermocouple comprised of *p*-type functionally graded and *n*-type segmented materials have been measured over a temperature range 200 K–450 K. The material efficiency of the thermocouple over the temperature gradient 223 K–423 K is estimated to be 10% compared with 8.8% for a standard Bi_2Te_3-based materials. *© 2002 Kluwer Academic Publishers*

1. Introduction

The figure of merit value of Bi_2Te_3-based thermoelectric materials peaks in a narrow temperature range (50–60 K). This is not a big disadvantage when thermoelectric modules are used in a cooling mode since the maximum temperature difference across each stage of a cooling module does not normally exceed 60 K. However, for thermoelectric generators the temperature difference across the thermoelectric module can be much larger. In this situation uniform Bi_2Te_3-based thermoelectric materials are not optimised for operation over a wide temperature range and the overall figure of merit value will be significantly lower than its maximum value.

The temperature of the maximum figure of merit of a thermoelectric material depends primarily upon the carrier concentration. The conversion efficiency of Bi_2Te_3-based thermoelements when operating over a large temperature difference can be substantially improved by adjusting the carrier concentration along the material's length to match the local properties of the material to the thermal field. This can be achieved by employing a functionally graded thermoelectric material (FGTM) with the carrier concentration optimised for operation over the specific temperature gradient. The optimum FGTM structure can also be approximated to by a segmented thermoelectric material comprised of two Bi_2Te_3-based materials joined together. Each material being optimised for a specific temperature within the temperature range of operation of a thermoelectric module.

The concept of employing a graded composition of thermoelectric materials to increase the overall conversion efficiency of a thermoelectric device operated over a wide temperature range was originally proposed by A. F. Ioffe in 1949 [1]. Recently several groups of researchers reported the development of segmented thermoelectric materials by joining Bi_2Te_3 and PbTe [2], Bi_2Te_3 and $FeSi_2$ [3], *n*, *p*-Bi_2Te_3 and *n*-$CoSb_3$ or *p*-Zn_4Sb_{12}/p-$CeFe_4Sb_{12}$ [4].

Fabrication of Bi_2Te_3-based FGTM can be attained by establishing a distribution of the dopant concentration along the growth direction of a crystal. The conventional preparation method of Bi_2Te_3-based thermoelectric materials by zone levelling technique is designed for the production of homogeneous ingots and cannot be used for fabrication of FGTM. However, the Bridgman or Czochralski techniques of crystal growth enable crystals with a steep gradient of the dopant concentration to be prepared.

Assuming complete mixing in the melt (by diffusion or stirring), the dopant concentration distribution along the crystal grown by Bridgman method is given by Equation 1:

$$C = kC_0(1 - g)^{k-1}, \tag{1}$$

where C is the dopant concentration in the crystal at the liquid-solid interface, C_0 is the initial dopant concentration in the melt, k is the distribution coefficient and g is the fraction of the melt which has solidified. The distribution of the dopant concentration along the ingot

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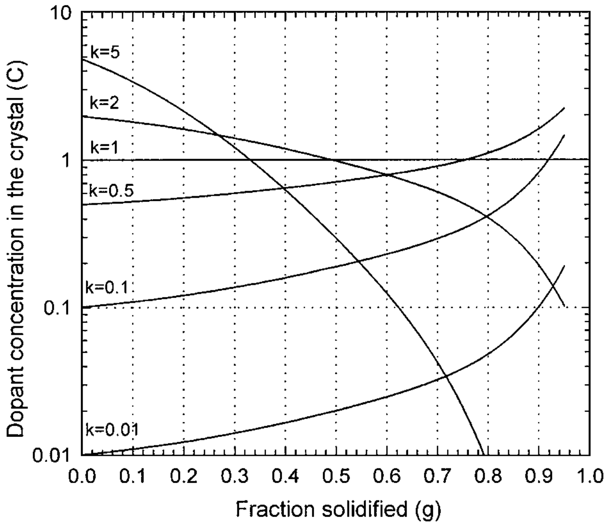

Figure 1 The dopant concentration distribution vs. fraction of solidified melt (Bridgman growth method).

length obtained from Equation 1 for different values of k is shown in Fig. 1.

As seen from Fig. 1, the gradient of the dopant concentration along the ingot is larger when the distribution coefficient of the dopant differs significantly from unity. Another factor which affects the dopant distribution is the ingot diameter (D) to length (L) ratio ($R = D/L$). For a fixed mass of the ingot, the ratio R determines the relationship between the ingot's length and parameter g. The larger R value is, the higher concentration gradient can be obtained for the same length of ingot.

Recently the double doping (Te excess + SbI_3) of solid solution $(Bi_2Te_3)_{1-x-y}(Sb_2Te_3)_x(Sb_2Se_3)_y$ was proposed that allows the preparation of p- and n-type materials with figure of merit values of up to 3.7×10^{-3} K^{-1} and 3.4×10^{-3} K^{-1}, respectively [5]. It has been reported that the double doping also enables materials to be prepared with greater variation of resistivity along the growth direction than using only Te as a dopant [5].

In this paper we report the preparation of p-type functionally graded and n-type segmented Bi_2Te_3-based thermoelectric materials optimised for operation over the temperature range 223 K–423 K. The results of the electrical property measurements of the materials and a thermocouple comprised of these materials are also presented.

2. Experimental procedure

Crystals of Bi_2Te_3-based solid solutions were grown by the Bridgman technique in evacuated quartz ampoules coated on the inside with a layer of pyrolytic graphite. Elements of 99.99% purity were used as source materials; the dopants (Te excess and SbI_3) were added in the amount of 1.5–4 wt% and 0.05–0.2 wt%, correspondingly. The charge was melted at 1073 K for 4–6 hours whilst being mechanically vibrated to ensure homogenisation of the melt. The ampoules were subsequently placed in the growth zone with a temperature gradient of ~25 K/cm and moved down at a rate of 0.5 cm/h. The crystals obtained were 0.6–0.9 cm in diameter and 1.5–4 cm long. All crystals had cleavage planes (111) predominantly aligned parallel to the growth direction.

Because of the high anisotropy of the electrical resistivity of Bi_2Te_3-based materials, the room temperature electrical resistivity has been measured on disks cut from the crystals perpendicular to the growth direction. The temperature dependence of the electrical transport properties of the materials was measured in the growth direction using techniques described previously [6]. The temperature dependence of the thermal conductivity was measured by a comparative method using stainless steel (NIST, USA) as a reference material.

Measurements of the electrical resistance and output voltage of p-type FGTM, n-type segmented material and a thermocouple comprised of these materials were conducted over the range 200 K–450 K and a temperature gradient of up to 230 K using a computerised apparatus. A small resistance heater and a copper rod cooled with liquid nitrogen were used for the hot and cold sides to provide the temperature gradient. Two copper plates (1 mm thick) were attached to the polished surfaces of the disks (3–5 mm thick) of crystals using a Ga-In alloy to provide contacts with low electrical and thermal resistance. Copper/constantan thermocouples were attached to each copper plate enabling measurements of both Seebeck coefficient and electrical resistivity. The resistivity of contacts and copper plates was preliminary assessed and did not exceed 5% of the resistivity of the materials.

3. Results and discussion

A solid solution $(Bi_2Te_3)_{0.25}(Sb_2Te_3)_{0.72}(Sb_2Se_3)_{0.03}$ doped with 2–4 wt% of Te excess and 0.05–0.2 wt% SbI_3 was used for the fabrication of p-type FGTM. Samples 4 mm long with a functional distribution of the carrier concentration were cut from the middle part of the crystals. The transport properties of the end parts of the samples were evaluated using thin disks (<1 mm) cut from both ends of the samples. The room temperature properties of the p-type FGTM are presented in Table I. The temperature dependence of the electrical transport properties of discs cut from both ends of the samples of FGTM is presented in Fig. 2. Measurements of the temperature dependence of thermoelectric properties revealed the figure of merit maximum at 260 K and 370 K for low- and high-temperature part of the samples, correspondingly.

TABLE I Room temperature transport properties of the p-type functionally graded and n-type segmented materials: α—Seebeck coefficient, ρ—electrical resistivity, λ—total thermal conductivity, R_H—Hall coefficient

Material	α (μV/K)	ρ (mΩ cm)	λ (mW/cm K)	R_H (cm^3/C)
Low temperature end of p-type FGTM	220	1.13	13.7	0.49
High temperature end of p-type FGTM	190	0.85	15.0	0.22
Low temperature n-type material	−201	0.94	14.0	0.83
High temperature n-type material	−172	0.67	15.8	0.38

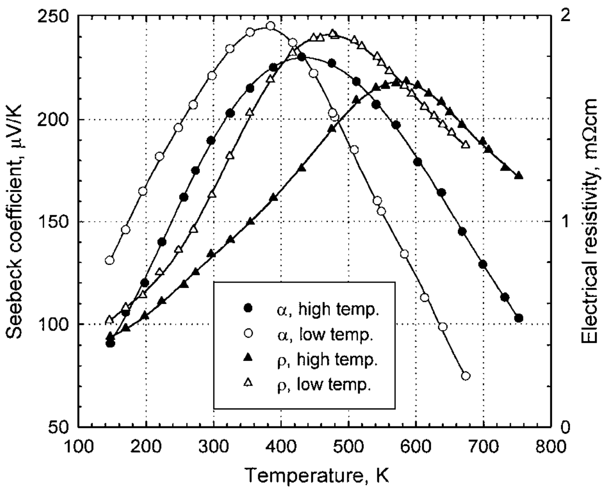

Figure 2 Temperature dependence of Seebeck coefficient and electrical resistivity for low- and high-temperature ends of the *p*-type functionally graded sample.

n-type $(Bi_2Te_3)_{0.7}(Sb_2Te_3)_{0.25}(Sb_2Se_3)_{0.05}$ solid solution has been prepared by the Bridgman technique. It has been reported [7] that this composition exhibits a prominent maximum of the parameter $\mu(m^*/m_0)^{3/2}/\lambda_L$ due to a lower lattice thermal conductivity λ_L and higher effective mass m^* in comparison with other compositions of solid solution. However until recently attempts to achieve a high figure of merit value for *n*-type materials of this composition using a single dopant (SbI_3) have not been entirely successful [7] due to a high concentration of negatively charged antistructural defects which increases with an increase in the Sb_2Te_3 content. Double doping (Te excess and SbI_3) of $(Bi_2Te_3)_{0.7}(Sb_2Te_3)_{0.25}(Sb_2Se_3)_{0.05}$ solid solution is reported to produce material with a lower thermal conductivity which resulted in a figure of merit value of 3.4×10^{-3} K^{-1} [5].

A number of *n*-type crystals has been grown with the dopant concentration 1.5–3 wt% of Te excess and 0.05–0.1 wt% SbI_3. However, the gradient of thermoelectric properties along the ingot length was insufficient to use the material as FGTM for operation over a wide temperature range. It is suggested that in *p*-type material the Te excess plays the major role in the doping process whereas in *n*-type solid solution the carrier concentration is mainly determined by the SbI_3 content. The distribution coefficient of Te in Bi_2Te_3-based materials is reported to be around 0.01 [8] which facilitates the preparation of crystals with a considerable gradient of thermolectric properties along the growth direction. The distribution coefficient of *n*-type dopants like SbI_3 [7] and $SbBr_3$ [9] is close to unity which determines the more uniform distribution of the halogen concentration along the crystal length. Further studies are required to understand the multiple doping mechanism.

A segmented thermoelement can be used to approach maximum thermoelectric performance of *n*-type material over a temperature difference of up to 200 K. This thermoelement consists of two materials joined together with each optimised for different temperature range. A shift of Z maximum to a temperature higher than 300 K requires higher carrier concentration than that of the standard material optimised for operation at room temperature. For *n*-type solid solution this can be achieved by an increase in the dopant concentration. A number of *n*-type samples with different carrier concentration has been prepared. The room temperature transport properties of *n*-type materials with Z maximum at 270 K and 380 K are presented in Table I.

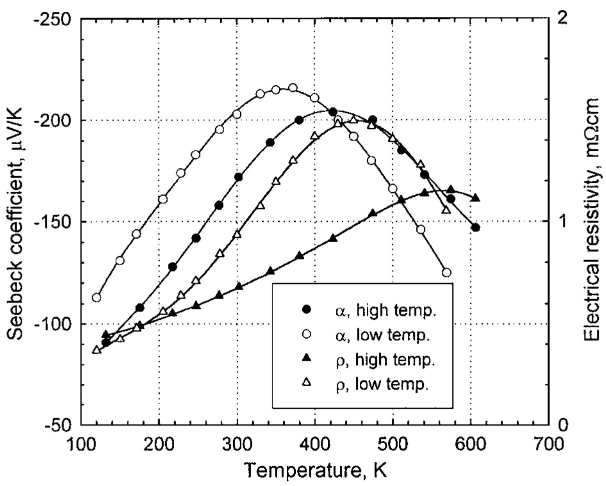

Figure 3 Temperature dependence of Seebeck coefficient and electrical resistivity for low- and high-temperature *n*-type materials.

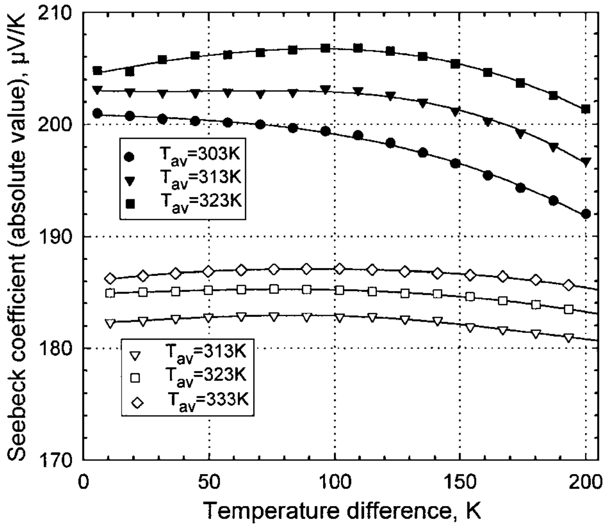

Figure 4 Absolute value of Seebeck coefficient of *p*-type FGTM (solid symbols) and *n*-type segmented material (open symbols) at different average temperatures as a function of temperature difference.

The temperature dependence of electrical transport properties of *n*-type samples is presented in Fig. 3. These samples were used to fabricate the segmented *n*-type material; the joining was performed by ordinary soldering.

The electrical transport properties of both *p*- and *n*-type materials were measured in the direction perpendicular to the *c*-axis of the crystal structure under a temperature gradient from 0 K to 230 K. The Seebeck coefficient and electrical resistivity of *p*-type FGTM and *n*-type segmented materials are presented in Fig. 4 and Fig. 5 as a function of temperature difference along the samples.

A broad maximum of the dependence of the overall Seebeck coefficient (Fig. 4) and power factor value

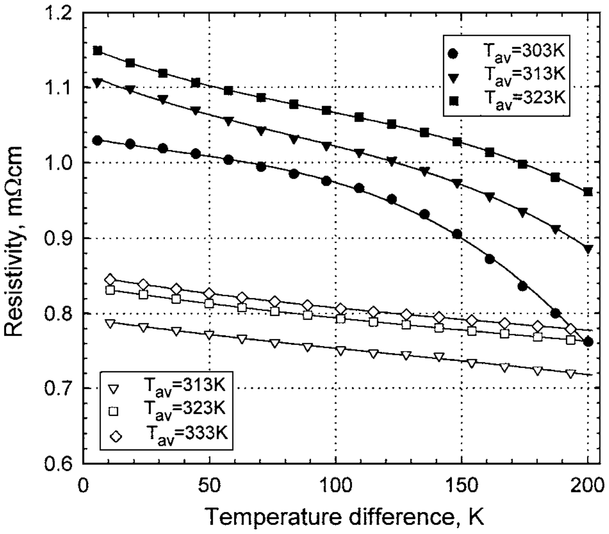

Figure 5 Electrical resistivity of p-type FGTM (solid symbols) and n-type segmented materials (open symbols) at different average temperatures as a function of temperature difference.

on the temperature difference reflects the broadening of the temperature range of efficient operation of the functionally graded and segmented materials.

The material conversion efficiency η was calculated using Equation 2:

$$\eta = \eta_c \frac{M - 1}{M + 1 - \eta_c}, \qquad (2)$$

where $\eta_c = (T_{\text{hot}} - T_{\text{cold}})/T_{\text{hot}}$ is the Carnot efficiency, $M = \sqrt{1 + Z\bar{T}}$, $Z\bar{T}$ is the average dimensionless figure of merit of materials over the temperature range from T_{hot} to T_{cold}, $\bar{T} = (T_{\text{hot}} + T_{\text{cold}})/2$. The thermal conductivity of the materials under different temperature gradients was obtained from the temperature dependence of the thermal conductivity of materials taking into account the distribution of carrier concentration along the length of the legs. The calculated conversion efficiency of p-type FGTM and n-type segmented materials at different average temperatures as a function of the temperature difference is displayed in Fig. 6.

As seen in Fig. 6, the conversion efficiency of both FGTM and segmented material reaches 10% over the 223 K–423 K temperature difference and slightly increases with decreasing average temperature. In Fig. 6 is also presented the conversion efficiency of the "standard" p-type material with the uniform distribution of the carrier concentration and the same composition of solid solution as that of FGTM. Over the whole temperature range of measurements the conversion efficiency of both FGTM and segmented materials exceeds that of the uniform material.

A thermocouple comprised of a p-type functionally graded leg and an n-type segmented leg was fabricated using the samples with electrical transport properties measured separately (Figs 4 and 5). The length of the samples was 3.5 mm and cross-section of around 0.3 cm^2. The electrical properties of the thermocouple were measured over the temperature range 200 K–450 K and temperature difference of up to 210 K. The results are presented in Table II.

TABLE II Measured (*) and calculated thermoelectric properties of the thermocouple under the temperature gradient of 223–423 K

Thermocouple parameters	Value
Total electrical resistance* (Ω)	2.28×10^{-3}
Total voltage* (V)	74.4×10^{-3}
Effective Seebeck coefficient* (μV/K)	372
Maximum electrical power output* (W)	0.61
Temperature difference along materials (K)	198
Total electrical contact resistance (Ω)	1.34×10^{-4}
Electrical resistance of materials (Ω)	1.98×10^{-3}
Thermocouple total electrical resistance (Ω)	2.23×10^{-3}
Total thermal conductance of materials (W/K)	0.0240
Total thermocouple thermal conductance (W/K)	0.0237
Z (materials) (K^{-1})	3.06×10^{-3}
Power factor (materials) (W/mK^2)	43×10^{-4}
Optimum current for the thermoelement (A)	14.3
Material efficiency of the thermocouple (%)	10.1
Conversion efficiency of the thermocouple (%)	9.2

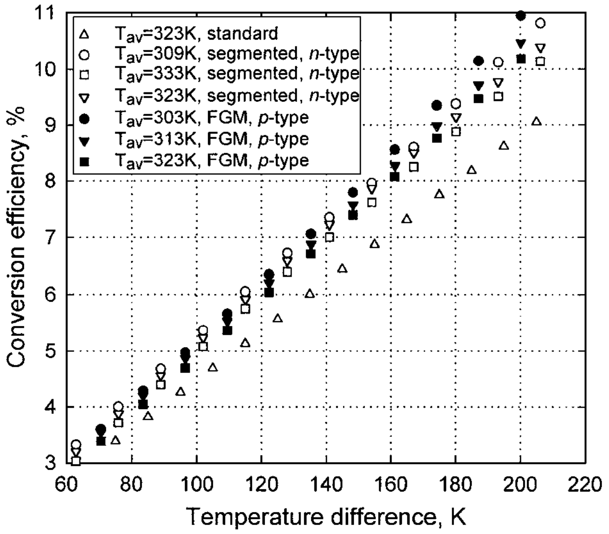

Figure 6 Calculated conversion efficiency of p-type FGTM, n-type segmented and "standard" p-type materials at different average temperatures as a function of temperature difference.

The thermoelectric properties of the thermocouple were calculated taking into account the experimentally measured Seebeck coefficient and electrical resistivity of n- and p-type materials over the temperature difference 223 K–423 K, the electrical and thermal resistance of copper and alumina plates and the electrical contact resistance of interfaces. The best agreement between the calculated and experimentally measured properties of the thermocouple (total electrical resistance and maximum electrical power output) was obtained for the electrical contact resistance value of 1.5×10^{-5} Ω cm^2. The results of the calculation of the electrical parameters of the thermocouple are presented in Table II.

The calculated conversion efficiency of the thermocouple reaches 9.2% over the 223 K–423 K temperature gradient (Table II) comparing with 10.1% of the material efficiency. Further increase in the material conversion efficiency is possible by optimisation of the functional distribution of the carrier concentration along the p- and n-type materials. The reduction in the electrical contact and copper plate resistance could also improve the conversion efficiency of the thermocouple.

4. Conclusions

The fabrication of thermoelements from FGTM and segmented materials is one of the promising methods to improve the efficiency of generating thermolectric modules. The functionally graded material with a continuously variable carrier concentration can be obtained using the Bridgman technique. The estimated conversion efficiency of both FGTM and segmented materials over the temperature difference of up to 200 K significantly exceeded that of the uniform material. The thermoelectric modules incorporating functionally graded and segmented Bi_2Te_3-based materials could be used to increase the temperature range of the efficient operation of thermoelectric generators.

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