# **Energy materials**



# Self-healing boron-doped  $Sb_2Se_3$  thermoelectric materials prepared using liquid metallic Ga–Sn alloys

Minsu Kim<sup>1</sup>, Dabin Park<sup>1</sup>, and Jooheon Kim<sup>1,2,3,\*</sup>

<sup>1</sup> School of Chemical Engineering and Materials Science, Chung-Ang University, Seoul 06974, Republic of Korea  $^2$ Department of Advanced Materials Engineering, Chung-Ang University, Anseong-si, Gyeonggi-do 17546, Republic of Korea <sup>3</sup> Department of Intelligent Energy and Industry, Graduate School, Chung-Ang University, Seoul 06974, Republic of Korea

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# ABSTRACT

Inorganic thermoelectric materials are typically brittle and unrecyclable. Among these inorganic thermoelectric materials, antimony selenide  $(Sb<sub>2</sub>Se<sub>3</sub>)$  is a promising material for preparing topological insulators and photovoltaic devi- $\text{ces.}$  Sb<sub>2</sub>Se<sub>3</sub> has a large Seebeck coefficient and extremely low electrical conductivity. To apply  $Sb_2Se_3$  as a thermoelectric material, its electrical conductivity must be improved, and self-healing must be realized. In this study, we fabricated self-healing thermoelectric composites using liquid metals from Ga–Sn and  $Sb_2Se_3$  thermoelectric materials.  $Sb_2Se_3$  nanowires and nanosheets were fabricated through hydrothermal reactions. To improve the thermoelectric performance, the Sb<sub>2</sub>Se<sub>3</sub> nanowire and nanosheet samples were doped with elemental boron. B-doping enhanced both carrier concentration and the carrier mobility, leading to improved electrical conductivity and Seebeck coefficient. The composite material with the highest thermoelectric performance was identified by adjusting the ratio of  $Sb_2Se_3$  nanowires to nanosheets. Subsequently, a liquid metal alloy Ga–Sn was prepared to achieve a melting point of 166 °C. Furthermore, a Ga–Sn and  $Sb_2Se_3$  hybrid composite with a weight ratio of 5:5 was prepared through hot pressing at 130  $^{\circ}$ C (temperature lower than the melting point). The fabricated composite was cut into two pieces and heated to approximately 130  $\degree$ C to induce self-healing. The cuts self-healed successfully, albeit with a certain loss of the Ga–Sn alloy. The electrical conductivity of the self-healed composites decreased slightly owing to the presence of voids and losses in the Ga–Sn liquid metal.

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Address correspondence to E-mail: jooheonkim@cau.ac.kr

#### GRAPHICAL ABSTRACT



# Introduction

In recent decades, Te-based thermoelectric materials, such as  $Bi_2Te_3$  [\[1–3](#page-11-0)],  $Sb_2Te_3$  [[4–6\]](#page-11-0), and Ag<sub>2</sub>Te [\[7](#page-11-0), [8\]](#page-11-0), have attracted considerable research attention owing to their high Seebeck coefficients. Te-based materials can easily be synthesized into diverse structures such as nanowires, nanorods, and nanosheets. However, the toxic nature of Te has prompted research focused on exploring less toxic and earth-abundant Se-based materials that have similar properties [[9–12\]](#page-11-0). Many researchers have investigated  $Bi<sub>2</sub>Se<sub>3</sub>$ - [\[13](#page-11-0), [14\]](#page-11-0),  $Bi<sub>2</sub>O<sub>2</sub>Se- [15–18]$  $Bi<sub>2</sub>O<sub>2</sub>Se- [15–18]$ , Cu<sub>2</sub>Se- [\[19–21](#page-11-0)], and SnSe-based materials [\[22](#page-11-0), [23\]](#page-11-0) to achieve enhanced thermoelectric performances. Among these materials, antimony selenide  $(Sb<sub>2</sub>Se<sub>3</sub>)$  are insulating materials, which has extremely low electrical conductivity and large Seebeck coefficient over 400  $\mu$ V/K [[24–26\]](#page-11-0). This extremely low electrical conductivity limits its application as a thermoelectric material. Similar to other Se-based thermoelectric materials,  $Sb<sub>2</sub>Se<sub>3</sub>$  can be synthesized in different structures such as nanosheets [\[27](#page-11-0), [28\]](#page-12-0), nanowires [[29,](#page-12-0) [30](#page-12-0)], and thin films [[25,](#page-11-0) [31](#page-12-0)]. Therefore, to enhance the thermoelectric performance of  $Sb_2Se_3$ , its electrical conductivity must be increased.

Inorganic thermoelectric materials such as rigid composite or flexible films exhibit several disadvantages such as low durability. Damaged thermoelectric materials cannot be repaired and should be replaced. To overcome this limitation, self-healing thermoelectric materials have been explored. Self-healing properties have been induced by introducing organic materials [[32](#page-12-0), [33\]](#page-12-0), polymer materials [\[34–36](#page-12-0)], phasechange materials [[37\]](#page-12-0), and liquid metals [\[38](#page-12-0), [39](#page-12-0)]. Unlike organic or polymeric materials, liquid metals can enhance the electrical conductivity of thermoelectric materials. A liquid metal that is commonly used is eutectic gallium–indium (EGaIn), which has a low melting point of 15.7 °C [[40,](#page-12-0) [41](#page-12-0)]. Owing to this low melting point, EGaIn is easy to process; however, the operating temperature range is reduced because the operating temperature  $(T_{op})$  must typically be lower than the melting point  $(T_{mp})$  (*i.e.*,  $T_{op} < T_{sh} < T_{mp}$ ). Malakooti et al. fabricated EGaIn-embedded thermoelectric supercooling materials, which can freeze temperature to  $- 84$  °C [\[42](#page-12-0)]. And Chen et al. fabricated flexible thermoelectric generator with bismuth telluride and bismuth antimony telluride nanowires and EGaIn contacts. The fabricated thermoelectric generator produced 127 nW at a 32.5 K temperature difference [[43\]](#page-12-0). However, compared to our study, EGaIn liquid metal was used to connect electrically each generator legs in series. In this study, we use Ga– Sn alloys with a melting point of 166  $°C$ . The melting points of gallium and tin are  $32 \degree C$  and  $232 \degree C$ , respectively. The melting point of the alloy can be controlled by adjusting the ratio of Ga and Sn contents.

The high melting point and electrical conductivity of the liquid metal Ga–Sn alloy can help enhance the thermoelectric performance of  $Sb<sub>2</sub>Se<sub>3</sub>$  composites. To establish the transport network of charge carriers to promote the recovery of the cut plane of the composite,  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowire and nanosheet composites are fabricated, and their thermoelectric performances are evaluated. The highest composite ratio is selected to fabricate a self-healing  $Ga$ – $Sn@B-Sb<sub>2</sub>Se<sub>3</sub>$  composite. When the composite is cut into two pieces and heated to 130  $\degree$ C, the Ga-Sn alloy melts at the cut surface, and the cut surface is restored.

## Experiments

#### **Materials**

Antimony (III) chloride (SbCl<sub>3</sub>; 99%) and sodium selenite (Na<sub>2</sub>SeO<sub>3</sub>; anhydrous; 99%) were purchased from Alfa Aesar. Boric acid (BH<sub>3</sub>O<sub>3</sub>; 99.5%), sodium borohydride (NaBH4; 98%), tin (Sb; shot, 99.999%), and gallium (Ga; 99.99%) were obtained from Sigma– Aldrich. Hydrazine monohydrate and cetyltrimethylammonium bromide (CTAB; 99%) were purchased from Daejung Chemical & Metals Co., Ltd (Seoul, Korea). Potassium antimony tartrate  $(C_8H_4K_2O_{12}Sb_2)$ -3H2O; 99.5%) was acquired from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan). All reagents were used as received without any purification process.

# Synthesis of  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowires and nanosheets

In 100 mL of distilled water (D.I. Water), 0.665 g of antimony potassium tartrate, and 0.51 g of sodium selenite were dissolved with vigorous magnetic stirring. The color of the solution approached white with stirring. Subsequently, 20 mL of hydrazine monohydrate was added to the solution, and the color became peach-like. The peach-colored solution was transferred to a Teflon-lined autoclave with 40 mL of tetrahydrofuran to fill 80% of the container. The sealed autoclave was heated at 135  $\degree$ C for 9 h. The product was washed with ethanol and D.I. water several times, and then dried in a vacuum oven at 60 °C overnight to obtain  $Sb_2Se_3$  nanowires [[44\]](#page-12-0).

The synthesis procedure of  $Sb_2Se_3$  nanosheets were referred previously reported studies  $[28]$  $[28]$ . Sb<sub>2</sub>Se<sub>3</sub> nanosheets were synthesized by the following process: 0.3423 g of antimony trichloride and 0.3375 g of CTAB were dissolved in 45 mL D.I. water. Subsequently, 0.3891 g of sodium selenite and 0.3390 g of sodium borohydride were dissolved in another 50 mL D.I. water. These two solutions were mixed separately with magnetic stirring for 30 min, and then, mixed together followed by 30 min of magnetic stirring to obtain a homogenous solution. The obtained solution was transferred to a 200-mL Teflonlined autoclave, and D.I. water was added to fill approximately 70% of the autoclave. The autoclave was placed in a drying oven and heated to 200  $^{\circ}$ C for 24 h. The product was washed with ethanol and D.I. water several times, and then dried in a vacuum oven at 60 °C overnight to obtain  $Sb_2Se_3$  nanosheets.

To dope  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowires and nanosheets, each nanowire and nanosheet materials was added to 1 M of  $H_3BO_3$  (boric acid) solution for 6 h and dried overnight.

# Fabrication of Ga–Sn alloys and Ga–Sn@B- $Sb<sub>2</sub>Se<sub>3</sub>$  composites

To fabricate the Ga–Sn alloy, Ga and Sn elements were mixed in various ratios. Each mixture was poured into a ceramic crucible and shifted to a muffle furnace purged with  $N_2$  gas. Considering the melting point of Sn (232  $\degree$ C), the muffle furnace was heated to 235 °C at a rate of 3 °C min<sup>-1</sup>. After melting Ga and Sn, the temperature of the muffle furnace was gradually decreased to room temperature to obtain the Ga–Sn alloy. Subsequently, differential scanning calorimetry (DSC; DSC 131 Evo, Setaram Instrumentation) was performed to determine the melting point of the Ga–Sn alloys.

The Ga-Sn@B-Sb<sub>2</sub>Se<sub>3</sub> composites were fabricated by mixing the Ga–Sn alloy and  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowire/nanosheet mixture with a weight ratio of 1:1 and hot-pressing at 130  $\degree$ C for 20 min to fabricate diskshaped pellets.

#### Characterization

The morphology and microstructures of the  $Sb<sub>2</sub>Se<sub>3</sub>$ nanowires and nanosheets were investigated using field-emission scanning electron microscopy (FE-SEM; SIGMA) and field-emission transmission electron microscopy (FE-TEM; JEM-F200). Moreover, the elemental mappings of the samples were obtained



using energy-dispersive X-ray spectroscopy (EDS; Thermo NORAN System 7, SIGMA) with FE-TEM. The crystalline structures of the  $Sb_2Se_3$  nanowires and nanosheets were confirmed using X-ray diffraction (XRD; D8 Advance, AXS Bruker) over a 2h range of  $10^{\circ}$  to  $80^{\circ}$  at 40 kV and 40 mA at a scan rate of  $0.1^{\circ}$  $s^{-1}$  under  $\lambda = 0.154056$  nm Cu K<sub>a</sub> radiation. The binding energies of  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowires and nanosheets were determined using X-ray photoelectron spectroscopy (XPS; K-Alpha, Thermo UK) using a 1486.6 eV Al  $K_{\alpha}$  X-ray source. The chemical structures in the samples were clarified using a Raman spectrometer II (DXR2xi, Thermo) with a near-infrared laser operating at 532 nm and a charge-coupled device detector.

The thermoelectric property  $S$  and  $\sigma$  values of the samples were measured using a homemade device. Specifically, the homemade device with a pair of voltmeters was used to implement a four-probe method. A pair of thermostats was used to quantify the  $\sigma$  between 298 and 373 K. The S value was calculated using the following equation:

$$
S = \Delta V / \Delta T \tag{1}
$$

where  $\Delta V$  is the change in the thermal electromotive force, and  $\Delta T$  is the temperature difference. The thermoelectric power force (PF) was calculated as follows:

$$
PF = S^2 \cdot \sigma \tag{2}
$$

In order to increase the accuracy of electrical conductivity and Seebeck coefficient measurement, each measurement was repeated more than 10 times, and the average value is shown in the figure of the manuscript.

In addition, the melting point of the Ga–Sn alloy was measured using DSC.

The charge carrier concentration and mobility were measured using Hall-effect measurements (HMS-300, Ecopia) under  $\pm$  1 T magnetic field with the van der Pauw method at room temperature.

# Results and discussion

## Thermoelectric performances of B-doped  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowires and nanosheets

Figure [1](#page-4-0) shows the thermoelectric Seebeck coefficients and electrical conductivity of  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowires and nanosheets before and after B-doping. The thermoelectric performances with increasing  $Sb<sub>2</sub>Se<sub>3</sub>$  nanosheet ratios were measured. The pristine Sb<sub>2</sub>Se<sub>3</sub> particles exhibited a high Seebeck coefficient of  $400 \mu V/K$  at room temperature, which indicated that  $Sb_2Se_3$  is a ptype thermoelectric material with hole charge carriers [[44\]](#page-12-0). The Seebeck coefficient of the  $Sb_2Se_3$  nanosheets was higher than that of the nanowires. In general, onedimensional nanowire/nanorod materials act as more effective transport channels for charge carriers compared with two-dimensional nanosheet materials and thus have a high electrical conductivity but low Seebeck coefficient. The pristine  $Sb_2Se_3$  exhibited an extremely low electrical conductivity  $(10^{-4} \text{ Sm}^{-1})$ , owing to which,  $Sb_2Se_3$  was considered to be a promising material for topological insulators. After B doping, the Seebeck coefficient and electrical conductivity increased slightly for both the nanowire and nanosheet samples. B is a representative p-type dopant that affects the charge carrier concentration and mobility. The carrier concentration and mobility of Sb<sub>2</sub>Se<sub>3</sub> nanowire was  $6.24 \times 1011$  cm<sup>-3</sup> and 10 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>, respectively. The electrical conductivity of Bdoped Sb<sub>2</sub>Se<sub>3</sub> nanowires and nanosheets increased owing to the increase in the carrier concentration and mobility. The measured carrier concentration and mobility of Sb<sub>2</sub>Se<sub>3</sub> nanowires were  $2.69 \times 10^{13}$  cm<sup>-3</sup> and 37  $\text{cm}^2 \text{V}^{-1} \text{ s}^{-1}$ . Due to the enhancement of carrier concentration and mobility, the power factor of  $Sb_2Se_3$ composite was improved as a whole nanosheet ratio, and the highest power factor value of  $3.22 \times 10^{-3} \mu W/$  $mK<sup>2</sup>$  was obtained at the 3:7 ratio of nanosheet and nanowire.

To confirm the synthesis of B-doped  $Sb_2Se_3$ , XRD and Raman analyses were performed, as shown in Fig. [2](#page-4-0). The XRD patterns of both  $Sb_2Se_3$  nanowire and nanosheets corresponded to the previously reported  $XRD$  pattern of  $Sb_2Se_3$  (JCPDS No. 15–0861) [\[44](#page-12-0), [45](#page-12-0)]. The hkl index for  $Sb_2Se_3$  nanowires is shown in Fig. S1. No other secondary peaks were observed, which indicated the successful synthesis of each nanowire and nanosheet. After B-doping, the XRD patterns shifted to slightly lower angles. This phenomenon likely occurred owing to the introduction of B atoms between the lattices of  $Sb_2Se_3$ , resulting in lattice expansion. The Scherrer equation,  $t = 0.94 \times \lambda/ B \cos(\theta)$ , was used to check grain size of  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowire using XRD patterns, where t is the grain size,  $\lambda$  denotes the X-ray wavelength

<span id="page-4-0"></span>

Figure 1 a Electrical conductivity and Seebeck coefficient, b calculated power factor of  $Sb_2S_8$  composites with various  $Sb_2S_8$ nanosheets ratio measured at room temperature.



Figure 2 XRD patterns of a  $Sb_2Se_3$  nanowires, nanosheets and b B-doped  $Sb_2Se_3$ . c High-resolution XRD pattern of b. d Raman spectra and e high-resolution of Sb<sub>2</sub>Se<sub>3</sub> nanowires, nanosheets, B-doped nanowires, and nanosheets.





Figure 3 XPS survey spectra of a B-doped  $Sb_2Se_3$  nanowire b B-doped  $Sb_2Se_3$  nanosheets. High-resolution B 1 s XPS spectra of c Bdoped  $Sb_2Se_3$  nanowires and **d** B-doped  $Sb_2Se_3$  nanosheets.

 $(0.154056 \text{ nm})$ , and B is the full width at half-maximum XRD peak width in radians [[46\]](#page-12-0). The calculated grain size of  $Sb_2Se_3$  nanowires was  $27 \pm 3$  nm, which corresponding to the diameter of nanowires from FE-SEM images discussed below. For nanosheet material, nanosheets were easily aggregated to form 5–600 nm size. After boron doping, the XRD peak was shifted slightly, and the morphology and diameter of nanowire were almost unchanged. For this reason, it is not sufficient to confirm boron doping using the change of grain size. However, boron doping was confirmed with Raman, XPS analyses

and expansion of lattice fringe in FE-TEM measurement which discussed below. Similarly, the Raman spectra of the  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowire and nanosheets corresponded to the Raman signature peaks of  $Sb<sub>2</sub>Se<sub>3</sub>$ located at 188, 208, and  $252 \text{ cm}^{-1}$ , respectively [\[47](#page-12-0)]. After B-doping, the Raman peaks exhibited a blue shift, indicating the expansion of the  $Sb_2Se_3$  lattice [[48\]](#page-12-0). An XPS analysis was conducted to examine the surface chemistry of B-doped  $Sb<sub>2</sub>Se<sub>3</sub>$ . Figure 3 shows the XPS survey spectra of the B-doped  $Sb_2Se_3$  nanowires and nanosheets. After B-doping, a B 1 s peak emerged located at 187 eV indicating B (0) state [\[49](#page-12-0)].



Figure 4 FE-SEM images of a  $Sb_2Se_3$  nanowires and b  $Sb_2Se_3$  nanosheets. EDS elemental mappings of c  $Sb_2Se_3$  nanowires and  $d$  Sb<sub>2</sub>Se<sub>3</sub> nanosheets.

FE-SEM and FE-TEM analyses were performed to examine the morphology and B-doping. The FE-SEM images of the Sb<sub>2</sub>Se<sub>3</sub> nanowires and nanosheets indicated the presence of highly crystalline structure, consistent with the XRD patterns. The  $Sb_2Se_3$  nanowires exhibited a thin and long morphology with a diameter and length of  $25-30$  nm and  $5-6$  µm, respectively. The size of the  $Sb_2Se_3$  nanosheets was 5–600 nm. The EDS elemental mapping indicates that the  $Sb_2Se_3$  nanowires and nanosheets were successfully synthesized. The FE-TEM images also indicated that the  $Sb_2Se_3$  nanowires had a highly crystalline wire morphology with a lattice fringe of 0.397 nm. The  $Sb_2Se_3$  nanosheets had a size of 5–600 nm with a lattice fringe of 0.216 nm. After B-doping, the lattice fringes of the  $Sb_2Se_3$  nanowires and nanosheet expanded to values of 0.416 nm and 0.229 nm, respectively. As mentioned previously, the introduction of B atoms between the  $Sb_2Se_3$  lattice led to lattice expansion. EDS elemental mapping was performed to confirm successful B-doping. For both the nanowire and nanosheet samples, the Sb and Se elements were uniformly distributed with a stoichiometric ratio of 2:3 confirmed by XPS data. Furthermore, the B elements were randomly distributed, indicating successful B-doping (Figs. 4, [5](#page-7-0)).

# Fabrication of Ga–Sn liquid metal alloys and performance evaluation of Ga–Sn@B- $Sb<sub>2</sub>Se<sub>3</sub>$  composites

To fabricate the Ga–Sn alloy with a melting point of 166  $\degree$ C, Ga and Sn were melted in a ceramic crucible by maintaining a temperature of 235  $\degree$ C (higher than the melting point of Sn, i.e., 232  $^{\circ}$ C) for 2 h and then allowing it to naturally decrease to room temperature. The DSC curve was obtained to confirm the melting point of the Ga–Sn alloy. The melting points of Ga and Sn were 32 and 232  $\degree$ C, respectively, as shown in Fig. [6](#page-8-0). For various ratio of Ga and Sn, the



<span id="page-7-0"></span>

Figure 5 High-resolution FE-TEM images of a  $Sb_2Se_3$ nanowires, b  $Sb_2Se_3$  nanosheets, d B-doped  $Sb_2Se_3$  nanowires, and **e** B-doped  $Sb_2Se_3$  nanosheets (Inset: inverse fast Fourier

transform image). EDS elemental mapping of  $c$  B-doped  $Sb<sub>2</sub>Se<sub>3</sub>$ nanowires and  $f$  B-doped  $Sb<sub>2</sub>Se<sub>3</sub>$  nanosheets.

melting points were located between the melting points of Ga and Sn. For a self-healing material, the self-healable temperature range of the liquid metal should be above the operating temperature and below the melting point (*i.e.*,  $T_{op} < T_{sh} < T_{mp}$ ). If the operating temperature  $(T_{op})$  is above the self-healable temperature  $(T_{sh})$ , the liquid metal materials (in this study; Ga–Sn alloys) that exist in the solid state can leak out of the composite as they begins to change to a liquid phase. Considering the performance of the thermoelectric materials in the low temperature range, the melting point of the Ga–Sn alloy was set to approximately 166  $\degree$ C by adjusting the ratios of Ga and Sn. When the Ga and Sn ratio was 1:3, the melting point was 1[6](#page-8-0)6  $°C$ , as shown in Fig. 6.

Before fabricating the self-healing  $Ga$ – $Sn@B-Sb<sub>2</sub>Se<sub>3</sub>$ composites, the B-doped Sb<sub>2</sub>Se<sub>3</sub> nanowires and nanosheets were mixed in various ratio, and the corresponding thermoelectric performances were

evaluated. As shown in Fig. [1,](#page-4-0) the composite with a nanowire and nanosheet ratio of 7:3 exhibited the highest power factor value of  $3.22 \times 10^{-3}$   $\mu$ W/mK<sup>2</sup>. Using this configuration, the Ga-Sn alloy and  $Sb_2Se_3$ NW/NS with a weight ratio of 5:5 were hot-pressed at 130  $\degree$ C for 20 min to fabricate disk-shaped pellets. The hot-pressed temperature was selected by considering DSC results as shown in Fig. [6.](#page-8-0) Because Ga– Sn alloys starts to melt over 120  $^{\circ}$ C, not a fully melting, the operating temperature of  $130 \,^{\circ}\text{C}$  can make Ga–Sn particles injected into the  $B-Sb<sub>2</sub>Se<sub>3</sub>$ composites. A high proportion of liquid metal in the  $Ga-Sn@B-Sb<sub>2</sub>Se<sub>3</sub>$  composite is required for a successful self-healing process. When the composite was cut, self-healing of the composite occurred during the process of melting and solidifying the liquid metal at the cross section. In addition, as the content of liquid metal in the composite increases, the electrical conductivity increases but the Seebeck coefficient

<span id="page-8-0"></span>

Figure 6 DSC curves of a Ga–Sn alloys with various ratio and b Ga (red line), Sn (blue line), and Ga–Sn alloys used in this study (sky blue line).

decreases, so the composite was manufactured by selecting a ratio of 1:1 in consideration of this. Because the melting point of Ga–Sn alloy was approximately 166  $\degree$ C and self-healing was expected to occur at a lower temperature, the thermoelectric performance of the  $Ga-Sn@B-Sb<sub>2</sub>Se<sub>3</sub>$  composite was evaluated at lower temperatures (up to  $100 \degree C$ ). As shown in Fig. [7\(](#page-9-0)a,b), owing to the high electrical conductivity of the metal elements Ga and Sn, the electrical conductivity increased, and the Seebeck coefficient decreased. The highest power factor value was  $2932 \times 10^{-3}$  µW/mK<sup>2</sup>, which is 910 times higher than B-doped  $Sb_2Se_3$  nanowires and nanosheets composite with a ratio of 7:3. To confirm the selfhealing properties, the  $Ga-Sn@B-Sb<sub>2</sub>Se<sub>3</sub>$  composite was cut into two pieces. The cut surface was attached and heated to 150  $°C$ . Before and after the self-healing process, FE-SEM images were recorded to confirm that the cut surface self-healed through the melting of the Ga–Sn alloy (Fig. [8](#page-10-0)). After self-healing, the relative electrical conductivity and Seebeck coefficient were measured again at 373 K to confirm the performance stability as shown in Fig. [7](#page-9-0)(c). The results indicated that the electrical conductivity slightly decreased owing to losses in the liquid metal melting and solidification processes and as the self-healing process was repeated, the electrical conductivity gradually decreased while Seebeck coefficient was almost unchanged. Due to these changes in electrical

conductivity and Seebeck coefficient, the power factor of the composite decreased with cycles. Through several cycles, liquid metal loss occurred, which can be seen as reducing the power factor value. However, the power factor of the composite maintained 96% value after 5 self-healing cycles.

In this work, we fabricated Ga–Sn alloys and Ga–  $Sn@B-Sb<sub>2</sub>Se<sub>3</sub>$  composites with enhanced thermoelectric performances with B-doping and reusable property. The  $Sb_2Se_3$  nanowires and nanosheets composites show extremely low electrical conductivity; however, the electrical conductivity was greatly improved by doping with element B and introducing Ga–Sn liquid metal. The liquid metal acts as a path of carriers and when the composite is damaged, it acts as a self-healing agent by applying heat to melt Ga–Sn alloys. Unlike conventional thermoelectric devices that could not heal damage, liquid metal was introduced to improve performance and introduce self-healing ability, which can be applied to other thermoelectric devices operating at low temperatures.

# **Conclusions**

We fabricated a self-healing thermoelectric composite using a liquid metal alloy Ga–Sn and  $Sb_2Se_3$  thermoelectric materials. Boron doping was performed

<span id="page-9-0"></span>

Figure 7 a Electrical conductivity and Seebeck coefficient, **b** calculated power factor of Ga–Sn $@B$ -Sb<sub>2</sub>Se<sub>3</sub> composites with increasing temperature. c Relative electrical conductivity, Seebeck

coefficient, and calculated power factor of  $Ga-Sn@B-Sb_2Se_3$ composites with self-healing cycles at 373 K.

for both the  $Sb_2Se_3$  nanowire and nanosheets samples to enhance their thermoelectric performance by modifying carrier concentration and mobility. B-doping enhanced the carrier concentration and carrier mobility, which led to improved electrical conductivity and Seebeck coefficient. By adjusting the  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowire and nanosheet ratios, the composite with the highest thermoelectric performance was identified. By B-doping, Raman spectra shows blue shift, which indicating the expansion of  $Sb_2Se_3$  lattice. This expansion of lattice was also confirmed by checking lattice fringe expansion of each  $Sb_2Se_3$ nanowire and nanowires. To give self-healable property for Sb<sub>2</sub>Se<sub>3</sub> composite, liquid metal was

chosen to also improve electrical conductivity. The self-healable property should be performed above the thermoelectric operating temperature and below the melting point of liquid metal (*i.e.*,  $T_{op} < T_{sh} < T_{mp}$ ). Subsequently, the liquid metal alloy Ga–Sn was fabricated to achieve a melting point of 166  $°C$ , which exceeds the set operating temperature of 100 °C. Ga-Sn alloy and  $Sb_2Se_3$  hybrid composites with a weight ratio of 1:1 were fabricated through hot-pressing at a temperature lower than the melting point (166  $^{\circ}$ C). The power factor of  $Ga$ – $Sn@B-Sb<sub>2</sub>Se<sub>3</sub>$  composite was improved to  $2932 \times 10^{-3} \mu W/mK^2$  which is 910 times higher than B-doped  $Sb<sub>2</sub>Se<sub>3</sub>$  nanowires and nanosheets composite with a ratio of 7:3. To confirm the self-

<span id="page-10-0"></span>

Figure 8 Photos of Ga–Sn@B-Sb<sub>2</sub>Se<sub>3</sub> composites a cut in two, b reattached by heating to 150 °C and c self-healing composite lifted using tweezers. FE-SEM images of Ga–Sn@B-Sb<sub>2</sub>Se<sub>3</sub> composites **d** before and **e** after self-healing process.

healable property, the fabricated composite was cut into two pieces and heated at approximately 150  $\degree$ C to induce self-healing. The truncated sections selfhealed successfully, albeit with a certain loss of Ga– Sn. The electrical conductivity of the composite after self-healing slightly decreased owing to the presence of voids and loss of Ga–Sn liquid metal. The power factor of Ga-Sn@B-Sb<sub>2</sub>Se<sub>3</sub> composite maintained over 96% after 5 self-healing cycles.

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# Author contributions

MK performed conceptualization, investigation, writing—original draft, data curation, formal analysis, and methodology. DP did investigation, data curation, and formal analysis. Prof. JK done supervision and project administration.

# **Declarations**

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Data and Code Availability Not Applicable.



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