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Short Communication

Microwave sintering and thermoelectric properties of p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ powder

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ABSTRACT

We report on the use of a modified multimode microwave cavity to sinter commercially available p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ powder. We have designed a special crucible containing SiC barrels to perform hybrid heating of the samples. Two different initial relative densities were studied (74 and 84%). The morphological evolution of the microstructure was studied by field emission scanning electron microscopy (FESEM). We have also observed that the densification of such powder is possible but that the final relative density reaches an upper limit of 86% due to the formation of Te gas, which results in closed porosity. The Seebeck coefficient was found to be independent of the process. The highest measured power factor is $2.9 \times 10^{-3}\,WK^{-2}m^{-1}$.

1. Introduction

For decades, bismuth telluride-based materials have been recognised as the best thermoelectric (TE) materials for cooling applications at approximately room temperature. These materials have a strongly anisotropic rhombohedral structure consisting of atomic layers ordered as $Te^{(1)}$-Bi-$Te^{(2)}$-Bi-$Te^{(1)}$ along the *c*-axis, which leads to strong anisotropies in the thermoelectric properties for single crystals [1]. Moreover, the weak Van der Waals bonding between $Te^{(1)}$-$Te^{(1)}$ layers leads to the poor mechanical behaviour of the single crystals [2].

Powder metallurgy has been used to overcome these difficulties [3]; in particular, spark plasma sintering (SPS) is regularly used to sinter such TE powders [4,5]. Hot pressing [6] and hot extrusion [7] techniques have also produced interesting results. All of these techniques are relatively expensive and complex to implement. In this work, we present a preliminary study of the sintering of $(Bi_{0.2}Sb_{0.8})_2Te_3$ commercial powders using microwave energy. This rapid sintering process has shown excellent results in the densification of several other ceramic materials [8]. The principal advantage of this process is the creation of a dense material with a fine microstructure as a result of the very brief sintering time at low temperature. This study focuses primarily on demonstrating the feasibility of sintering such TE materials with microwaves.

2. Materials and methods

2.1. Green compacts

Commercially available p-type $(Bi_{0.2}Sb_{0.8})_2Te_3$ powder supplied by 5N Plus Inc. was used in this study. Two different processes were used in this work. For the first process, green compacts were prepared by uniaxial pressing at 100 MPa to form pellets with diameters of 10 mm. Then, these pellets underwent a cold isostatic pressing at 400 MPa. The green compact density was approximately 84% of the theoretical value ($6.79\,g\,cm^{-3}$). In the second process, green compacts were only prepared by uniaxial pressing at 200 MPa to form pellets with diameters of 10 mm. The density reached was approximately 74% of the theoretical value.

2.2. Sintering run

Considering the geometry and the small size of the samples, direct microwave heating was not sufficient to sinter the green compacts. Densification was thus performed by microwave hybrid heating in a specially designed crucible placed in a $430 \times 430 \times 490\,mm^3$ multimode cavity under a nitrogen atmosphere ($P_{N2} = 1$ bar). The crucible consisted of silicon carbide (SiC) barrels that are regularly arranged around the sample. This design allowed homogenous heating of the inner cavity. The applied microwave power was 600 W with a frequency of 2.45 GHz. An optical pyrometer placed on top of the cavity enabled temperature monitoring with very good reproducibility, as shown in Fig. 1 for a heating ramp of approximately $100\,K\,min^{-1}$. The maximum sintering temperature varied from 400 to 440 °C and the plateau duration varied from 0 to 20 min.

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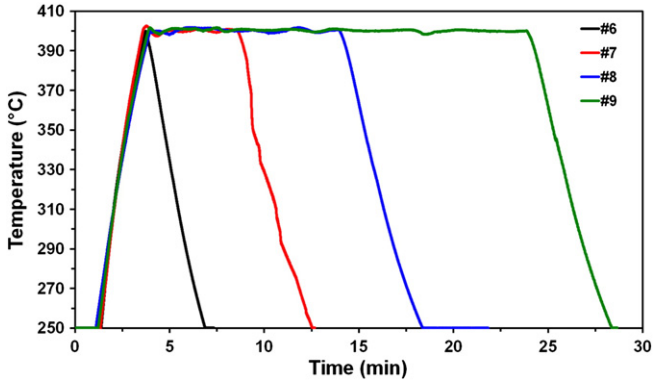

Fig. 1. Temperature cycles of experiments for samples with an initial relative density of 74% (increasing cycle duration from sample 6 to sample 9).

2.3. Characterisations

The final relative density and distribution of porosity were measured by Archimedes' method in alcohol (99.95%). The microstructures in the fractured surfaces were observed by field emission scanning electron microscopy (Model Supra 55 VP, ZEISS, Germany). The average grain sizes were obtained from the micrographs by the intercept method. Taking into account that the aspect ratio of the grains is greater than unity and the number of intercepts is approximately 300, we used the average grain sizes only to compare the different samples. The Seebeck coefficient was calculated from the ratio of the Seebeck tension and the differential temperature to which the sample was submitted. The Seebeck tension was measured using a homemade apparatus where the differential temperature was obtained by maintaining a cold region at 288 K and heating the hot region from ambient temperature up to 478 K to determine the Seebeck coefficient as a function of the temperature. The electrical conductivity was measured at ambient temperature using an HMS-3000 apparatus (Ecopia, BRIDGE TECHNOLOGY, USA).

3. Results and discussion

3.1. $D_{ini} = 84\%$

Several experiments were performed to attempt to improve the final density of the pellets. The sintering conditions used for this set of experiments and the results of the morphological characterisations are presented in Table 1. The corresponding microstructures observed by FESEM are shown in Fig. 2. A comparison of the sample heated 5 min at 400 °C with the green compact shows that the applied sintering cycle results in a slight increase in the relative density (from 84.2 to 85.6%). To further increase the final relative density, two different methods were explored: using a higher temperature or a longer temperature plateau. A 20-K temperature increase results in the same relative density value (85.6%), but the density slowly decreases for higher temperatures (84.6% for 440 °C). A longer temperature plateau results in a significant decrease in the final relative density (82.7%). When the temperature varies from 400 to 440 °C, the percentage of open pores decreases from 7.0 to 5.8%, whereas the percentage of closed pores increases from 7.4 to 9.6%. This trend is exaggerated in the case of the utilisation of a longer plateau, in which almost all of the pores are closed. The corresponding microstructures are shown in Fig. 2. In general, the microstructures of the microwave-sintered samples presented in this paper are very homogeneous. The presented micrographs are taken from a random location in the samples, which indicates that there are no significant thermal gradients present inside the samples during this process. In Fig. 2, it is obvious that even for the softest treatment, the differences from the green compact in terms of morphology are significant. The large agglomerates with sizes of several tens of μm have disappeared upon sintering. The grains are more faceted, and their size dispersion is far less pronounced. The morphologies of samples heated 5 min at 400 and 420 °C are very similar and are quite dense, with an average grain size on the order of approximately 1.1 μm, which increases further for a longer plateau. The presence of pronounced closed porosity in the samples treated 5 min at 440 °C and 10 min at 400 °C is also of note, which is not surprising when considering the structure of Bi-Te-based materials. The weak bonding between $Te^{(1)}$-$Te^{(1)}$ atoms makes this material quite unstable. Such pore formation has already been observed with the hot pressing technique and has been attributed to the evaporation of tellurium [9]; this increase in porosity has also been observed for long annealing times of n-type Bi-Te materials sintered by SPS [10]. To analyse the gases that formed during the microwave sintering experiment, a glass lid was placed on top of the cavity to condense and collect the products of decomposition. As shown in Fig. 3, a metallic deposit composed of micro-needles was found on the glass lid after microwave heating of a p-type green compact for 15 min at 400 °C. An X-ray analysis of this deposit unambiguously shows that the micro-needles are made of pure tellurium. The outgassing is attributed to the decomposition of the $(Bi_{0.2}Sb_{0.8})_2Te_3$ pellets that takes place during the microwave cycle if the cycle is too long or if the temperature is too high. As a consequence, Te_2 gases that are trapped inside the sample cause closed porosity. In order to limit the Te volatilization, we have tried to decrease the sintering temperature by 20 K (i.e. 380 °C) with 10 min plateau duration. This experiment did not show successful results because the temperature was too low to initiate densification of the material

Table 1
Experimental conditions and thermoelectric properties (Seebeck coefficient, electrical conductivity and calculated power factor) of samples used in this study.

Initial relative density*	Temperature	Plateau duration	Final relative density*	Open porosity	Closed porosity	Average grain size	Seebeck coefficient**	Electrical conductivity	Power factor**
[%]	[°C]	[min]	[%]	[%]	[%]	[μm]	[μV.K^{-1}]	[S.m^{-1}]	[W K^{-2}m^{-1}]
84	–	–	84.2	14.4	1.4	<0.7	170	13300	0.4×10^{-3}
84	400	5	85.6	7.0	7.4	1.12	215	62700	2.7×10^{-3}
84	420	5	85.6	5.9	8.5	1.12	217	65000	2.8×10^{-3}
84	440	5	84.6	5.8	9.6	1.13	–	–	–
84	400	10	82.7	0.4	16.9	1.50	–	–	–
74	400	0	76.5	19.2	4.3	0.74	–	–	–
74	400	5	81.0	12.4	6.6	0.88	–	–	–
74	400	10	82.6	9.4	8.0	0.94	–	–	–
74	400	20	83.8	6.6	9.6	1.39	213	69700	2.9×10^{-3}

* Relative densities are calculated with the theoretical value of 6.79 g cm^{-3}.
** These are ambient temperature values.