

## Transport Properties of $\text{Bi}_{43}\text{Se}_4\text{Te}_{53}$ Thermoelectric Alloy Made By Mechanical Grinding and Pulse Discharge Sintering

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### Introduction

In this work, a combination of mechanical grinding followed by pulse discharge sintering (MG-PDS) has been applied to fabricate the n-type  $\text{Bi}_{43}\text{Se}_4\text{Te}_{53}$  thermoelectric alloy. The original alloy is composed of coarse grains (about 10  $\mu\text{m}$  diameter). It is shown that the current MG-PDS process not only produce fine crystallites, but also alters the constituent phases in the sintered samples. Calorimetric measurements demonstrate that, in addition to the  $\text{Bi}_2(\text{Se},\text{Te})_3$  phase, a Se-rich phase is developed after 10 h of milling. However, when the milling time reaches 25 h or longer, instead of the Bi-rich phase, a Te-rich phase is formed. Hall measurements further show that the development of the Se/Te-rich phase considerably increases the carrier concentration, while, in the meantime, decreases the carrier mobility. The thermoelectric property measurement results indicate that the current MG-PDS process does not yield any favorable room-temperature figure of merit over the as-received alloy. The influences of oxygen contamination and additives on the thermoelectric properties are discussed.

### Experimental Procedures

The as-received sample is composed of coarse grains (about 10  $\mu\text{m}$  diameter). Smashing of the as-received sample was done in air. The smashed powders were sieved and the powders under 75  $\mu\text{m}$  diameter were used for the subsequent mechanical grinding. MG was carried out in a vibratory ball mill under a fixed vibration frequency of 25 Hz. The ball-to-powder mass ratio used is 75:1. The milling was conducted in Ar atmosphere. The handling of the mechanically ground powders was made in an argon-filled glove box, in which the oxygen level is kept below 5 ppm. Typically, about 38 g of powders were obtained after each run. The MG powders were then consolidated into bulk by PDS. PDS was carried out at 618 K for 10 min in vacuum. Both MG powders and the sintered bodies were characterized by XRD and SEM. The oxygen content in the MG powders and the sintered samples was determined using an oxygen analyzer. The structural evolution of the sintered samples upon heating/cooling was monitored by means of a DSC under a flowing Ar atmosphere. The electrical, thermal and thermoelectric properties of the sintered samples were investigated. Seebeck coefficient (S) and the electrical resistivity ( $\rho$ ) were determined from room temperature to 433 K in He gas. The temperature gradients were 10-30 K during Seebeck coefficient measurement.

### Result and Discussions

The microstructure in the samples made by MG-PDS process is much finer than the as-received and the sample processed by smashing-PDS. Longer time mechanical grinding makes little difference to the crystal morphology and size. The sample made by either smashing-PDS or MG-PDS has much lower absolute values of Seebeck coefficient than the as-received sample. For all the samples, the absolute value of Seebeck coefficient decreases with increasing the temperature. For all the samples studied, the resistivity

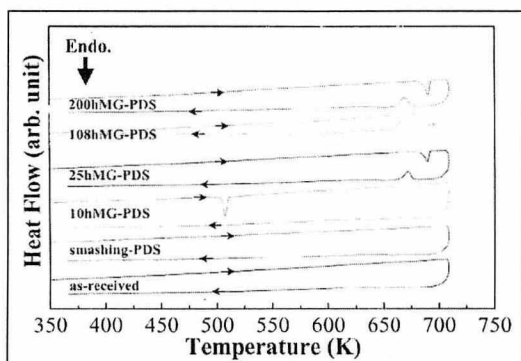


Figure 1 DSC traces of the bulk  $\text{Bi}_{43}\text{Se}_4\text{Te}_{53}$  samples by various processings

endothermal peak around 507 probably corresponds to the melting of the Se-rich phase because this temperature is quite close to the melting point of pure Se. In case of 10h MG-PDS, a Se-rich phase was developed. It is considered that this phase formed by the Se atoms that escape from the lattice of the  $\text{Bi}_2(\text{Se},\text{Te})_3$  hexagonal phase during MG-PDS process. The occupation of these Se vacancies by Bi atoms produces electrons. As the milling time reaches 25 h, rather than the Se-rich phase, a Te-rich phase was identified by DSC in Fig. 1. The Te-rich phase is formed in the same way as the former Se-rich phase. Since the ionized Te vacancies act as donors, adding electrons to the conduction band, the development of the Te-rich phase will contribute a number of electrons to the sintered samples. Also, the increased carrier density in the sintered samples partly comes from the contribution of oxygen contamination. Because, as a donor, oxygen adds electrons to the conduction band of the  $\text{Bi}_{43}\text{Se}_4\text{Te}_{53}$  semiconductor. We studied the influence of additives on the thermoelectric performance and phase evolution of  $\text{Bi}_{43}\text{Se}_4\text{Te}_{53}$  alloy. The additives were deliberately mixed to the smashed powders prior to mechanical grinding. It is found that the additives under the current content remarkably altered the properties of the sintered samples. But, no favorable result was realized in the figure of merit.

## Conclusion

In this work, the mechanical grinding followed by pulse discharge sintering process was introduced to fabricate the n-type  $\text{Bi}_{43}\text{Se}_4\text{Te}_{53}$  thermoelectric samples. The main results can be summarized as follows:

- (1) The MG-PDS processes not only produces fine crystallites, but also alters the constituent phases in the sintered samples. In addition to the  $\text{Bi}_2(\text{Se},\text{Te})_3$  phase, a Se-rich phase is developed after 10 h of milling. However, when the milling time reaches 25 h or longer, a Te-rich phase is formed.
- (2) The development of the Se/Te-rich phase as a result of mechanical grinding gives rise to a number of electrons and simultaneously decreases the carrier mobility and finally leads to a degradation in the room-temperature figure of merit of the sintered samples.
- (3) The oxygen contamination in the smashed powders is also an important consideration for the degeneration in the figure of merit of the sintered samples.
- (4) Preliminary studies on the addition of  $\text{SbI}_3$ , Sb, Te as well as Sb+Ag to the original  $\text{Bi}_{43}\text{Se}_4\text{Te}_{53}$  alloy are carried out. Unfortunately, no improvement in the figure of merit over the as-received samples has been achieved in the experiments.

increases linearly with temperature. For the samples made by MG-PDS the resistivity fails to vary monotonously with the milling time. From Hall measurement, it is found that both the smashing-PDS and MG-PDS processes, especially the MG-PDS, significantly increase the carrier concentration. In order to understand the origin for the carrier concentration enhancement, the phase evolution of the samples made by various processings during heating/cooling was studied by DSC. Some DSC traces were displayed in Fig. 1. The endothermal peak at around 690K can be ascribed to the melting of the Te-rich phase. The