Effect of current on the microstructure and performance of $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ thermoelectric material via field activated and pressure assisted sintering*

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Abstract: $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ thermoelectric material was sintered via a field activated and pressure assisted sintering (FAPAS) process. By applying different current intensity (0, 60, 320 A/cm^2) in the sintering process, the effects of electric current on the microstructure and thermoelectric performance were investigated. This demonstrated that the application of electric current in the sintering process could significantly improve the uniformity and density of $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ samples. When the current intensity was raised to 320 A/cm^2, the preferred orientation of grains was observed. Moreover, positive effects on the thermoelectric performance of applying electric current in the sintering process were also confirmed. An increase of 0.02 and 0.11 in the maximum figure of merit ZT value could be acquired by applying current of 60 and 320 A/cm^2, respectively.

Key words: thermoelectric material; $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$; microstructure; performance; current; field activated and pressure assisted sintering

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1. Introduction

Thermoelectric materials are of interest for applications as heat pumps and power generators. The conversion efficiency of a thermoelectric material is dependent on the dimensionless figure of merit, $ZT = \alpha^2\sigma T/\kappa$, where α is the Seebeck coefficient, σ is the electric conductivity, T is the absolute temperature and κ is the thermal conductivity. P-type Bi–Sb–Te compounds have been widely used to fabricate electronic cooling devices because of the highest ZT value near room temperature among the p-type thermoelectric semiconductors.

Characterized by the application of electric current to assist or activate the sintering process, electric current activated pressure assisted sintering (FAPAS) technology has advantages over conventional sintering methods, such as faster heating rate, lower sintering temperature, shorter holding time, and less sensitivity to initial powders characteristics[1, 2], and it has been introduced into the preparation of Mg_2Si and β-$FeSi_2$ thermoelectric materials[3]. However, the intrinsic role of electric current in the sintering process of $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ thermoelectric material needs to be further explored[4]. In the present study, the FAPAS process was modified. Different current intensities (0, 60, 320 A/cm^2) were applied in the sintering process, and the effects of electric current on the microstructure and thermoelectric performance were investigated.

2. Experimental materials and procedure

The constituent elements, Bi, Sb, Te, with purity of 99.999%, according to the stoichiometric ratio of $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$, were melted at 1323 K in a sealed, evacuated quartz tube for 10 h before being quenched and ball-milled into powders of 200 mesh. Then, in an FAPAS apparatus, the $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ powders were consolidated to coin-like samples of 20 mm in diameter and 3 mm in thickness.

Three kinds of sintering process, such as no-current sintering (NCS), low density current sintering (LCS) and high density current sintering (HCS), were used to obtain different current densities, which are depicted in Fig. 1. For the NCS process, the sample is typically heated by radiation from external heating elements, and no electric current flows through the graphite die and powders (Fig. 1(a)). For the LCS process, when applying electric current of 1000 A, the maximum electric current intensity is limited to less than 60 A/cm^2 because of the by-pass current flowing through the graphite mould (Fig. 1(b)). In the present study, an innovative mould (Fig. 1(c)) with an Al_2O_3 tube was adopted to restrict the by-pass current so that high-intensity electric current flowing through the compound powders could be realized. When applying 1000 A electric current, the current intensity can achieve 320 A/cm^2. When applying the sintering process, a cold-formed compact of $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ was inserted into the graphite mould and placed in the sintering apparatus. Simultaneously, a load of 50 MPa was applied on the upper punch electrode. The temperature of powders was raised to 673 K in 5 min and maintained for 20 min. All processes were performed under vacuum circumstances ($\leqslant$ 5 Pa).

The Seebeck coefficient and electrical conductivity were measured by a Seebeck coefficient/electric resistance measuring system (ZEM-1, ULVAC Inc., Japan). The temperature difference between the cool and hot ends of the samples in the Seebeck coefficient measurement was 4 K. The thermal conductivity was calculated from $\kappa = \alpha D C_p$, where α is the thermal dif-

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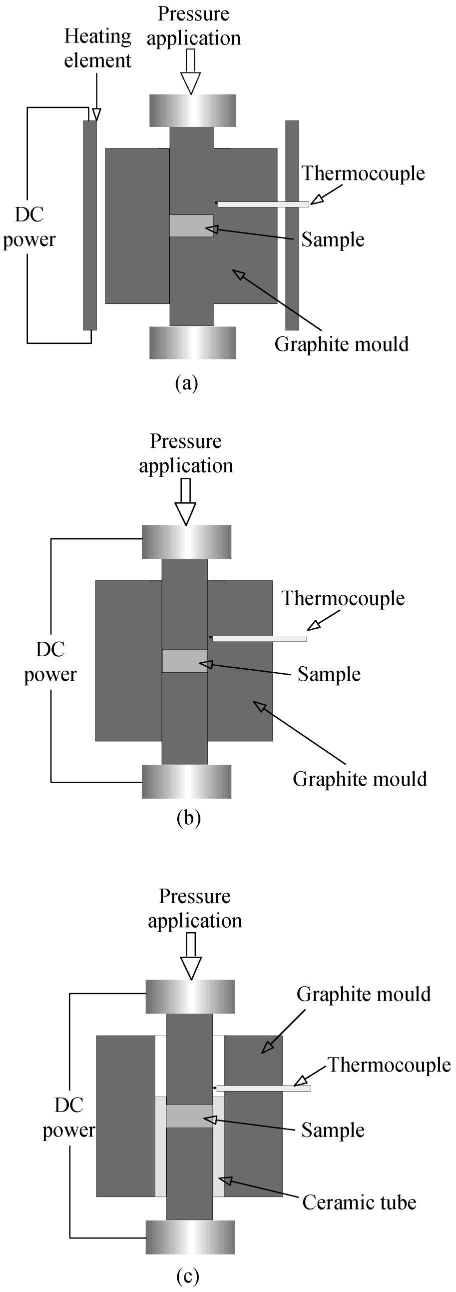

Fig. 1. Schematic diagram of the sintering apparatuses. (a) NCS. (b) LCS. (c) HCS.

fusivity, D is the sample density measured by the Archimedes method, and C_p is the specific heat capacity, which was measured on a NETSCH LFA457/DSC404.

3. Results and discussion

3.1. Comparison of microstructures

The SEM fracture morphologies of samples sintered via NCS, LCS, and HCS processes are shown in Fig. 2. The fractures are along the direction of electric current and pressure being supplied. Layer structures can be observed in all the samples. Not like the uniform and dense LCS-sample and HCS-sample, there are pores (marked by circles) dispersed in the NCS-sample. In the FAPAS process, powders are heated by the Joule heat generated from the electric current flowing through the powder particles. This heating mode contributes to obtaining uniform and dense samples. Measured by Archimedes method, the densities of the NCS, LCS and HCS samples are 6.318, 6.545 and 6.549 g/cm^3, respectively.

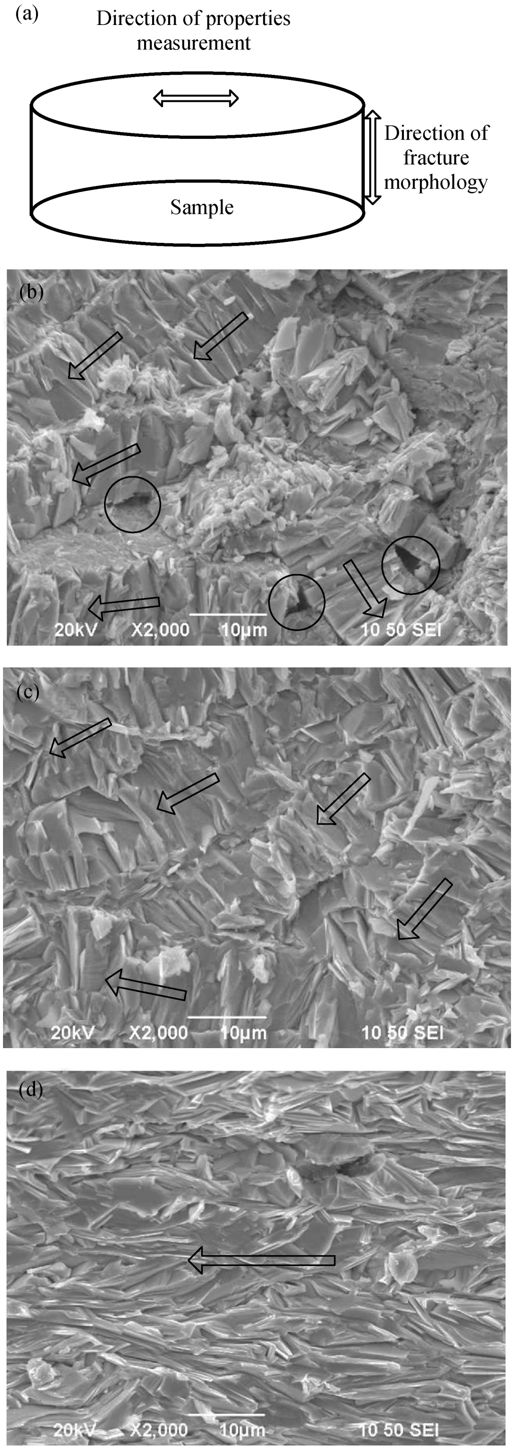

Fig. 2. SEM fracture morphology of (a) observing direction, (b) NCS, (c) LCS and (d) HCS samples.

Furthermore, in contrast to the random distribution in the NCS-sample and LCS-sample, the layer structure in the HCS-sample demonstrates a preferred orientation (marked by arrows), which indicates that the application of a high density of electric current in the sintering process could enhance the

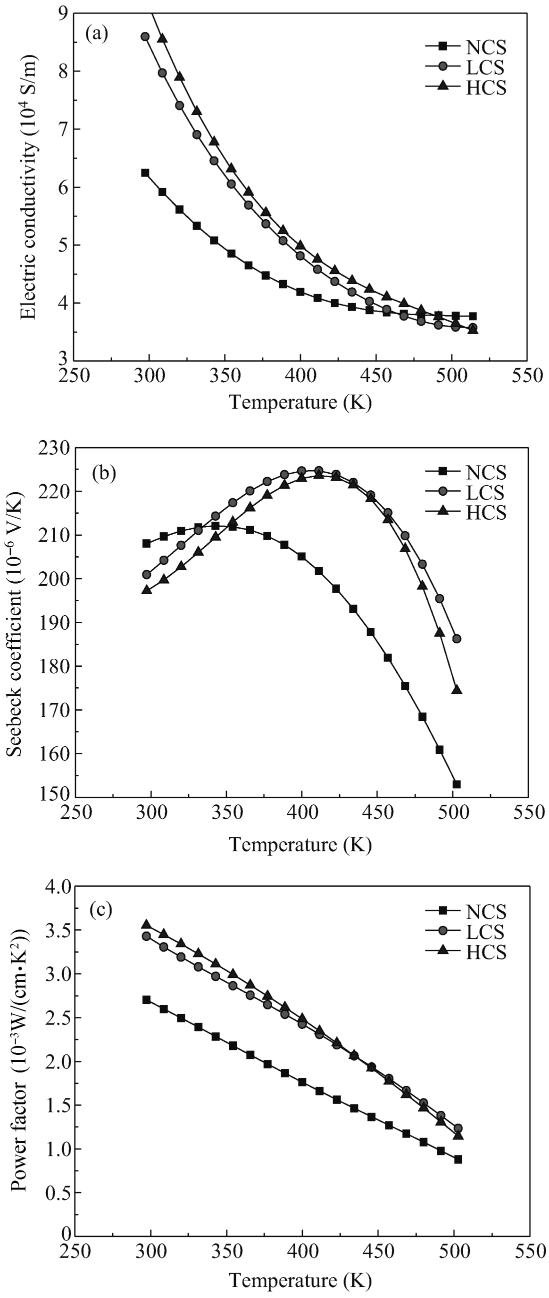

Fig. 3. Comparison of (a) electric conductivity, (b) Seebeck coefficient, and (c) power factor of the samples sintered by different processes.

mass migration along the current direction[2], leading to the preferred orientation of layer structures.

3.2. Comparison of electrical properties

The temperature dependence of the electric conductivity (σ) is depicted in Fig. 3(a). All of the samples' electric conductivity decreases with a rise in temperature. In the temperature range of 297–513 K, the electric conductivity of the samples is 6.25–3.77 × 10^4 S/m (NCS), 8.59–3.58 × 10^4 S/m (LCS) and 9.29–3.53 × 10^4 S/m (HCS), respectively. The values of the LCS-sample and HCS-sample are higher than that of the NCS-sample in the temperature range of measurement.

For semi-conductive thermoelectric materials, electric conductivity is a function of carrier density and carrier mobility[5],

$$\sigma = ne\mu, \tag{1}$$

where n is the carrier concentration, e is the carrier charge and μ is the carrier mobility. Before the intrinsic excitation, the lattice vibration increases with a rise in temperature, and hence the scattering effect from lattice vibration is enhanced and the carrier mobility is suppressed. As shown in equation 1, decreased carrier mobility leads to decreased electric conductivity. When the intrinsic excitation takes place, large amounts of carriers are excited, increased carrier density counteracts the scattering effect from the lattice vibration, and the electric conductivity remains steady, as shown in Fig. 3(a). The higher electric conductivity of the LCS-sample and HCS-sample compared with the NCS-sample can be attributed to their high density. In general, samples with high density possess a high carrier concentration and the electric conductivity can be improved.

The temperature dependence of the Seebeck coefficient (α) is depicted in Fig. 3(b). In the temperature range of 297–513 K, the Seebeck coefficient values of all of the samples increase first and then decrease with a rise in temperature. In the temperature range of 297–330 K, the Seebeck coefficient of the NCS-sample is higher than that of the LCS-sample and HCS-sample. The maximum Seebeck coefficient values of the samples are 211.15 × 10^{-6} V/K (NCS, 366 K), 224.70 × 10^{-6} V/K (LCS, 411 K), 223.60 × 10^{-6} V/K (HCS, 413 K), respectively.

In the degeneracy condition, the Seebeck coefficient can be described as

$$\alpha = \mu\frac{\pi^2}{3}\frac{k_B}{e}\frac{s+\dfrac{3}{2}}{\eta_F}, \tag{2}$$

where k_B is the Boltzmann constant, μ is the carrier mobility, s is the scattering factor and η_F is the simple Fermi level. Equation (2) indicates that a higher carrier mobility can contribute to a rise in Seebeck coefficient. In Bi–Sb–Te compounds, the origin of the charge carrier is related to the antisite defects (Sb_{Te} or Bi_{Te}), where Sb or Bi atoms occupy the Te sites, and charged vacancy defects (V_{Bi}, V_{Sb} and V_{Te})[6]. For p-type $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ material, Sb_{Te} defects are the primary source of hole carriers[7]. In the FAPAS process, the application of electric current in the sintering process could eliminate the Sb_{Te} defects by the improved mass migration[2]; this is helpful in improving the carrier mobility[5, 6]. As a result, higher carrier mobility contributes to a rise in Seebeck coefficient.

The temperature dependence of the power factor ($P = \alpha^2\sigma$) is depicted in Fig. 3(c). The power factor is the comprehensive indicator of the electrical properties of a thermoelectric material. The power factor values of all of the samples decrease with a rise in temperature. The maximum values of the NCS-sample, LCS-sample and HCS-sample are 2.70 × 10^{-3}, 3.43 × 10^{-3}, and 3.55 × 10^{-3} W/(m·K^2), respectively. For the LCS-sample and HCS-sample, both higher electric conductivity and Seebeck coefficient values compared with the NCS-sample lead to their higher power factor values. This indicates that applying electric current in the sintering process is helpful

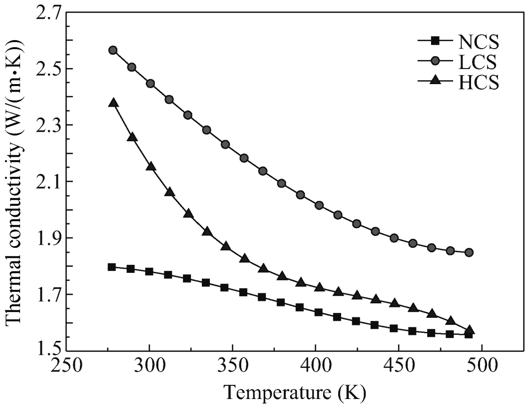

Fig. 4. Comparison of thermal conductivity of the samples sintered by different processes.

in improving the electric properties of $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ material.

3.3. Comparison of thermal conductivity

Figure 4 illustrates a comparison of thermal conductivity of the samples sintered by different processes. Compared to the lowest value of 1.55 W/(m·K) in 490 K for the NCS-sample, the thermal conductivity of the LCS-sample deteriorates (1.85 W/(m·K) in 490 K) and the HCS-sample has a moderate value (1.57 W/(m·K) in 490 K).

The thermal conductivity of a material can be described as $k = k_{\rm el} + k_{\rm ph}$, where $k_{\rm el}$ and $k_{\rm ph}$ are the electronic and lattice thermal conductivities, respectively. The $k_{\rm ph}$ is related to the phonon scattering occurring at lattice distortions, pores, and grain boundaries[5, 8]. As shown in Fig. 2(b), the dispersed pores in the NCS-sample can enhance the phonon scattering and severe phonon scattering leads to a depression of the thermal conductivity. For LCS and HCS samples, as mentioned above, a higher density means fewer pores and less phonon scattering. Furthermore, the application of electric current eliminates the Sb_{Te} defects in $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ compound and the phonon scattering by the Sb_{Te} defects is suppressed too. The decrease in phonon scattering by pores and defects leads to a high thermal conductivity of the LCS-sample.

However, what should be noticed is that the HCS-sample, also being subjected to electric current in the sintering process, possesses much lower thermal conductivity than the LCS-sample. With the temperature increasing, the thermal conductivity of the HCS-sample gradually approaches that of the NCS-sample, and it achieves the lowest value of 1.57 W/(m·K) in 490 K. This ought to be related to the preferred orientation layer structure caused by applying high intensity electric current in the sintering process. As shown in Fig. 2(a), the direction of thermal conductivity measurement is perpendicular to the fracture direction, and also perpendicular to the direction of the electric current applied. For the HCS-sample, low thermal conductivity between the layers leads to a low thermal conductivity in the direction perpendicular to the fracture surface (which is parallel to the direction of applied electric current).

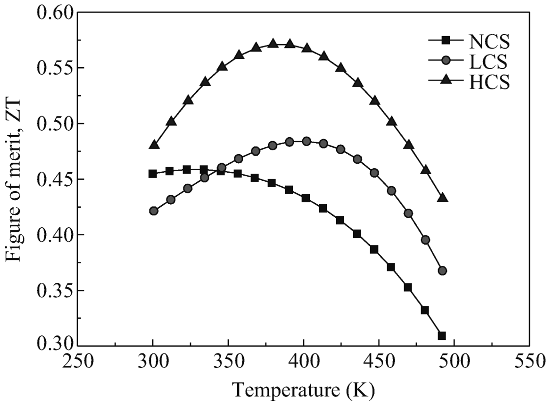

Fig. 5. Comparison of the ZT value of samples sintered by different processes.

3.4. Comparison of ZT values

The ZT values of the samples sintered by different processes are depicted in Fig. 5. The maximum value of the NCS, LCS and HCS samples were 0.46, 0.48 and 0.57, respectively.

It is well known that all of the transport properties, such as electric conductivity, Seebeck coefficient and thermal conductivity, are functions of carrier density and scattering mechanism, and they need to be optimized in order to reach maximum ZT values for specific thermoelectric material. As mentioned above, benefiting from the high electric conductivity and Seebeck coefficient, the ZT value of the LCS-sample is higher than that of the NCS-sample across most of the temperature range of measurement. An increase of 0.02 in the maximum ZT value compared with the NCS-sample was achieved. For the HCS-sample, integration of high electrical properties and low thermal conductivity leads to a highest ZT value in the entire temperature range of measurement. An increase of 0.11 in the maximum ZT value compared with the NCS-sample was achieved.

4. Conclusion

$(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ thermoelectric material was sintered via a field activated and pressure assisted sintering (FAPAS) process. The effects of electric current in the FAPAS process on the microstructure and thermoelectric performance were investigated by adopting the NCS, LCS and HCS sintering processes. The maximum ZT values of the NCS, LCS and HCS samples were 0.46, 0.48 and 0.57, respectively. This demonstrates that the application of electric current in the sintering process could significantly improve the uniformity and density of $(Bi_2Te_3)_{0.2}(Sb_2Te_3)_{0.8}$ samples. When the current intensity was raised to 320 A/cm^2, the preferred orientation of the layer structure was observed. Applying electric current in the sintering process can contribute to acquiring higher electric conductivity and Seebeck coefficient. By applying a high intensity of electric current (320 A/cm^2) in the sintering process, both high electrical properties and low thermal conductivity could be acquired. The preferred orientation of the layer structure caused by applying high intensity electric current leads to the low thermal conductivity of the HCS-sample.

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