Journal of Power Sources 343 (2017) 316–321

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

# An additive approach to low temperature zero pressure sintering of bismuth antimony telluride thermoelectric materials

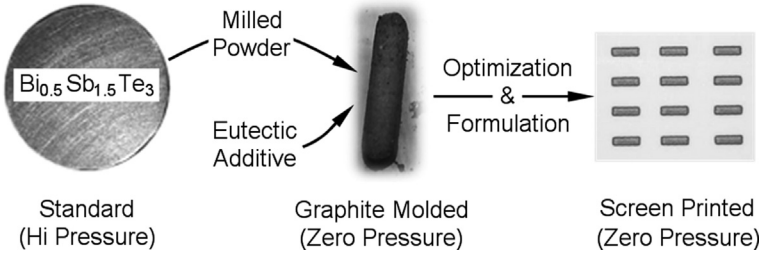
Glenn C. Catlin*, Rajesh Tripathi, Geoffrey Nunes Jr., Philip B. Lynch, Howard D. Jones, Devin C. Schmitt

*Materials Science, Central Research & Development, DuPont Experimental Station, 200 Powder Mill Rd., Wilmington, DE, 19083, USA*

## HIGHLIGHTS

- An additive-based approach for producing screen-printable thermoelectrics is outlined.
- Low pressure and low thermal budget thermoelectric materials processing.
- Thermoelectric paste is used to produce printed thermoelements with a ZT of 0.74.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 10 October 2016
Received in revised form
20 December 2016
Accepted 23 December 2016

*Keywords:*
Thermoelectrics
Power generation
Solid state cooling
Printable electronics
Composites
Seebeck coefficient

## ABSTRACT

This paper presents an additive-based approach to the formulation of thermoelectric materials suitable for screen printing. Such printing processes are a likely route to such thermoelectric applications as micro-generators for wireless sensor networks and medical devices, but require the development of materials that can be sintered at ambient pressure and low temperatures. Using a rapid screening process, we identify the eutectic combination of antimony and tellurium as an additive for bismuth-antimony-telluride that enables good thermoelectric performance without a high pressure step. An optimized composite of 15 weight percent $Sb_{7.5}Te_{92.5}$ in $Bi_{0.5}Sb_{1.5}Te_3$ is scaled up and formulated into a screen-printable paste. Samples fabricated from this paste achieve a thermoelectric *figure of merit* (*ZT*) of 0.74 using a maximum processing temperature of 748 K and a total thermal processing budget of 12 K-hours.



## 1. Introduction

Thermoelectric materials act as solid state transducers that can convert the flow of thermal energy into electrical energy, or vice versa. Use of thermoelectrics as a solid state heat pump for refrigeration is well known [1], and has even been extended to such applications as cooled seats in luxury automobiles [2]. The history of thermoelectrics in power generation is equally long. NASA, for example, has used radioisotope-powered thermoelectric generators to power satellites since the 1960s [3] and a similar generator is currently powering the Curiosity rover on Mars [4]. Recently, there has been renewed interest in thermoelectrics for waste heat recovery, for boosting the efficiency of microelectronics, and as power sources for wireless sensor networks, medical devices, and wearable electronics [2] and [5].

These newer applications require thinner, more flexible form

* Corresponding author.
*E-mail address:* glenn.c.catlin@dupont.com (G.C. Catlin).

http://dx.doi.org/10.1016/j.jpowsour.2016.12.092
0378-7753/

factors [6] and [7], in contrast to more traditional rigid, block-like designs. Peltier coolers with a thin form factor can offer significant increases in cooling power over more conventional designs, provided the thermoelectric material retains a substantial fraction of the bulk material performance [8] and [9]. Interest in these novel form factors is driving interest in alternative deposition techniques. Recent work has employed dispenser [10] and [11], stencil [12], screen [13] and [14], and spray [15] printing as the deposition technology, with an eye to the development of flexible energy harvesters [14] [16], and [17]. These approaches face a common problem: the as-deposited material is a powder, often in a liquid paste form, that must be consolidated at atmospheric pressure. In addition, the thermal budget (processing temperature integrated over time) needs to be compatible with flexible, *i.e.,* polymeric substrates. Reported consolidation methods include laser heating of the printed material [10] and a high temperature sintering step in which additional Te powder is introduced into the heating chamber to limit the loss of vaporized tellurium from the $Sb_2Te_3$ thermoelectric [18]. Evans and co-workers have added selenium [16] and additional tellurium [19] to their powders to lower the sintering temperature and improve the electrical properties of their dispenser-printed formulations.

In the above mentioned works, the challenge of fabricating a consolidated material from a powder is met primarily by adjusting the processing conditions. In the work reported here, we address this challenge through a materials chemistry approach. In particular, we have investigated the use of low-melting point, tellurium-based compounds as additives to $Bi_{0.5}Sb_{1.5}Te_3$ (BST) thermoelectric material. These additives act as low temperature sintering aids for zero pressure processing of powders into consolidated thermoelectric elements. This study was enabled by the development of a rapid screening technique based on reusable graphite molds. The molds allowed us to process small amounts of material directly into bar-shaped samples suitable for electrical measurement. The combination of sample consolidation during heating and graphite's exfoliating properties allowed for a clean and easy sample release after heat treatment (during the development of this screening tool, we learned that Talapin et al. [20] developed a similar approach for shaping thermoelectric composite materials). Using these molds enabled us to quickly investigate a substantial number of additives over a range of concentrations.

One of the main advantages of the paste formulation in this work is that the paste can be used in the screen-printing process, which is a high throughput manufacturing technique and is commonly used in the production of photovoltaic devices. Furthermore, the screening technique and formulation developed in this work can be adapted for use in other additive manufacturing techniques, such as 3D-printing and stereolithography [21]. These manufacturing techniques enable the production of electronic elements with complex geometries, which can increase the performance and efficiency of energy devices [22].

As a result of these investigations, we were able to identify the eutectic compound $Sb_{7.5}Te_{92.5}$ as the best candidate additive, scale up a composite material based on that additive, and formulate a screen-printable thermoelectric paste. Parts printed and processed from that paste were found to have a thermoelectric figure of merit, calculated from individual measurements of Seebeck coefficient, thermal conductivity, and electrical conductivity, of $ZT = 0.74$.

## 2. Experimental

### 2.1. Synthesis and sample preparation

Bismuth antimony telluride (BST) powders were generated through mechanical alloying of elemental Bi, Sb, and Te powders in a 0.5/1.5/3.01 M ratio. The ball-to-material ratio (BMR) was kept between 2.0 and 3.5. The additives were generated through melt synthesis in a quartz tube furnace under an argon atmosphere. As a standard practice, the furnace was purged (by evacuation and backfilling with process gas) a minimum of 3 times prior to each use. The additives were then cryogenically ball-milled for particle size reduction. Composite materials were created by cryogenic milling BST and additive powders together in 5 mL stainless steel vials with a BMR of 1.0 and a powder loading of 2.0 g per vial. A scaled-up process for larger batches of composite used a 50 mL stainless steel milling jar with a BMR of 2.0 and a powder loading of 20.0 g per jar.

Samples of thermoelectric material were formed by heat treating the composite powders in graphite molds. The molds were fabricated by cutting 2 mm wide, 11.2 mm long, 1.2 mm deep channels in blocks of graphite. The molds were prepared by overfilling each channel to form a small mound, and then hand-compressing the mound using the flat bottom of a quartz crucible. A second iteration of this mounding/compaction process was carried out to ensure homogeneous material distribution within the channel. The three channels in each mold were always filled with the same composite. The filled molds were then heat treated in a quartz tube furnace under forming gas. All molded samples were held at the maximum temperature indicated in Table 2 for 1 min. After heat treatment, the samples were removed by simply inverting the molds (Fig. 1).

Baseline comparison samples were formed by hot pressing in a standard plate press using 12.7 mm diameter stainless steel dies. Additives were hot pressed at 120 ± 20 MPa with the platens held at 613 K for a minimum of 30 min. A BST control sample was hot pressed in an argon atmosphere using a graphite die at a temperature of 723 K for 20 min.

Screen printable pastes were formulated by blending BST (or BST composite) powder (89.4 wt%), ethyl cellulose binder (0.7 wt%), and Texanol™ organic vehicle (9.9 wt%) in a speedmixer. Texanol™ is an ester alcohol and has a boiling point of 254 °C (at 760 mm Hg), a molecular weight of 216.321 g $mol^{-1}$, and is a trademark of Eastman Chemical Company. The resulting pastes were then

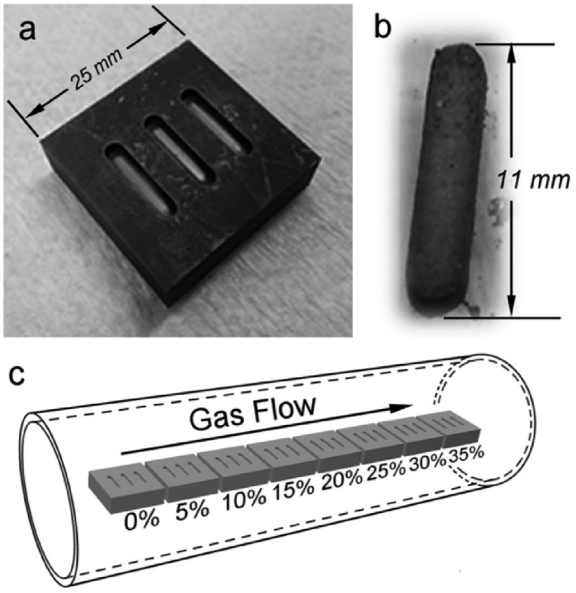



**Fig. 1.** (a) Graphite mold used in processing the samples. (b) Typical sample pellet after release from the mold. (c) Arrangement of the samples in the tube furnace for heat treatment.