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Fabrication of Thermoelectric Bismuth Telluride Films using the Novel Resin 3D Printing Technique

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ABSTRACT

The global drive for clean energy sources to replace carbon-based fossil fuels necessitates the development of advanced fabrication processes for thermoelectric materials. Thermoelectric materials can generate electricity from ambient heat, making them promising for low-power generating devices that typically rely on batteries with limited lifespans. Compared to bulk materials, thermoelectric thin films offer enhanced performance due to increased Seebeck coefficient and reduced thermal conductivity. However, fabricating high-quality thermoelectric thin films often involves complex and costly vacuum deposition techniques, hindering their widespread application. This study explores the fabrication of thermoelectric Bismuth Telluride (Bi_2Te_3) films using a resin-based 3D printing method aimed at reducing synthesis costs while enhancing thermoelectric properties. Bi_2Te_3 films were synthesized via photopolymerization, commercially known as resin 3D printing. In this method, Bi_2Te_3 was mixed with a flexible photopolymer resin to facilitate film formation. Ratios of resin to Bi_2Te_3 tested were 60:40, 70:30, 80:20, and 90:10. As the resin content increased, the films became more durable and sturdier, despite a potential trade-off in performance. Phase analysis of the films was conducted using X-ray diffraction (XRD), confirming the presence of Bi_2Te_3 peaks. Elemental and microstructural characterization via Scanning Electron Microscope (SEM) revealed the presence of Bi_2Te_3, including pores that are potentially associated with the resin content. This study demonstrates a novel and cost-effective approach to fabricating Bi_2Te_3 thermoelectric films using photopolymerization 3D printing, maintaining desirable thermoelectric properties without the need for complex fabrication processes.

1. Introduction

Thermoelectric (TE) materials are gaining traction as a promising renewable energy source. They have the potential to efficiently utilize widely available waste heat, offering a sustainable and long-

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term energy solution without the need for battery replacements or frequent recharging [1]. The TE performance of materials in TE devices directly dictates their overall energy conversion efficiency. TE materials are crucial components in TE devices as their performance substantially affects the device's ability to convert heat into electricity efficiently [2,3].

The dimensionless figure of merit (ZT) governs the conversion efficiency of thermoelectric (TE) materials. ZT is defined as $ZT = \sigma S^2 T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and κ represents the total thermal conductivity which includes electronic (κ_e), bipolar (κ_b), and lattice (κ_l) contributions [4]. Optimizing TE performance therefore requires minimizing κ while maintaining high values for both σ and S. Near room temperature applications favor bismuth telluride (Bi_2Te_3) as the leading TE material. This is due to its unique combination of inherently low lattice thermal conductivity, κ_l and high electronic weighted mobility [5,6]. For instance, Bi_2Te_3 and its alloys like Sb_2Te_3 or Bi_2Se_3 have established themselves as the leading TE materials for near-room temperature applications [7,8]. This dominance stems from their successful implementation in commercially available TE devices and modules for both power generation and solid-state cooling within this temperature range [9].

On the downside, the fabrication process of Bi_2Te_3 is time- and cost-consuming. For example, zone melting (ZM) which remains the dominant method for commercial production of Bi_2Te_3-based TE materials suffers from drawbacks such as being time-consuming and energy-intensive [10]. Additionally, prolonged high-temperature annealing can cause compositional deviations, ultimately degrading TE performance. Furthermore, ZM-produced materials exhibit high orientation and a propensity to cleave along the basal plane, leading to poor mechanical properties and hindering long-term durability [11]. Extensive research has explored alternative fabrication methods to address the limitations of zone melting, particularly its high energy consumption, extended processing times, and associated costs. Techniques like high-energy ball milling, melt spinning, and various wet chemical methods have been successfully developed for synthesizing Bi_2Te_3-based compounds with desirable features like fine grain size and modulated microstructure [12-15].

Combining these synthesis methods with hot pressing (HP) or spark plasma sintering (SPS) can achieve both robust mechanical properties and high TE performance in Bi_2Te_3 bulk materials [16,17]. However, these alternative methods still present challenges. They can be time-consuming and energy-intensive, and the products may suffer from oxidation or contamination by residual media and organic impurities during synthesis, ultimately leading to degraded TE performance. In an attempt to overcome these drawbacks, this work explores 3D printing as a novel and potentially cost-effective approach to fabricating Bi_2Te_3 films for TE applications. 3D printing technology, first reported by Hull [18,19], has seen rapid advancements in recent years due to progress in precision measurement and control. One prominent 3D printing method utilizes photopolymer resins, implemented primarily through stereolithography apparatus (SLA), digital light processing (DLP), and 3D spray printing (3DSP) techniques [19,20,21]. This technology builds objects layer-by-layer by optically curing liquid photopolymer resins [22,23]. 3D printing with photopolymer resins offers advantages such as cost-effective utilization, high building accuracy, and rapid fabrication, making it a popular choice for rapid prototyping and manufacturing [24-26]. Therefore, this work investigates a novel approach for fabricating Bi_2Te_3 films via photopolymer resin-based 3D printing. The pre-printing mixture ratio of photopolymer resin and Bi_2Te_3 powder was carefully considered towards fabrication. Subsequently, the microstructure and elemental composition of the printed films were characterized to assess the feasibility of this fabrication process.

2. Methodology

The 3D printed Bi_2Te_3 films were prepared firstly by manually mixing Bi_2Te_3 powders with photopolymer resin (Magma Flexible Photopolymer Resin Series). Here, the ratio of Bi_2Te_3 powders and photopolymer resin was determined by the following equation:

$$\frac{x}{n\%} \times \frac{y}{m\%} \tag{1}$$

where x and y are the weight of photopolymer resin and Bi_2Te_3 powder respectively in gram, while n is the percentage of photopolymer resin and m is the percentage of Bi_2Te_3 powder, both in the final mixture. Then, these mixtures were stirred manually for 10 minutes using a glass rod. As illustrated in Figure 1, these mixtures were placed in the printer (Creality LD-002H Mono LCD UV Resin 3D printer) with the printing setting associated with the design dimension of 20 mm-wide, 20 mm-long and 0.1 mm-thick. The mixtures were then imprinted on the soda lime substrate to obtain the resin-Bi_2Te_3 layer for further procedure.

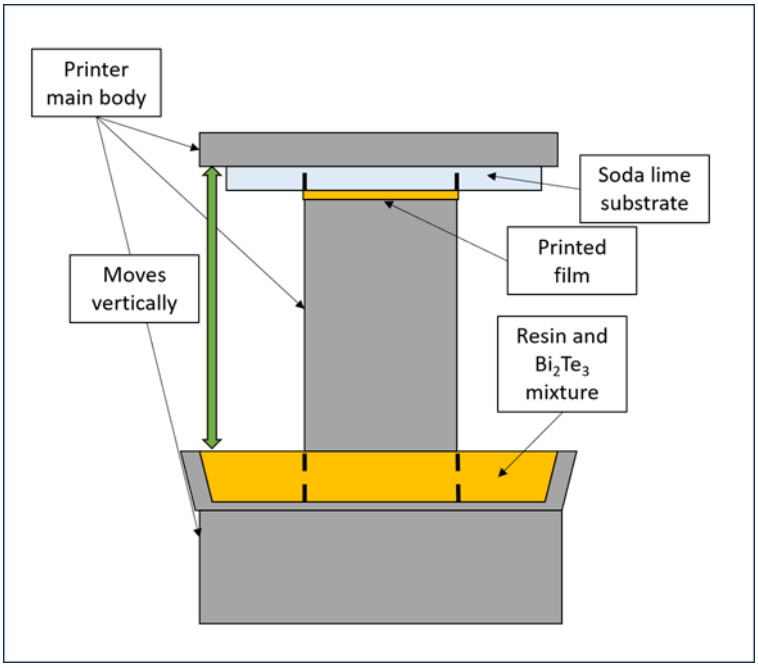

Fig. 1. Schematic diagram of 3D printing fabrication procedure

After printing, these films were exposed to UV light for 9 seconds to solidify them. With the purpose of densification and resin elimination, these films were placed on aluminum oxide (Al_2O_3) boats for the following annealing procedure. Annealing conditions were set to 200 ℃ of holding temperature, and 40 minutes of holding time in a muffle furnace (Furnace Carbolite 301). This condition was selected based on previous works where an annealing temperature of 350 ℃ for 90 minutes showed the best TE performance [17]. However, during the preliminary step for the current work, the samples turned into powder with the same annealing condition, showing a possible sudden loss of binding effect expected by the photopolymer resins. Hence, 200 ℃ of holding temperature, and 40 minutes of holding time were found to be the most suitable annealing condition for this work. The sample names associated with its photopolymer resin-powder ratio and annealing conditions are summarized in Table 1 below.

Table 1
Sample composition and annealing condition

Sample name	Mixing ratio in wt% (resin: powder)	Annealing condition
10BT	90:10	Unannealed
20BT	80:20	Unannealed
30BT	70:30	Unannealed
40BT	60:40	Unannealed
40BTa	60:40	200 ℃, 40 minutes

Following the fabrication process, the 3D printed films' microstructure and elemental composition were observed using the Low-Vacuum Secondary Electron Microscope (LV-SEM) and its attached Energy Dispersive X-ray Analyzer (EDS).

3. Results

As shown in Figures 2(a-d), increasing the photopolymer resin ratio led to the enhanced physical integrity of the fabricated films, suggesting improved mechanical strength. This aligns with the expected binding effect of the photopolymer resin, contributing to enhanced printability [27]. However, a potential trade-off may arise as the increased resin content could compromise TE performance due to decreased Bi_2Te_3 powder proportion. SEM images in Figure 3 illustrate a flaky morphology for the Bi_2Te_3 powders, appearing as lighter gray regions. Image analysis determined an average particle size ranging from 10 to 100 µm.

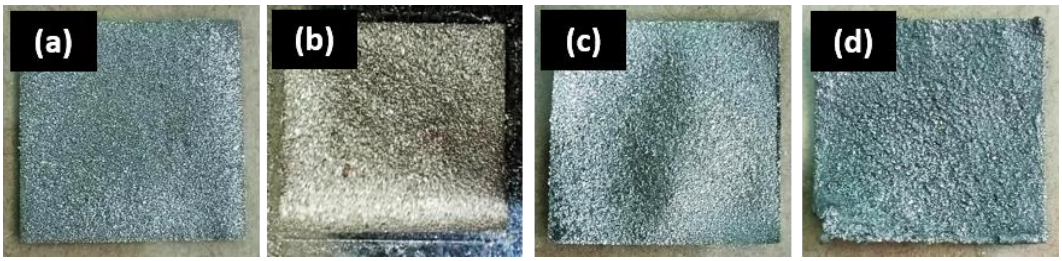

Fig. 2. Images of fabricated films with the photopolymer resin to Bi_2Te_3 ratio at (a) 90:10 (b) 80:20 (c) 70:30 (d) 60:40

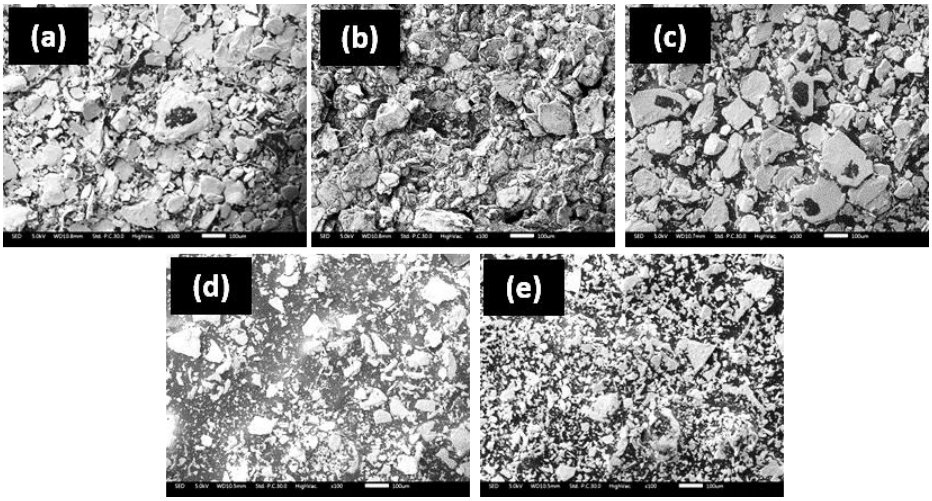

Fig. 3. SEM images of fabricated film before annealing with the photopolymer resin to Bi_2Te_3 ratio at (a) 90:10 (b) 80:20 (c) 70:30 (d) 60:40 (e) 60:40 after annealed at 200℃ for 40 minutes

The surface of the Bi_2Te_3 appeared smooth with no visible defects. The darker grey region is believed to be the photopolymer resin or pores, agreeing with the EDS quantitative analysis, summarised in Figure 4 and Table 2. This morphology is consistent with previous studies on similar materials [19]. Furthermore, there is a sign of densification after the annealing process as shown in Figure 3(d) and Figure 3(e). For powdered materials, annealing can cause the particles to bond together through atomic diffusion, reducing their porosity and increasing density [28]. This is promising towards TE performance enhancement with the increase in density in fabricated films. Further studies are required to identify quantitively the amount of remaining photopolymer resins or pores associated with the annealing process which was expected to eliminate traces of photopolymer resins.

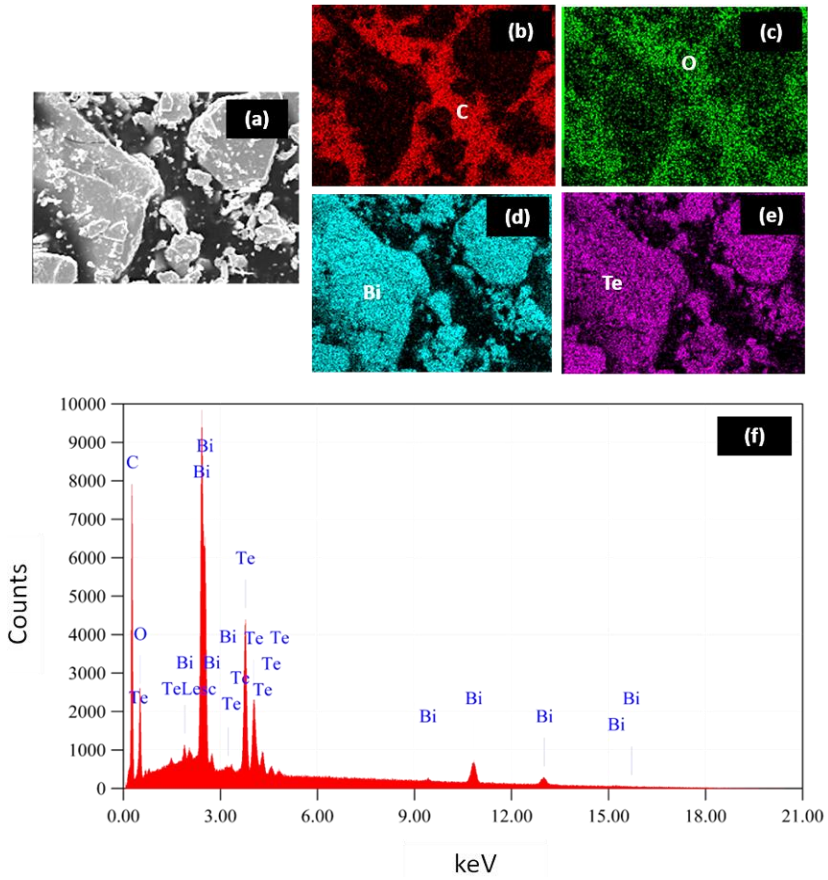

Fig. 4. (a) SEM image (b-e) EDS mapping of C, O, Bi and Te (f) Elemental composition, for sample 40BTa

EDS mapping (Figure 4) and corresponding quantitative analysis (Table 2) indicate a predominant distribution of Bi and Te within the film. Oxygen (O) and carbon (C) were detected throughout the sample, exhibiting higher concentrations in regions depleted in Bi and Te.

Table 2
Quantitative analysis of sample 40BTa

Elements	Mass (%)
C	14.99
O	1.90
Te	25.80
Bi	57.31
Total	100

The presence of O suggests the formation of oxide phases, porosity, or residual photopolymer resin, which may influence material properties. To elucidate the precise nature of C and O, further characterization using Raman or FTIR spectroscopy is recommended. In summary, the phase and elemental analyses collectively demonstrate the feasibility of fabricating Bi_2Te_3-based films via photopolymerization 3D printing.

4. Conclusions

A novel resin 3D printing method successfully was successfully implemented in the fabrication of promising high-performance Bi_2Te_3 films, with a minimum resin content of 60 wt%. SEM images confirmed the films' microstructure and EDS analysis verified their elemental composition. However, further quantitative analysis is needed to assess porosity and resin content. Additionally, thermoelectric property evaluation is crucial to definitively determine the viability of this Bi_2Te_3 film fabrication method.

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