Perfectly Flawed: Leveraging on Defects in $AgSbTe_2$ via Ge Doping for Thermoelectric Waste Heat Harvesting

Research Report

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Date

10 July 2023

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Abstract

Hitherto, the two main causes of global warming are the burning of fossil fuels which release greenhouse gases, and the emission of waste heat as a byproduct of processes. Thermoelectrics have the ability to convert waste heat into electricity, which makes them perfect as a clean energy alternative while making use of waste heat. Recently, $AgSbTe_2$ has emerged as a promising thermoelectric due to its relatively high thermoelectric figure of merit (*zT*), a way to measure the performance of thermoelectrics. However, the performance of $AgSbTe_2$ needs to be improved for practical applications. My study aims to investigate the effect of a novel dopant, Germanium (Ge), on the *zT* of $AgSbTe_2$ by varying the amount of Ge in each sample to produce $AgSb_{1-x}Ge_xTe_2$ (x = 0 - 0.15). The electrical and thermal properties of each sample were measured, and the results demonstrated that 6% Ge produced the optimal trade-off between the properties and enhanced the *zT* of the sample by 92% as compared to undoped $AgSbTe_2$. After characterization using electron microscopy and x-ray diffraction techniques, it was discovered that the *zT* enhancement was due to the Ge doping inducing the formation of an ideal amount of Ag_2Te secondary phase. These findings would create opportunities to discover more sustainable synthesis and processing methods to enhance the performance and cost-effectiveness of $AgSbTe_2$, thus realizing the potential of $AgSbTe_2$ as a promising thermoelectric for combating global warming by cooling the environment and serving as a clean energy alternative.

Keywords: **Thermoelectric, $AgSbTe_2$, Ge Doping, Ag_2Te secondary phase**

Acknowledgement:

The author would like to thank Ms Chong Ai Lin[1] and Asst Prof Ady Suwardi[2,3] for their advice and mentorship throughout this research project.

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3. observe the common standard of academic integrity adopted by most journals and degree theses.
4. have declared all the assistance and contribution we have received from any personnel, agency, institution, etc. for the research work.
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(Signatures of full team below)

X ______________________

Name of team member: Ivan Joel YOU Wen Jie

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Name of supervising teacher: CHONG Ai Lin

Noted and endorsed by

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Table of Contents

Background and Purpose of the Research Area

The ability to convert waste heat into electricity has made thermoelectric generators good, not only for recycling of waste heat, but also for reducing the pollution caused by using fossil fuels.[1] Applications of thermoelectric generators include harnessing waste heat emitted by processes involving the use of heat engines. For example, a thermoelectric device can be placed at the exhaust of a car to tap on the waste heat emitted by the engine. The electricity generated can be used to power up the electrical devices of the car. These thermoelectric materials work based on the Seebeck effect, where heating one end of each material causes their majority charge carriers to diffuse to the cooler end or heat sink, establishing a potential difference across the temperature gradient. The potential difference generated per unit temperature gradient is measured as the Seebeck coefficient. The figure of merit (zT) has been widely used to determine the efficiency of thermoelectric materials in generating electricity from waste heat, whereby a higher zT value would represent a more efficient material. zT is calculated by $zT=S^2\sigma T/\kappa$, where S, σ, T and κ represent Seebeck coefficient, electrical conductivity, temperature and thermal conductivity respectively.[1] To increase the efficiency of thermoelectric materials, we would have to improve the parameters that make up the figure of merit, however this would not be straightforward as the parameters are inter-related.[2, 3] For example, in the relationship between Seebeck coefficient and carrier concentration is given by $S \propto \left(\frac{1}{n}\right)^{2/3}$, and the formula for electrical conductivity is given by $\sigma = ne\mu$, where n, e, and μ represents carrier concentration, electronic charge, and mobility respectively. Seebeck coefficient is inversely proportional to carrier concentration, while electrical conductivity is proportional to carrier concentration.[4] This means that with an increase in carrier concentration, electrical conductivity increases while Seebeck coefficient decreases, leading to an opposite effect on zT.

One way to increase the value of zT is doping, which is adding a small amount of another element to modify the material's electrical properties, such as the concentration of the majority free charge carriers.[2] By doping, an intrinsic semiconductor can be converted into an extrinsic semiconductor, hence increasing the electrical conductivity of the material. There are 2 types of extrinsic semiconductors: p-type and n-type. N-type semiconductors have electrons as its dominant free charge carrier, while p-type semiconductors have holes as its dominant free charge carrier. To make n-type semiconductors, an electron-donor should be doped to ensure that there is a majority of electrons. Vice-versa, to make p-type semiconductors, electron-acceptor should be added to ensure that there is a majority of holes.[5] The signs of the Seebeck coefficient for p-type and n-type semiconductors are positive and negative, respectively. Light doping will also scatter phonons (which are quanta of vibrational mechanical energy), thus reducing the thermal conductivity of the material.

$AgSbTe_2$ is a well-known thermoelectric material for near room temperature use as it has a high Seebeck coefficient and a low thermal conductivity due to its high likelihood of secondary phases forming, which results in a high zT value.[6] However, for many decades, this material suffers from atomic disorder, hindering its potential for widespread use and real application.[7, 8] By doping Ge into $AgSbTe_2$, it is hypothesized that the zT value can be further increased as doping Ge will result in $AgSb_{1-x}Ge_xTe_2$, which is a p-type semiconductor. In this project, $AgSbTe_2$ was doped with various amounts of Ge and the effect on the Seebeck coefficient, electrical conductivity, thermal conductivity and thus zT value of $AgSbTe_2$ was investigated.

Experimental Methods

Six samples were prepared, comprising of one pure $AgSbTe_2$ and 5 samples of Ge-doped $AgSbTe_2$, where Ge was added to replace 3%, 6%, 9%,12% and 15% of Sb respectively. To prepare the samples, Ag powder and Sb, Ge, and Te chunks were weighed to match their stoichiometric ratios such that the total mass of each sample was ~10 g. The powders and chunks were placed in a quartz ampule, evacuated until 10^{-3} Pa, and flame sealed to ensure that the elements would not oxidize. The quartz ampules were then heated in a furnace at 1273 K to melt the elements so that they would be homogenized, and then cooled to form an ingot. The ingot was grinded into powder using a pestle and mortar. Next, the powder was loaded into graphite dies, and then sintered using Spark Plasma Sintering at 673 K and 50 MPa. Sintering is a process to soften and compress the powder into a solid piece, under high temperature and pressure. Note that the temperature during sintering does not exceed the melting point of the powder, thus the powder does not liquify during any part of the process. This sintering process would produce dense cylindrical pellet samples with 12.7 mm diameter and approximately 11 mm in height, with densities that are > 95% of the theoretical density of single crystalline $AgSbTe_2$.

Next, the samples were cut into rectangular pieces (2 x 2 x 10 mm^3) for electrical properties measurement, and a square piece (6 x 6 x 1 mm3) for thermal properties measurement. The electrical properties were measured using a variable temperature 4-point probe measurement system (ULVAC ZEM-3), and the thermal properties measured using a variable temperature Laser Flash Analysis system (Netzsch LFA 457). Then, Scanning Electron Microscope (SEM), Energy-dispersive X-ray spectroscopy (EDS), and X-ray Diffraction (XRD) were used to study the composition of the samples.

Results and Discussion

From Figure 1a, it is observed that the electrical conductivity increases significantly when 3% of Ge is doped. This is because of the increase in hole concentration when Ge is doped, thus increasing the amount of charge carriers and thus electrical conductivity. However, as more Ge is doped (6 – 15%), the electrical conductivity decreases. This is because the added dopants induced the formation of more secondary phases, which causes charge carrier scattering, thus decreasing the mobility of charge carriers. This dominates over the increase in charge carrier concentration from the doping, ultimately causing the electrical conductivity to decrease.

From Figure 1b, it is shown that the pristine sample has the highest Seebeck coefficient. This is due to low carrier concentration as there are less holes in the material. When 3% of Ge is doped, the Seebeck coefficient decreases drastically. This is due to the increase in holes and thus carrier concentration from the added dopants. However, as more Ge is doped (6 – 15%), the Seebeck coefficient starts to improve. This is the result of the trend in electrical conductivity, which showed that the electrical conductivity decreases when more Ge is added above 3%. Intuitively, a lower electrical conductivity implies higher electrical resistance, which results in a higher voltage drop based on Ohm’s law when a unit of current passes through the sample, thus translating to an increase in Seebeck coefficient.

Figure 1c demonstrates that for 3 – 6% Ge doped samples, the thermal conductivity decreases. This is due to the dopants inducing the formation of well-dispersed secondary phases, which lead to effective phonon scattering, thus decreasing the thermal conductivity. However, as more Ge was doped (9 – 15%), more secondary phases were formed, which lead to the secondary phases being more aggregated, increasing the contribution from secondary phase to the overall thermal conductivity of the final sample. It is likely that the pure secondary phase has a higher thermal conductivity than the pure $AgSbTe_2$ matrix, thus resulting in an ineffective phonon scattering and a higher thermal conductivity.

By obtaining the Seebeck coefficient, resistivity, and thermal conductivity of the 6 samples, the figure of merit as a function of temperature for the 6 samples can be plotted as shown in Figure 2. Interestingly, by doping a small amount of Ge (6%), the zT value of the material $AgSbTe_2$ can be significantly improved. For example, at 673K, the zT value of $AgSbTe_2$ doped with 6% Ge improved by 92% as compared to the pristine sample.

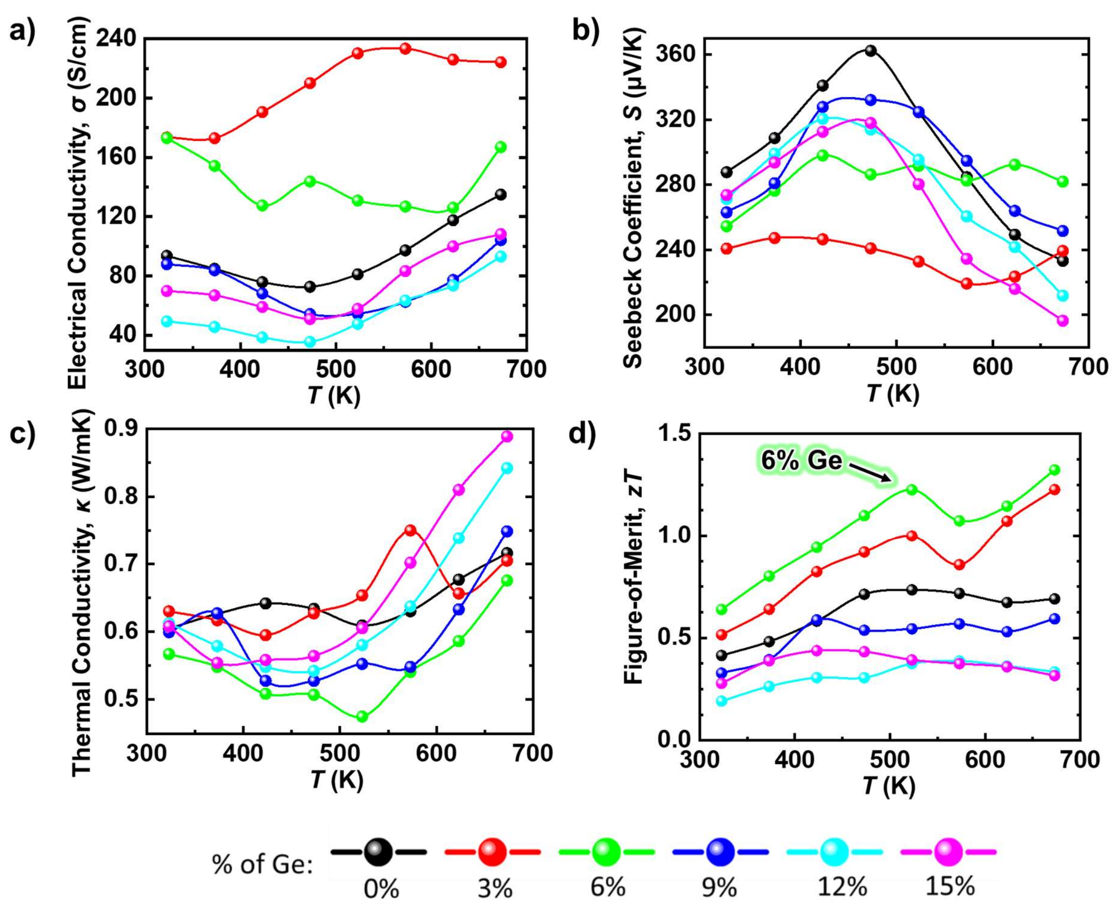
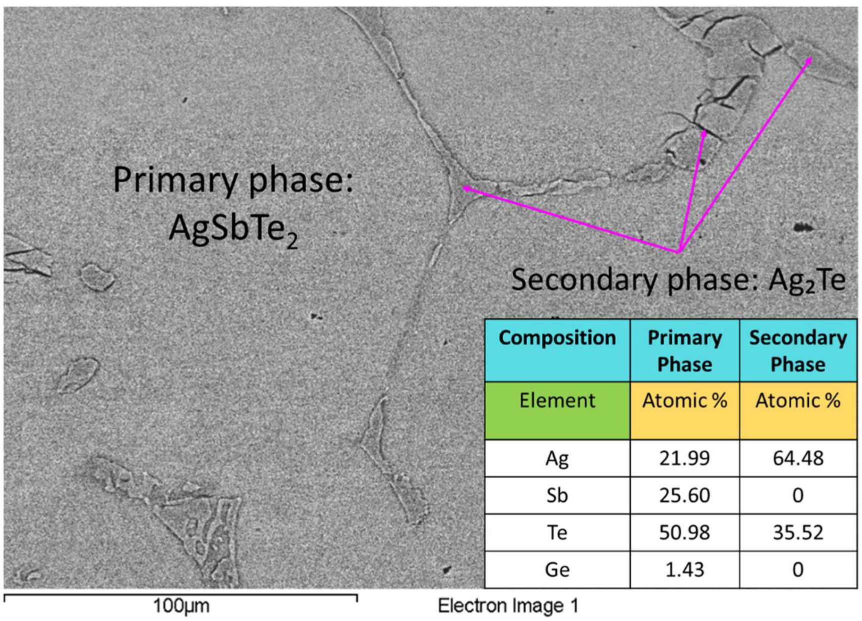


Figure 1: Properties of the 6 samples as a function of temperature: (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity, (d) figure of merit

Next, to further investigate the microstructure and composition of the sample with the highest *zT* value, which is the sample doped with 6% Ge, SEM EDS was used to obtain the image shown in Figure 2. Figure 2 shows that there are 2 phases in the sample. When an area of the sample with secondary phases was scanned using EDS, it was found that the secondary phase comprised of Ag and Te in a 2:1 ratio. Thus, a possible composition of the secondary phase is Ag_2Te.



Composition	Primary Phase	Secondary Phase
Element	Atomic %	Atomic %
Ag	21.99	64.48
Sb	25.60	0
Te	50.98	35.52
Ge	1.43	0

Figure 2: SEM images of the 6% Ge sample, and composition of the primary and secondary phases scanned by EDS

The elemental map in Figure 3 shows that the secondary phase regions comprise of high concentration (bright cyan) of Ag, lower concentration (dark yellow) of Te, and an absence (black) of Sb, as compared to the surrounding $AgSbTe_2$ main phase.

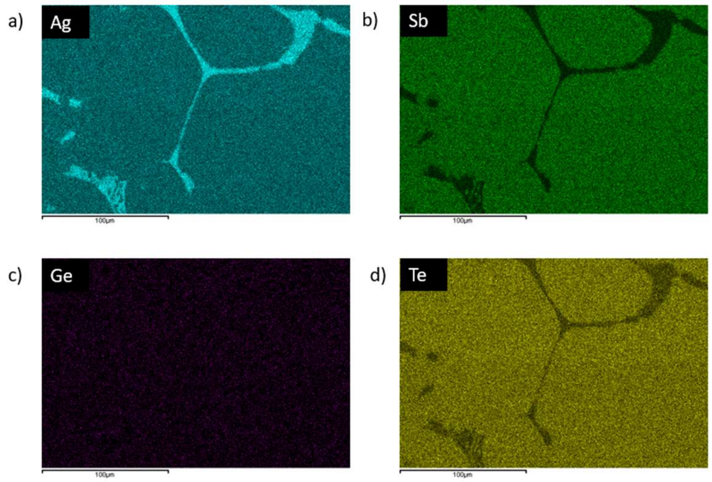


Figure 3: Elemental map of Ag (a, blue), Sb (b, green), Ge (c, purple) and Te (d, yellow)

Lastly, X-ray Diffraction (XRD) was used to investigate the lattice structure of the samples. By comparing the measured XRD peaks of the samples with the Powder Diffraction Files (PDF) from the PDF-4+ 2022 Database of the International Centre for Diffraction Data (ICDD), the crystallographic phase purity of the samples can be characterized. From Figure 4, the XRD peaks of all samples can be mostly matched with the database pattern of pure cubic $AgSbTe_2$ (PDF #96-901-1031, black vertical lines), which shows that the main phase is indeed cubic $AgSbTe_2$. However, there were also some small secondary phase peaks that cannot be matched to that of cubic $AgSbTe_2$, where the intensities of these secondary phase peaks increase with the amount of Ge doping. These secondary phase peaks can be matched to pure monoclinic Ag_2Te (PDF #96-591-0145, purple vertical lines), which agrees with the SEM EDS elemental quantification where the Ag:Sb:Te:Ge ratio of the secondary phase region is approximately 2:0:1:0, as shown in Figure 2. Since Ag_2Te has been reported to be a n-type material with a near room temperature thermal conductivity of ~0.7 W $m^{-1}K^{-1}$,[9] this supports the reasoning behind the decrease in electrical conductivity and the increase in thermal conductivity for the samples with higher Ge content stated earlier. The free electrons from the n-type Ag_2Te will cancel out some of the free holes from the p-type $AgSbTe_2$, thus reducing the p-type carrier concentration and electrical conductivity. In addition, the near room temperature thermal conductivity is significantly higher than that of the pristine $AgSbTe_2$ main phase (~0.6 W $m^{-1}K^{-1}$), which explains why having too much Ag_2Te secondary phases will increase the thermal conductivity of the samples.

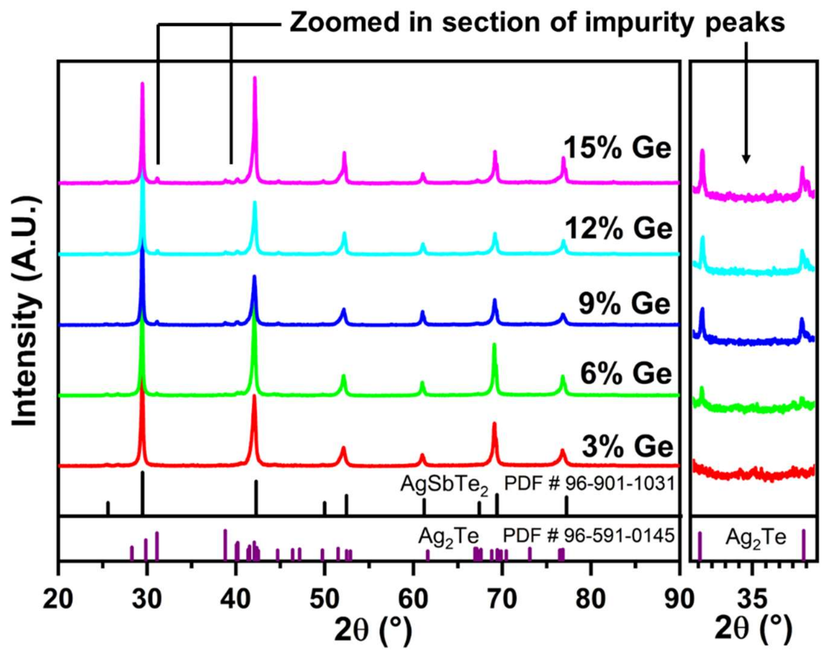


Figure 4: XRD patterns of Ge doped $AgSbTe_2$ samples

Conclusion

In this project, various amounts of Ge were doped into $AgSbTe_2$ to increase the *zT* value of the material. The doping of Ge resulted in different changes to the parameters that make up *zT*, where certain amounts of Ge improved some parameters but worsened other parameters. Notably, doping a small amount of Ge (6%) resulted in the highest *zT*, due to (1) optimal trade-off between Seebeck and electrical resistivity, and (2) lowest thermal conductivity. On the contrary, doping excessive Ge resulted in the formation of excessive secondary phases in the material, which lead to a lower *zT*. In conclusion, Ge doped $AgSbTe_2$ has good potential to be used as a thermoelectric material, since only a small amount of Ge is required to increase the *zT* value of the material significantly.

This work has paved the way for other future work to be done, such as further optimization of the efficiency of Ge doped $AgSbTe_2$ by exploring other synthesis methods such as slow cooling. This work has also shown that Ge has good use as a dopant, and Ge could be explored in other materials to improve zT. With further optimization, there is immense potential for $AgSbTe_2$ to be realized as a leading thermoelectric material for near room temperature waste heat harvesting. This would result in less wasted energy from any processes, indirectly improving the efficiency of processes. Since less fossil fuels would need to be burnt, thermoelectrics could help in the fight against global warming.

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Declarations:

This research work and report have been submitted to the following competitions:

Name of Competition	Date	Awards Won
Singapore Science and Engineering Fair	Mar 2023	Gold Award
National STEM Talent Search	Apr 2023	2nd place
International Science and Engineering Fair	May 2023	4th award