

# Preparation and Characterization Of $\text{Sb}_2\text{MnTe}_4$

A Summer Project Report  
by

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# 1 Introduction

Most of the energy utilised in the industries, transportation and household purposes is in the form of heat. But much of the heat produced is actually lost to the environment. One of the example is powering of cars where only 10% of the energy produced from combustion of diesel and petrol is utilised for useful work. So need of the hour is to convert the lost heat into electricity. This is where thermoelectric materials come into picture. The phenomenon of thermoelectricity is known from 19th century from the discoveries of Seebeck and Peltier. This can convert heat into electricity directly via solid state mechanism. The principle is simple, when such materials are heated the thermal gradient created causes the charge carriers to flow from hotter side to cooler side and potential difference is created.

The performance of thermoelectric materials is found out by  $ZT = \frac{s^2 \sigma}{k} T$ , where  $s$  is the seebeck coefficient,  $\sigma$  is the electrical conductivity,  $k$  is the thermal conductivity and  $T$  is the temperature. Thermoelectric materials with  $ZT > 1$  are considered good, but to increase  $ZT$  is not straightforward job because  $s$ ,  $\sigma$ ,  $k$  are interrelated. In the last two-three decades there have been great advances in thermoelectric field and various strategies have been incorporated to increase  $ZT$ <sup>[1][2]</sup>.

Many layered semiconductors are studied for thermoelectricity.  $\text{Bi}_2\text{Te}_3$  and  $\text{Sb}_2\text{Te}_3$  are one of the widely studied layered thermoelectric material. Many new compounds have been developed from intergrowth between layers.  $\text{Bi}_2\text{MnTe}_4$  is one such compound that has been studied<sup>[3][4]</sup>. In this project we have tried to prepare and study one such compound,  $\text{Sb}_2\text{MnTe}_4$ .

## 2 Preparation

### 2.1 First sintering

Raw materials of Sb, Mn, Te were taken in the stoichiometric ratio of  $\text{Sb}_2\text{MnTe}_4$  and uniformly mixed by grinding inside the glove box. The mixed powder was divided into three parts for further preparation. The first part of the powder was put in the die inside the glove box and pellets were formed. Second part of the powder was put in the die outside the glove box to make pellets. Third part was kept for ball milling. (A) and (B) were kept for sintering at 600°C for 10 hours. Heating rate and cooling rate were fixed at 50°C/hr. (C) was kept for ball milling for 400 mins.

### 2.2 Second sintering

The pellets from first sintering were brittle. To increase the density the pellets from first sintering were grinded, mixed and kept for second sintering. (A) and (B) were kept for second sintering at 600°C for 24 hours. Heating rate and cooling rate were fixed at 50°C/hr.

### 2.3 Observation

XRD was done after every sintering on all samples (A),(B),(C). The main phase had formed for first sintered samples-(A),(B) (Figure 1). (C) had individual peaks from precursors and no main phase had formed (Figure 2). XRD of second sintering samples had secondary phases besides the main phase. The secondary phases were index to be from  $\text{Sb}_2\text{Te}_3$ . The main phase peaks have shifted to higher angles thus crystal structure has shrunk (Figure 3).

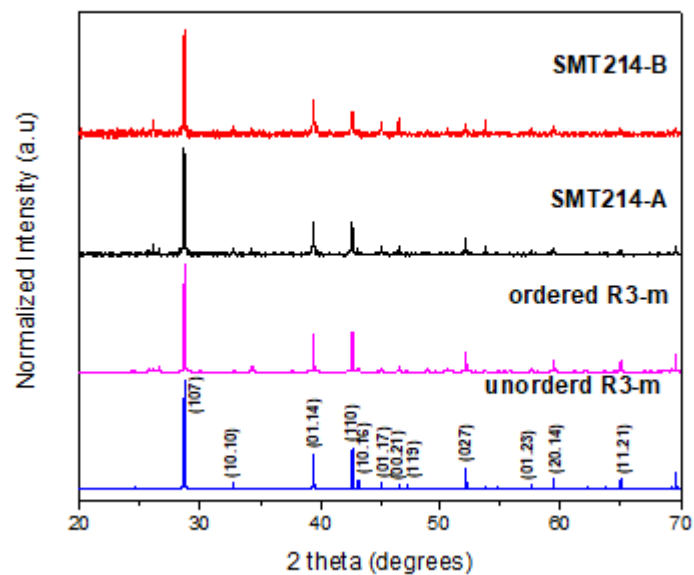


Figure 1: XRD compared with simulated ordered and unordered phase

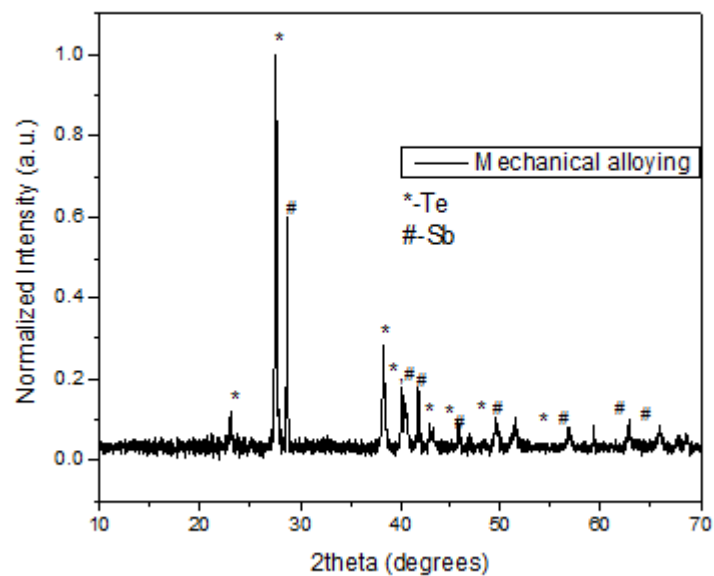


Figure 2: XRD of ball milled sample

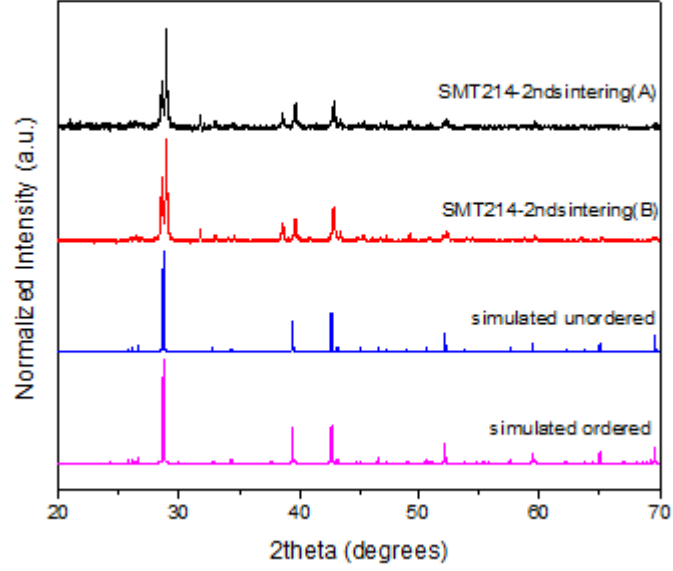


Figure 3: XRD of 2nd sintered sample

### 3 Preparation-II

In the first preparation we observed that sample formed from 1st sintering were brittle and cannot be properly used for measurements. The 2nd sintered sample was dense but had secondary peaks. Second preparation was kept for sintering for longer time so that sample formed would be dense. Raw materials of Sb, Mn, Te were taken in the stoichiometric ratio of  $\text{Sb}_2\text{MnTe}_4$  and uniformly mixed by grinding inside the glove box. Pellets were prepared out of the mixed powder and kept for sintering at  $600^\circ\text{C}$  for 24 hours. Heating rate and cooling rate were fixed at  $50^\circ\text{C/hr}$ . From XRD analysis we observe that most intense peak (hkl plane 107) has some secondary peak (Figure 4) and therefore formed sample has some secondary phases. Figure 5 compares all preparations with simulated ordered and unordered phase.

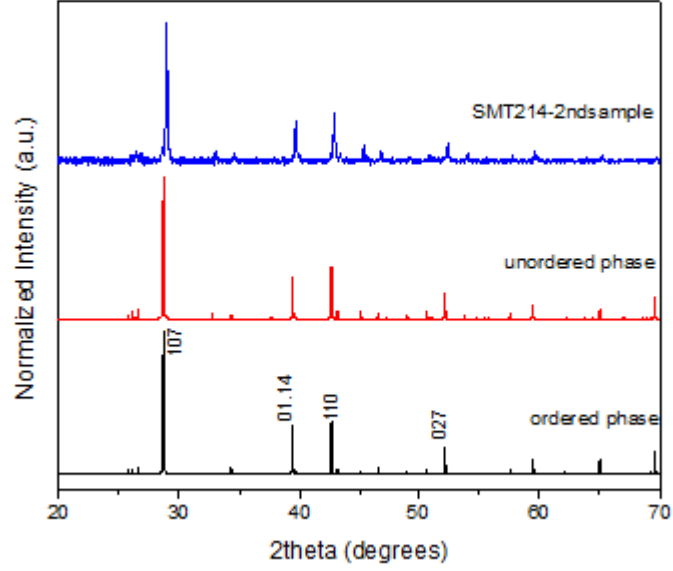


Figure 4: XRD analysis of 1st sintered sample of second preparation

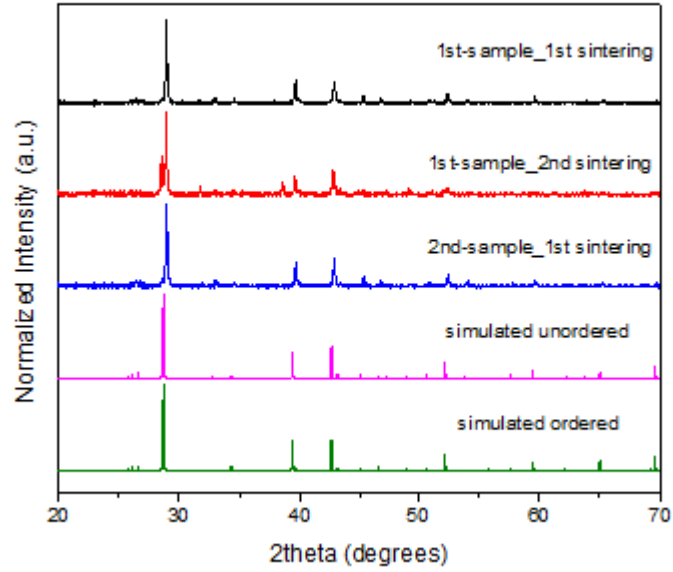
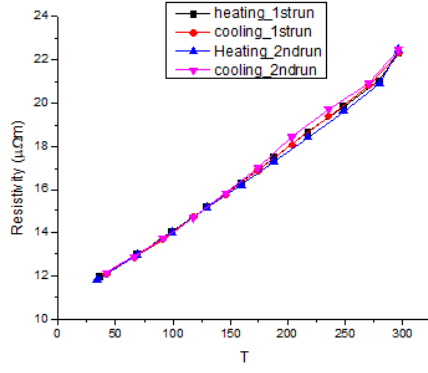


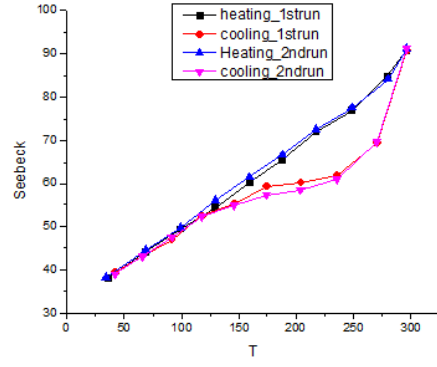
Figure 5: XRD analysis of all samples formed

## 4 Thermoelectric measurements

Seebeck and resistivity measurements are made on 2nd sintered sample of 1st preparation (sample-B). Measurements were done up to 300°C. Measurements were done during heating and cooling and repeated for two cycles. From the graph (Figure 6a) of resistivity we can observe that it increases with temperature and heating and cooling curves perfectly match for both the runs. Seebeck (Figure 6b) and power factor (Figure 7) values are observed to increase with temperature but heating and cooling curves do not match.



(a) Resistivity dependence on temperature



(b) Seebeck dependence on temperature

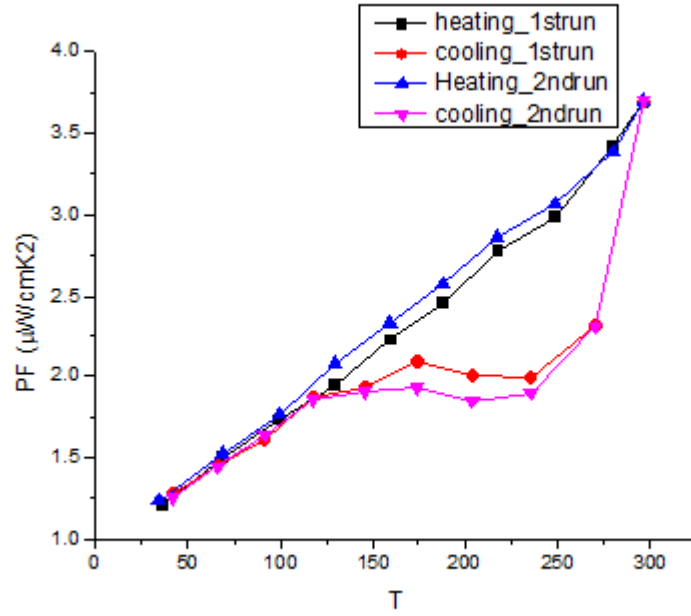


Figure 7: Calculated power factor with temperature

## 5 TG/DSC

TG/DSC measures mass loss and heat changes in the sample with temperature. Thermogravimetry(TG) records mass of the sample with temperature. In Differential scanning calorimetry(DSC) temperature of sample is compared with that of a reference with change of temperature. In case of thermal events like melting, crystallisation, the sample temperature is greater or lesser than reference and peak is observed. TG/DSC was done on sintered second sample to study secondary phase formation on temperature. The first TG/DSC was done upto 600°C. A small blip was noted on DSC curve around 300°C (Figure 8). To verify the blip observed two more TG/DSC measurements were done, one before reaching 300° upto 270° and keeping an isotherm there for 10 mins and other upto 600°C and keeping isotherm at that temperature for 30 mins. DSC upto 270°C showed no changes in enthalphy of the sample with temperature (Figure 9), but the XRD of the sample from DSC/TG measurement showed formation of secondary phases (Figure 12). DSC upto 600°C and keeping isotherm for 30 mins was observed to increase the intensity of blip near 300°C and there is mass loss of about 1.6% (Figure 10). The XRD of the sample from DSC was observed and showed to increase in the intensity of the secondary phases (Figure 12).

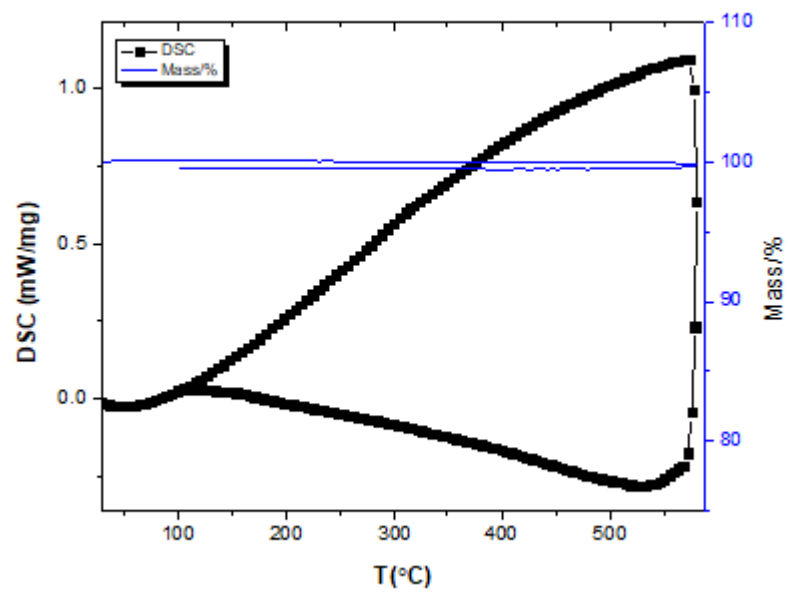


Figure 8: TG/DSC first run while heating and cooling upto 600°C

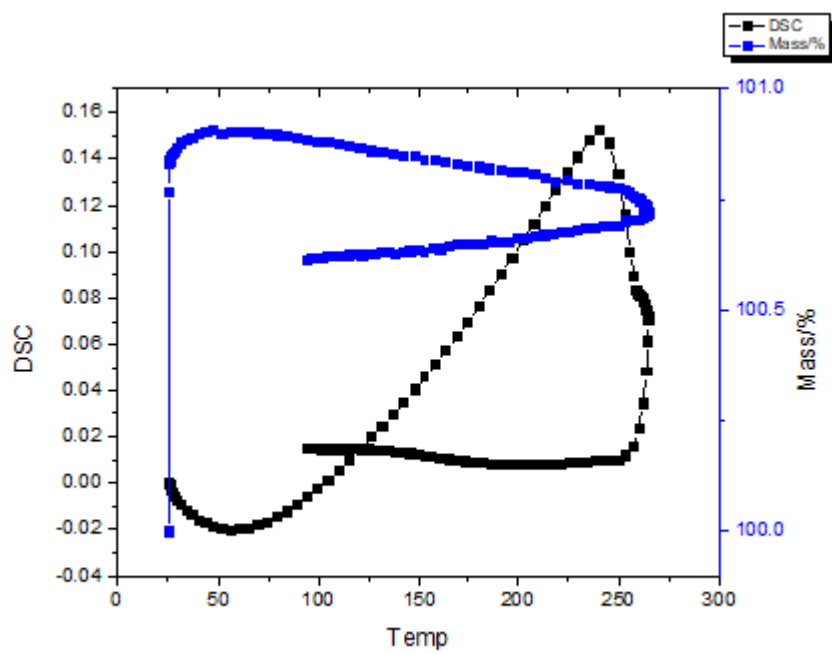


Figure 9: TG/DSC while heating and cooling upto 270°C and isotherm at 270°C

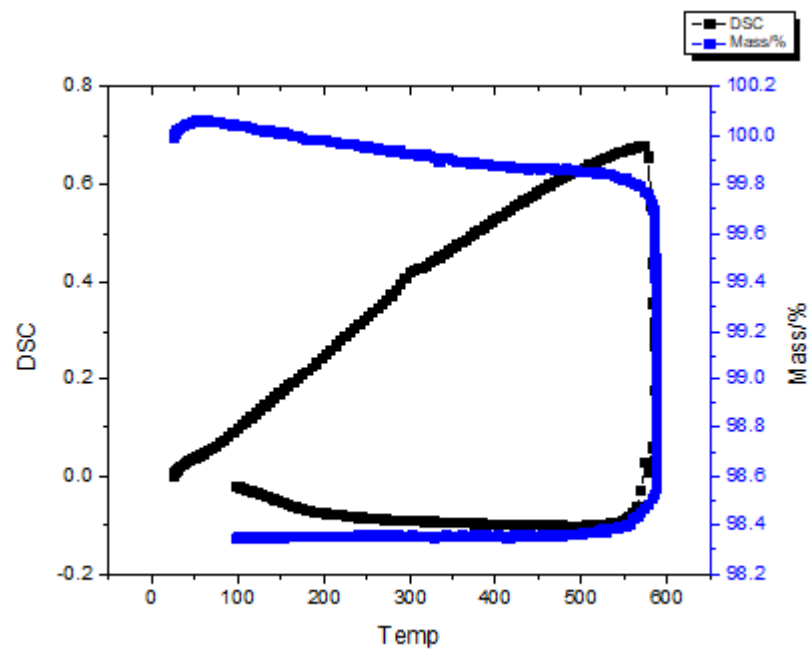


Figure 10: TG/DSC while heating and cooling upto 600°C and isotherm at 600°C

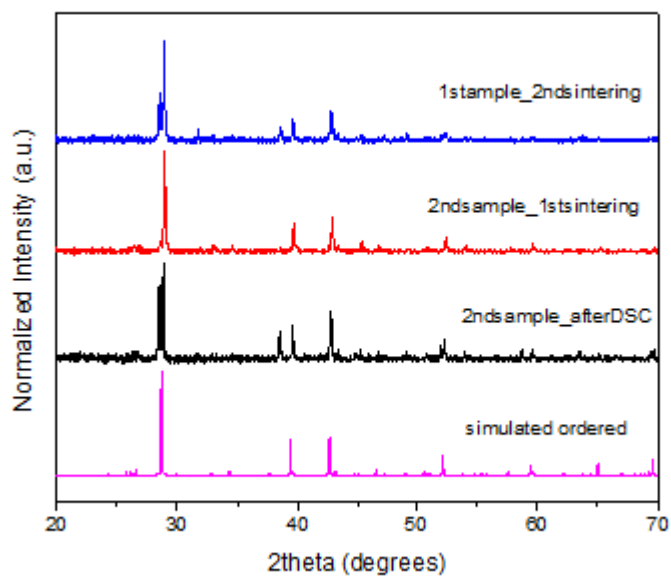


Figure 11: XRD analysis after TG/DSC upto 600 °C



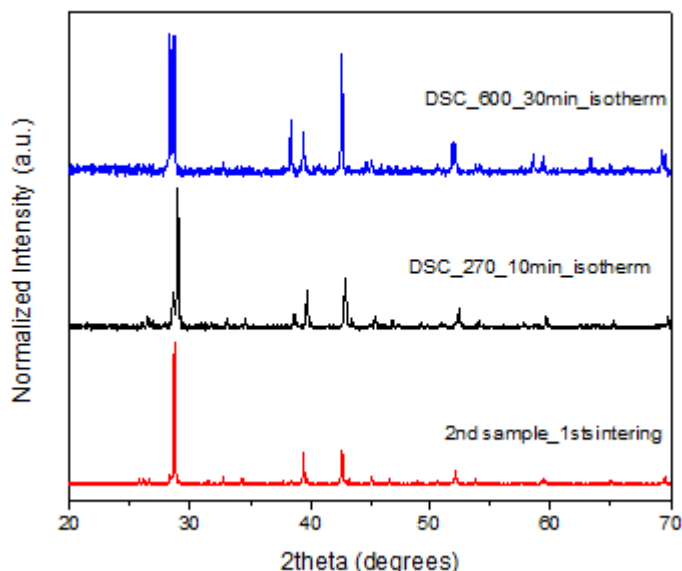


Figure 12: XRD analysis after TG/DSC upto 270°C and 600°C and isotherm at highest temperature

## 6 Conclusions

$\text{Sb}_2\text{MnTe}_4$  prepared was unstable at higher temperatures about 600°C. This was confirmed from DSC measurements and XRD of samples from DSC. The secondary phase was indexed to be  $\text{Sb}_2\text{Te}_3$ . Thermoelectric measurements were done on decomposed sample that had  $\text{Sb}_2\text{Te}_3$  which is also a thermoelectric material. The powerfactor increased with temperature but heating and cooling curve did not match.

We have planned to obtain thermal diffusivity on the composite sample (decomposed phase that had  $\text{Sb}_2\text{Te}_3$ ) and calculate its ZT. We have planned to carry forward this study and to achieve phase stabilisation at higher temperatures. This would allow us to obtain thermoelectric properties of pure phase at higher temperatures.

## 7 Acknowledgement

I would take this opportunity to thank my supervisor Dr. Surjeet Singh who gave the opportunity to work in his lab and gave direction to this project. I would also like to thank Navita Jakhar, my PhD guide with whom I learned the skills required during the project and guided me at every step. I am also grateful for labmates without whom summer would not have been enjoyable, taking out time from their busy life and helping me in the project, in various fruitful discussions and above all helping me to have a great time inside and outside lab. I am thankful to IISER Pune for having summer project in their curriculum and giving us a taste of research in such early stages. I am thankful to DST-INSPIRE for scholarship during my stay in IISER.

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