CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

In this chapter, the results of all measurements are presented and discussed. Eight newly developed samples of Bi_2Te_3- and PbTe-based thermoelectric materials were successfully fabricated using a hot press machine with different specifications. The specifications such as temperature, pressure and time holding to fabricate samples were different based on thermoelectric materials and the machine used. For instance, both Bi_2Te_3- and PbTe-based alloys were pressed using a hot press machine in UKM under the same pressure of 20 MPa for about 30 minutes at different temperatures such as 473 K and 523 K respectively. Meanwhile for samples fabricate using hot-pressed in USIM, Bi_2Te_3 and PbTe based samples were pressed under 13 MPa pressure for 17 minutes at temperatures 473 K and 493 K respectively.

Besides that, the amount of material needed to construct the samples from powder to bulk was calculated in two different methods which are volume ratio (VR) and atomic mass (AM) techniques as discussed in Chapter 3. The compositions of the fabrication samples were confirmed using EDS and its thermoelectric properties of Seebeck coefficient and electrical resistivity were measured. In addition, measurements of the Seebeck coefficient under large temperature differences were carried out in a special develop high-temperature vacuum chamber to represent the actual operating condition.

4.2 Samples Analysis

N- and p-type Bi_2Te_3 and PbTe based thermoelectric samples fabricate using AM method are labelled as samples A, C, E, and G while samples fabricated using the VR method are labelled as samples B, D, F, and H. The weight and thickness of the successfully fabricated samples were measured and recorded in Table 4.1. The weight of samples before and after the HP process was slightly different might be because some powder melted and some of it remained unpressed. In addition, the expected thickness of samples based on both calculations for Bi_2Te_3-based n-$Bi_2Te_{2.7}Se_{0.3}$ and p-$Bi_{0.5}Sb_{1.5}Te_3$ (samples A-D) was 0.2 cm and 0.35 cm, meanwhile, the expected thickness for PbTe-based samples of n-$PbTe_{0.8}Se_{0.2}$ and p-$Pb_{0.4}Sn_{0.6}Te$ (samples E-H) was 0.35 cm and 0.4 cm.

The thickness and compound ratio of fabricated Bi_2Te_3 based samples using the atomic mass (AM) method shows a great agreement with the expected thickness. It is observed that the thickness after being constructed was significantly different with a percentage difference between 3% to 25%. The difference is bigger with VR method calculation compared to AM method with 3% and 9% for sample Bi_2Te_3-based respectively. The temperature of the HP process for samples A and B is 473 K which is lower than the melting point (MP) of Se. Therefore, the difference between both samples is because of the different pressure and holding time used during the HP process. The same goes for samples C and D where it is fabricated below the melting point (MP) of Sb (903 K). For these Bi_2Te_3-based samples, both methods are affected by pressure and holding time during the HP process. Samples A and C can prove that AM method in calculating the weight of raw powders is more accurate due to the % difference in thickness being lower when using AM method compared to the VR method.

On the other hand, for sample PbTe-based, AM method produces a greater % difference from the expected thickness of the samples compared with the VR method. This becomes more obvious for p-type samples as shown in Table 4.1. The difference between samples E and F might be because of the duration of holding time that was applied during the HP process. Although both samples undergo temperature beyond the melting point of Se (494 K), it can be seen that holding time plays a role which the more holding time during the HP the less % difference will be produced. It can also be observed for samples of p-$Pb_{0.4}Sn_{0.6}Te$ (sample G and H) during the pressing temperature of 523 K which is above the melting point (MP) of tin (Sn) which is 504.9 K, percentage error of 20% for its thickness is obtained. From the results obtained, AM method is better in calculating the raw powder weight before the fabrication process. In addition, for samples in low-temperature range materials, the melting point (MP) of dopant doesn't matter because the samples will only be measured at low temperatures. However, for higher temperature range samples, the melting point, pressure and holding time matter as these samples will experience a high-temperature measurement.

Although the fabricated thickness of sample E using the atomic mass (AM) method is slightly higher than sample F using the volume ratio (VR) method, its compound ratio is almost the same as the expected compound ratio. This might be because fabricated n-$PbTe_{0.8}Se_{0.2}$ samples (atomic mass method) have unpressed powder left after the pressing process making the thickness a little bit lower than the expected sample.

Table 4.1: Thickness and weight of fabricated samples.

Samples	**Expected Compositions**	**Place (Temperature, Pressure, Holding time)**	**Calculation Method**	**Expected Thickness (cm)**	**Thickness After HP (cm)**	**% Difference Thickness**
A	n-$Bi_2Te_{2.7}Se_{0.3}$ (MP Se: 494 K)	USIM (473 K, 13 MPa, 17 min)	AM	0.2	0.21	5
B	n-$Bi_2Te_{2.7}Se_{0.3}$ (MP Se: 494 K)	UKM (473 K, 20 MPa, 30 min)	VR	0.35	0.32	9
C	p-$Bi_{0.5}Sb_{1.5}Te_3$ (MP Sb: 903 K)	USIM (473 K, 13 MPa, 17 min)	AM	0.2	0.19	5
D	p-$Bi_{0.5}Sb_{1.5}Te_3$ (MP Sb: 903 K)	UKM (473 K, 20 MPa, 30 min)	VR	0.35	0.32	9
E	n-$PbTe_{0.8}Se_{0.2}$ (MP Se: 494 K)	USIM (493 K, 20 MPa, 30 min)	AM	0.4	0.425	6
F	n-$PbTe_{0.8}Se_{0.2}$ (MP Se: 494 K)	UKM (523 K, 20 MPa, 30 min)	VR	0.35	0.34	3
G	p-$Pb_{0.4}Sn_{0.6}Te$ (MP Sn: 504 K)	USIM (493 K, 20 MPa, 30 min)	AM	0.4	0.3	25
H	p-$Pb_{0.4}Sn_{0.6}Te$ (MP Sn: 504 K)	UKM (523 K, 20 MPa, 30 min)	VR	0.35	0.27	20

4.2.1 Compositions of Elements in Samples

To confirm the composition of elements in a sample, an analysis of elemental composition using EDS of FESEM has been done (Figure 4.1). The measurement analysis was focused on different surface areas of samples with a magnification of 100x. All of the composites can be seen in the synthesized composite thru the EDS spectrum. Details of measured percentage weight, as well as the calculated average ratio for each sample, are shown in Table 4.2.

Each sample was measured five times at a different spot. It shows from the analysis that most of the sample fabricated using HP in USIM and atomic mass (AM) calculation method (sample A, C, E) has the closest ratio to the expected compound ratio. As for samples E and F, even though the % difference in thickness from sample E is higher than sample F, the composition obtained from EDS shows that sample E has a better result. This shows that AM method is better in calculating the raw powder weight before the samples can be fabricated.

Figure 4.1: EDS machine for elemental composition measurement.

Table 4.2: Weight % of elemental composition in each sample obtained from EDS measurement.

Samples	**Expected Compositions**	**Weight % EDS**			**Ratio of Element**
A	n-$Bi_2Te_{2.7}Se_{0.3}$	**Bi**	**Te**	**Se**	2.2 : 2.6 : 0.2
		44.14	51.39	4.46	
B	n-$Bi_2Te_{2.7}Se_{0.3}$	**Bi**	**Te**	**Se**	0.9 : 3.5 : 0.6
		18.95	69.55	11.50	
C	p-$Bi_{0.5}Sb_{1.5}Te_3$	**Bi**	**Sb**	**Te**	0.6 : 1.6 : 2.8
		12.63	31.13	56.24	
D	p-$Bi_{0.5}Sb_{1.5}Te_3$	**Bi**	**Sb**	**Te**	0.2 : 1.6 : 3.2
		3.67	32.96	63.37	
E	n-$PbTe_{0.8}Se_{0.2}$	**Pb**	**Te**	**Se**	1.1 : 0.7 : 0.2
		56.94	33.49	9.57	
F	n-$PbTe_{0.8}Se_{0.2}$	**Pb**	**Te**	**Se**	0.5 : 1.1 : 0.4
		23.31	56.10	20.60	
G	p-$Pb_{0.4}Sn_{0.6}Te$	**Pb**	**Sn**	**Te**	0.7 : 0.2 : 1.1
		33.81	10.81	55.38	
H	p-$Pb_{0.4}Sn_{0.6}Te$	**Pb**	**Sn**	**Te**	0.5 : 1.1 : 0.4
		9.77	33.50	56.72	

4.3 Seebeck Coefficient (α)

One of the properties to determine the performance of thermoelectric materials is by measuring the Seebeck coefficient. Seebeck coefficient, α can be obtained with thepresence of temperature difference (ΔT) and voltage, V measurement of samples. It can becalculated as,

$$\alpha = \frac{V}{\Delta T} \tag{4.1}$$

In this study, the Seebeck coefficient of all samples was measured under a large temperature difference (lΔT< 385 K). The measurements were taken outside and inside the vacuum chamber (Figure 3.7). For comparison and benchmarking, samples A and E were also measured under a small temperature difference (sΔT < 25 K) using apparatus outside of the chamber (Figure 3.17).

4.3.1 Small Temperature Difference (sΔT)

To confirm the samples that were fabricated using this method, the Seebeck coefficient at sΔT was measured and compared with the literature. Samples A and E were selected which represented Bi_2Te_3 - and PbTe-based thermoelectric materials. Few sets of measurement were made, thus error bar plotted in graphs represented the deviation of the measured value from the average value. The Seebeck coefficient of sample A (n-$Bi_{2.2}Se_{0.2}Te_{2.6}$) under sΔT measured using a hot probe setup outside the vacuum chamber is shown in Figure 4.2. The highest error bar calculated from sample A is ±0.013. For comparison, samples from You et al. (2019) were used. They prepared the sample of

$Bi_2Se_{0.3}Te_{2.7}$ using ball milling and hot-pressing method with the pressure of 50 MPa at a temperature of 700 K for 50 minutes holding time. Sample A has α of -53 µV/K which is 65% lower compared to samples that were reported by You et al. which was -150 µV/K reported in 2019 at room temperature. The difference in α in both samples is because of the different fabrication methods and composition of the sample. It is expected for the HP sample to have a lower α value than the SPS sample. However, these results still comply with Gharsallah et al., in their report that pure Bi_2Te_3 compounds fabricated by different physical and chemical methods have a Seebeck coefficient in the range of -50 to -260 µV/K (Gharsallah et. al,2017).

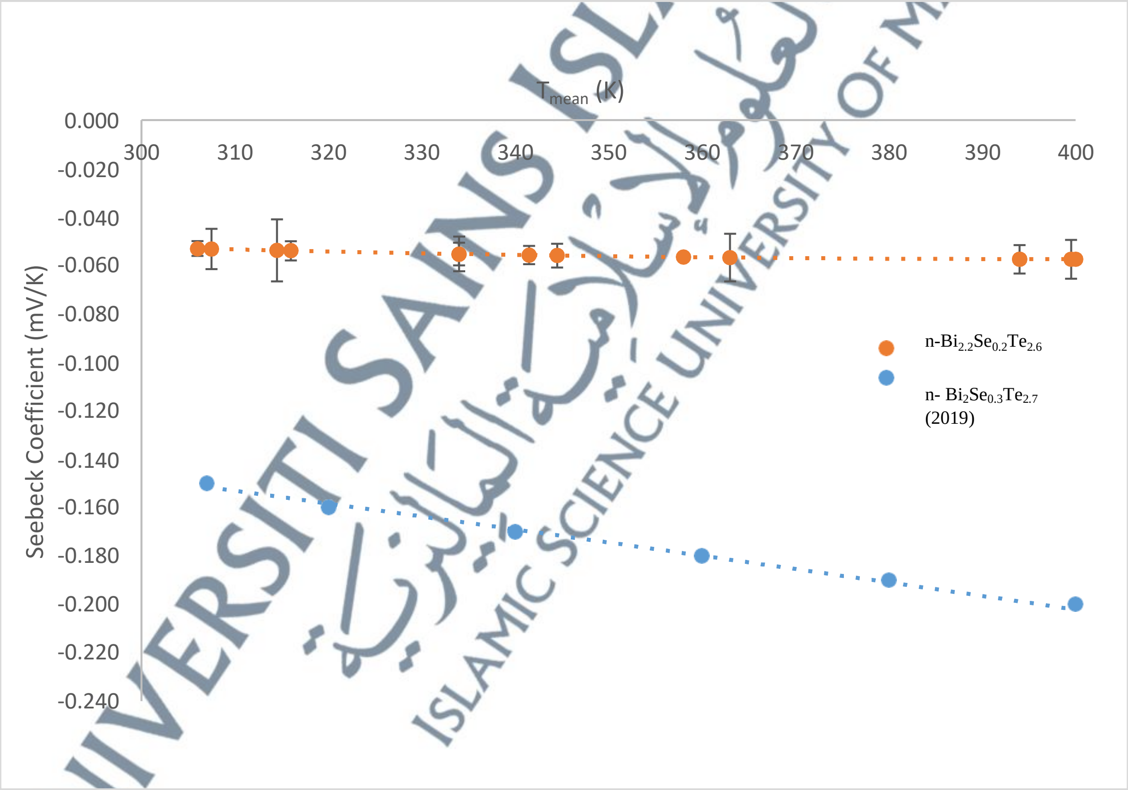

Figure 4.2: Average Seebeck coefficient of sample A obtained from different sets of measurements for sΔT and You et al., (2019).

The α value of sample E measured under sΔT using a hot probe outside the vacuum chamber compared with Li et al. is shown in Figure 4.3. The α of sample E (n-$Pb_{1.1}Te_{0.7}Se_{0.2}$) is -245 µV/K measured at room temperature which is ~63% higher than the α of n-$PbTe_{0.85}Se_{0.15}$ was -150 µV/K reported by Li et al., (2011). Li et al., prepared the samples using ball milling and then SPS methods. Thus, this HP sample are having a higher Seebeck than the reported sample. Although it has a higher α value it cannot be compared directly as the ratio and fabrication method are not the same. The measured α is in the range of -200 to -250 µV/K at a temperature range of (300-500 K) which is almost similar to pure PbTe (-230 to -310 µV/K) fabricated with the same method by Li et al. at the same temperature range. This is because the sample contains more Pb which makes it behave like pure PbTe.

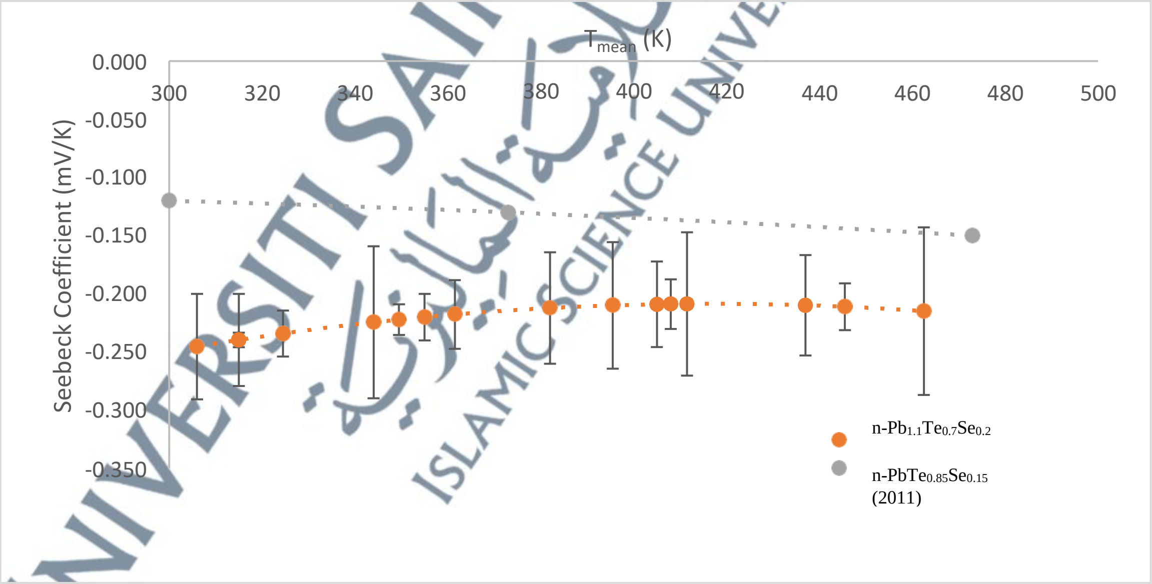

Figure 4.3: Average Seebeck coefficient of sample E obtained from a few different sets of measurements for sΔT compared with $PbTe_{0.85}Se_{0.15}$ by Li et al., (2011).

4.3.2 Large Temperature Difference (lΔT)

A large temperature difference (lΔT) measurement was made with $\Delta T > 10$ K, by increasing hot side temperature T_h while maintaining cold side temperature T_c. In general, all measurement outside the vacuum chamber under lΔT has a higher error bar than measurement inside the vacuum chamber because of the high heat loss to the surrounding during outside measurement. Samples A and G represent Bi_2Te_3 and PbTe samples to show the different error bars produce from both measurements.

As for sample A, the highest error bar for inside vacuum measurement is ±0.005 while outside measurement is ±0.025 shown in Figure 4.4. The bigger error can also be seen in Figure 4.5 which shows the measurement of sample G outside and inside measurements. The highest error bar value of outside measurements is ±0.014 higher than the error of inside measurements which is ±0.007. Due to that, the discussion regarding measurement under lΔT will consider more the measurements inside the vacuum chamber.

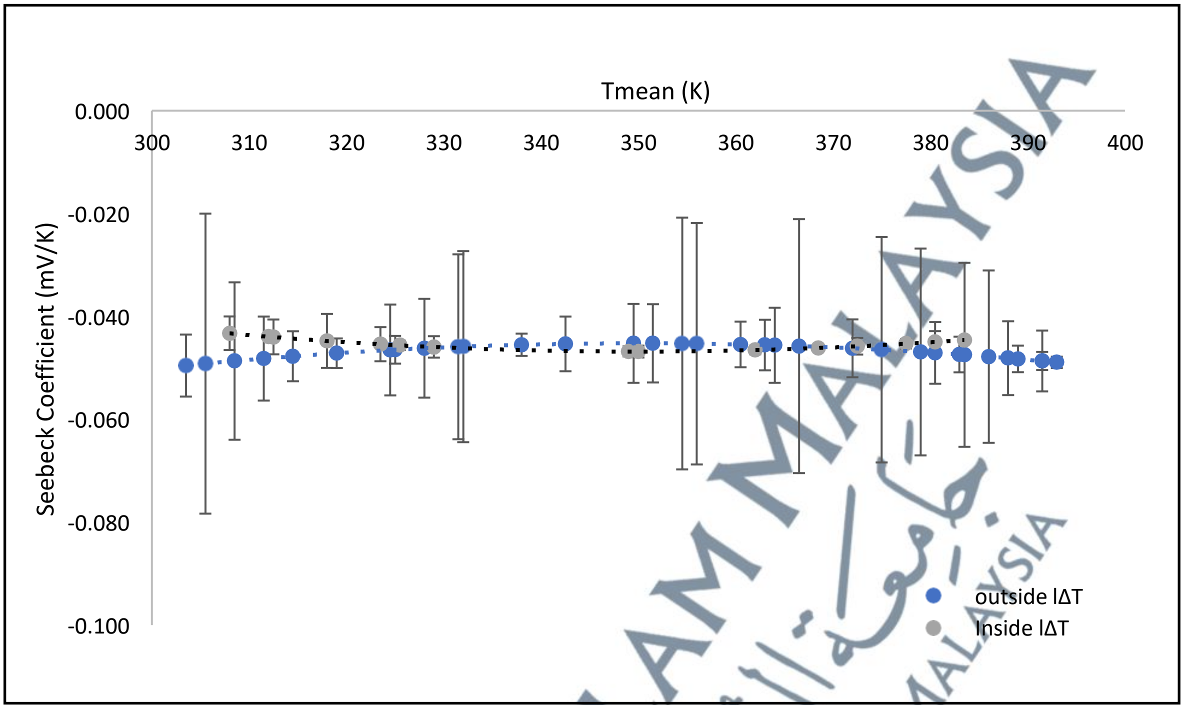

Figure 4.4: Average α of sample A obtained from several different sets of measurements outside and inside of vacuum chamber under lΔT.

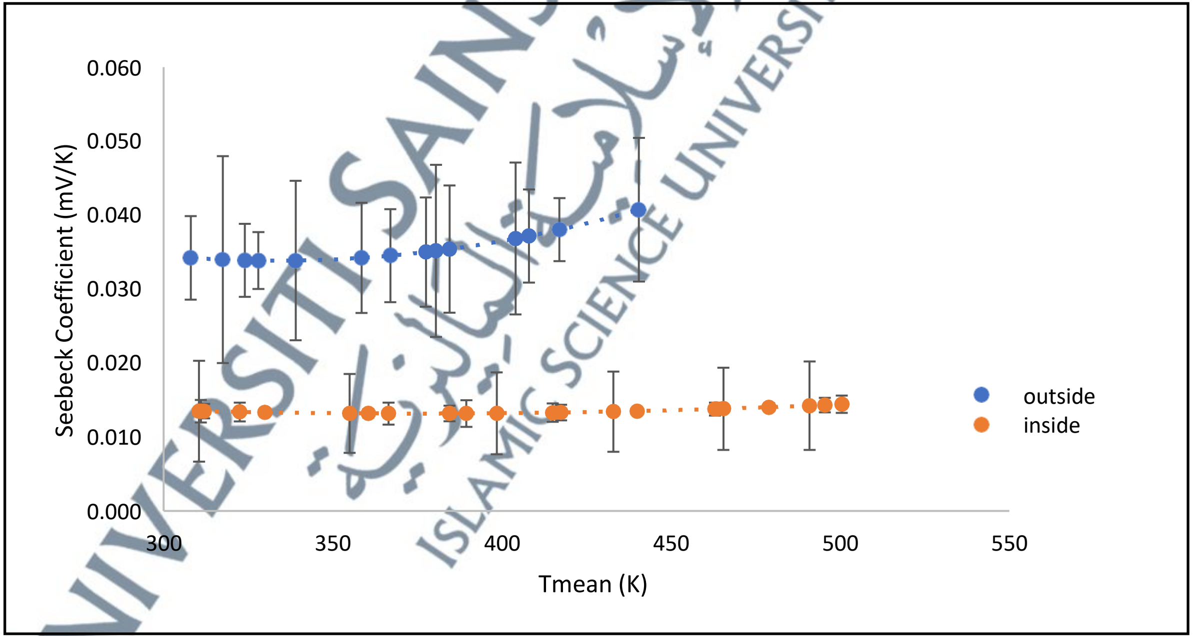

Figure 4.5: Average α of sample G obtained from several different sets of measurements outside and inside of vacuum chamber under lΔT.

Based on Figure 4.6, The results of the α value of sample A (n-type Bi_2Te_3) are comparable to the n-type Bi_2Te_3 from previous researcher Nadhrah MY (2012) which also measure α under lΔT. The α value of measurement inside the vacuum chamber shows a similar trend to the previous study. The different α value is because the sample of the previous study was fabricated using the SPS technique.

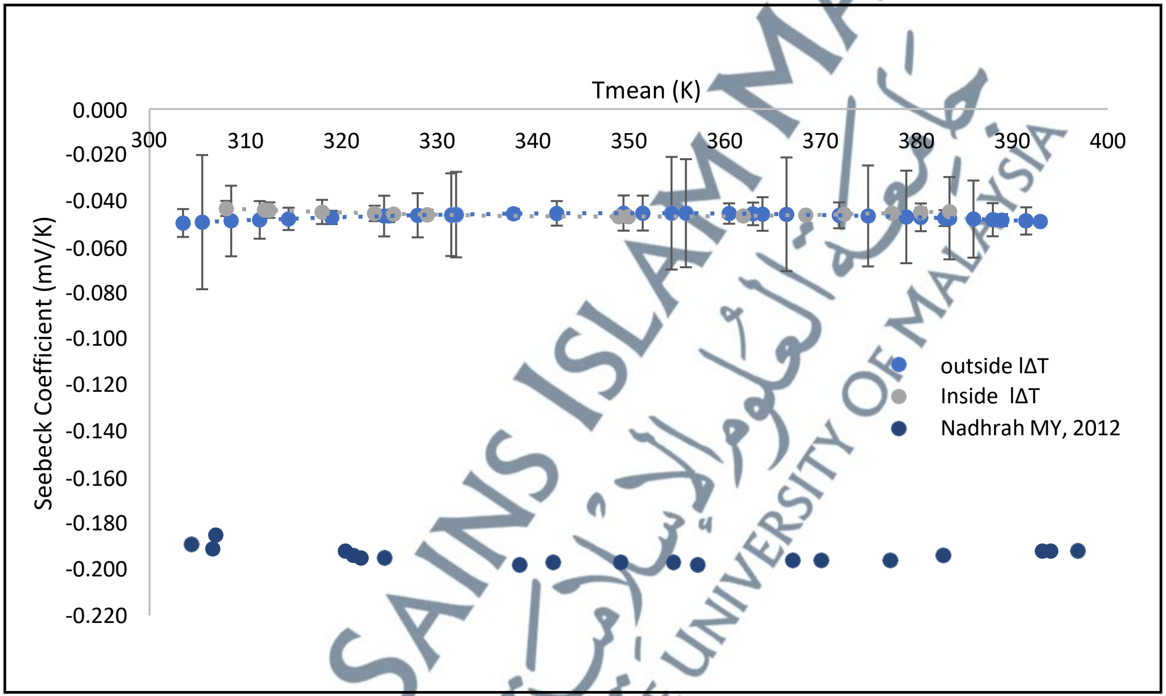

Figure 4.6: Average α measurements of sample A outside and inside vacuum chamber under lΔT.

The α value measured under lΔT for fabricated samples using different calculation methods is being compared. The results for n-type Bi_2Te_3 of sample A using AM method and sample B using the VR method are measured inside a vacuum chamber as shown in Figure 4.7. The temperature difference for lΔT was kept in the range of up to 122 K. The α value of sample A at room temperature is -50 µV/K. The average Seebeck coefficient of sample B calculated from a series of data at room temperature is -25 µV/K which has a

50% lower value than sample A. It is expected that sample B produce an α value less than sample A due to its composition that is way too far from the expected ratio. The highest error was ±0.005 for measurements of sample A whereas a higher error is observed in measurement of sample B with ±0.013 error.

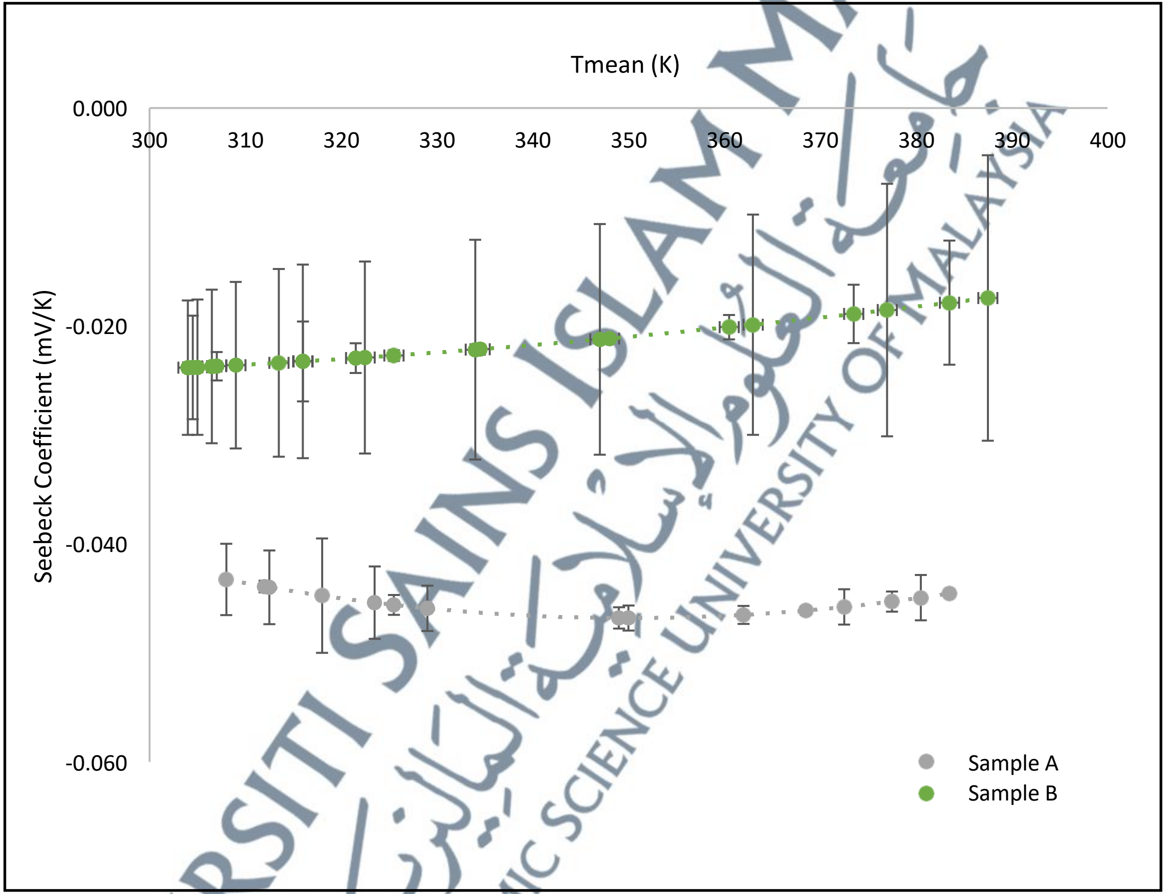

Figure 4.7: Average α of samples A and B under lΔT.

The α of fabricated samples C and D are shown in Figure 4.8. The measurements were done under lΔT up to 177 K with a temperature range (T_{mean}) up to 391 K. It is observed that the results of sample C and D obtained from measurements inside of vacuum chamber has a similar pattern to those reported by Kim et. al, (2011) where the α increase with the increase of temperature until it reached T_{mean}= 450 K, then it will slowly decrease by temperature.

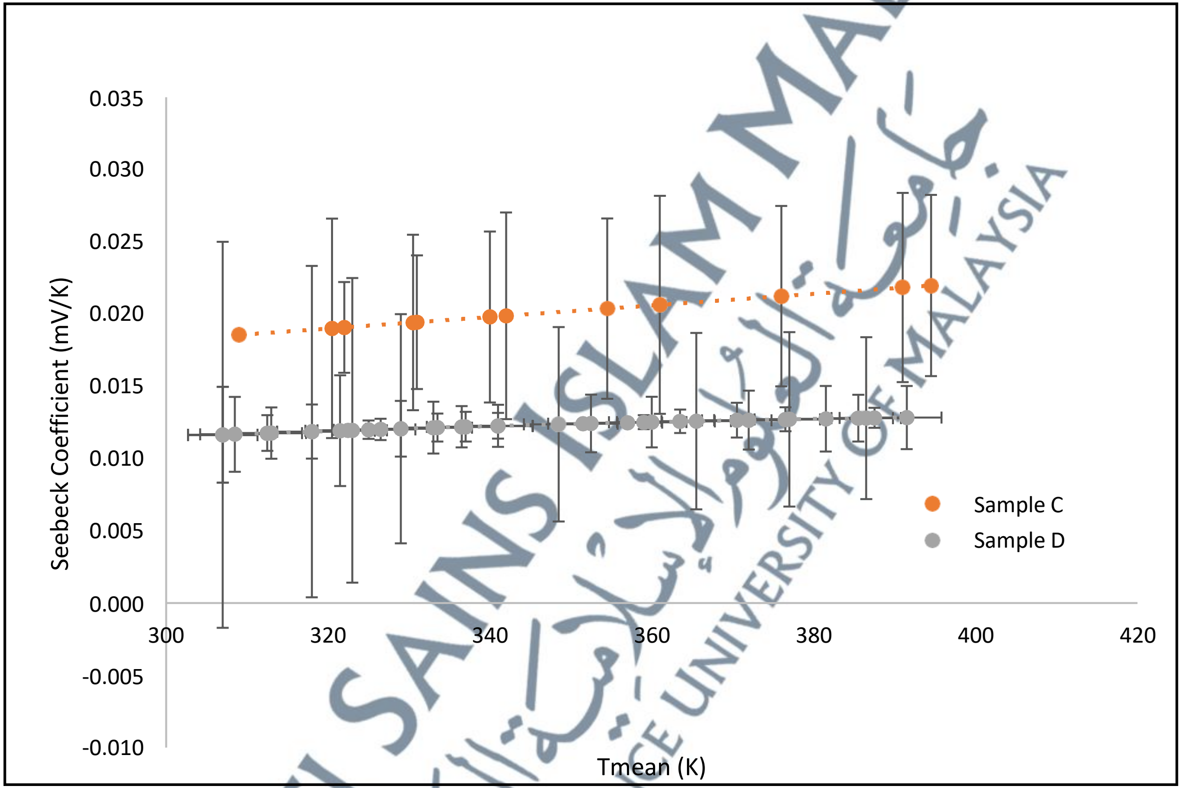

Figure 4.8: Average α of samples C and D obtained from several different sets of measurements inside of vacuum chamber under lΔT.

4.3.3 Comparison between sΔT and lΔT

Only two samples were measured for their Seebeck coefficient (α) under sΔT which were samples A and E to represent Bi_2Te_3-based and PbTe-based respectively. Moreover, the fabricated ratio of the compound is closer to the required compound ratio. The α measured under sΔT and lΔT are compared to see the difference between both conditions. Figure 4.9 shows the measurement of sample A under sΔT and lΔT. The α of sample A measured under sΔT and lΔT inside the vacuum chamber. Although the α values were slightly different in both conditions the pattern shows similarity. The difference in α value is feasible as this agrees with the measurement from the previous researcher that α under lΔT is lower than under sΔT.

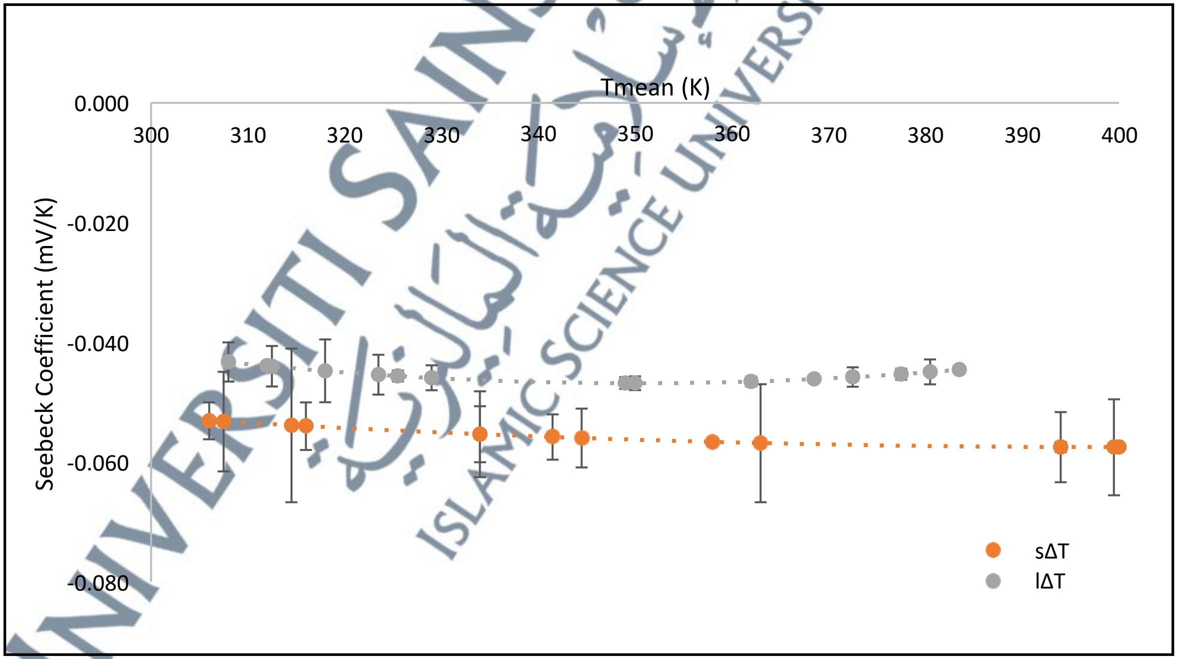

Figure 4.9: α comparison of sample A under sΔT and lΔT.

4.4 Electrical Resistivity

This is the added value to this study whereby the electrical resistivity of all samples was measured using a 4-point probe (Jandel RM3000+). 10 mA of current was supplied to all samples and the electrical resistivity was recorded in Table 4.3. However, there is no further study on resistivity. Thus, only a comparison to a previous study has been made. The 4-point probe measured sheet resistance, Rs therefore the bulk resistance is calculated using the average Rs measurement of the samples. Equation 3.3 is used to calculate the bulk sample resistance. For example, sample A has average Rs of 0.07 Ω/sq with a height (thickness) of 0.21 cm:

$$Bulk\ Resistivity, R\ \left(\frac{\Omega}{cm}\right) = Height, H\ (cm) * \ Resistance, Rs\ \left(\frac{\Omega}{sq}\right)$$

$$= 0.21 \text{ cm x } 0.07\ \Omega/\text{sq}$$

$$= 15 \text{ x } 10^{-3}\ \Omega/\text{cm}$$

Since samples A and B were expected to have a compound ratio of $Bi_2Te_{2.7}Se_{0.3}$, produced the ratio of fabricated samples of $Bi_{2.2}Te_{2.6}Se_{0.2}$ and $Bi_{0.9}Te_{3.5}Se_{0.6}$ respectively, thus electrical resistivity of M. Fusa et. al, (2014) is compared. M. Fusa et. al, (2014) reported that the electrical resistivity of $Bi_2Te_{3-x}Se_x$ (x = 0.2 - 0.6) was in the range of 10 to 21 mΩ.cm at room temperature. Therefore, the electrical resistivity of samples A and B is a bit higher than the range of the reported values which is 15 and 27 mΩ.cm respectively.

In addition, the electrical resistivity of $Bi_{2-x}Sb_xTe_3$ (x = 1.4 to 2.0) and (x = 1.2 to 2) prepared by various methods had been reported to have electrical resistivity in the range of 0.2 to 2.4 mΩ.cm and 2.5 to 0.8 mΩ.cm respectively (Xie et.al, 2013, Zhang et.al, 2015).

Meanwhile, Nagami et. al (2019) recorded that electrical resistivity for $Bi_{0.5}Sb_{1.5}Te_3$ was ~4 mΩ.cm at room temperature. Wang et.al, (2018) revealed that the electrical resistivity at room temperature for $Bi_{0.4}Sb_{1.6}Te_3$ was 1.3 mΩ.cm. In this study, the measured electrical resistivity at room temperature for samples C and D were 11 and 5.8 mΩ.cm respectively which is slightly higher than the reported value. This may be affected by the presence of an oxidation layer on the surface of samples that are not properly removed.

Li et. al, (2011) reported that the electrical resistivity of $PbTe_xSe_{1-x}$ (x = 0.2, 0.3, 0.5, 0.85 and 1.0) was between 2.8 – 9.5 mΩ.cm at temperature of 300 – 673 K. They also obtained ~6.8 mΩ.cm at 300 K for a pure PbTe sample. In addition, Unuma et al. (1998) fabricated a pure PbSe sample using pressureless sintering where they obtained electrical resistivity of 167 Ω.m at room temperature (300K). The measured electrical resistivity for samples E ($Pb_{1.1}Te_{0.7}Se_{0.2}$) and F ($Pb_{0.5}Te_{1.1}Se_{0.4}$) measured was 33.8 and 2.7 Ω.cm at room temperature respectively. The electrical resistivity of both samples in this study is much higher than the one reported in Li et al. might be caused by the low pressure and holding time used in the HP process of this study. This is because they were using the ball milling and SPS techniques which are known to be the best method for modifying the grains interface between compounds. However, this study's method is better than pressureless sintering as the electrical resistivity of this study lower than Unuma et al.

Last but not least, the electrical resistivity of samples G and H are 0.18 and 1.8 mΩ.cm at room temperature respectively. Zhu et. al, (2002) reported that $Pb_{0.8}Sn_{0.2}Te$ has an electrical resistivity of 0.51 to 0.25 mΩ.cm at room temperature. Therefore, themeasured result for both samples agrees well with the reported electrical resistivity.

Table 4.3: Electrical resistivity of all samples.

Samples	**Compositions Sample**	**Electrical Resistivity (Ω.cm)**	**Literature Composition**	**Electrical Resistivity (Ω.cm)**
A	$Bi_{2.2}Te_{2.6}Se_{0.2}$	$15x10^{-3}$	$Bi_2Te_{3-x}Se_x$ (x = 0.2 - 0.6) M. Fusa et al., (2014)	$(10–21)$ x 10^{-3}
B	$Bi_{0.9}Te_{3.5}Se_{0.6}$	$27x10^{-3}$		
C	$Bi_{0.2}Sb_{1.6}Te_{2.8}$	$11x10^{-3}$	$Bi_{0.5}Sb_{1.5}Te_3$ Nagami et. al., (2019)	$\sim 4x10^{-3}$
D	$Bi_{0.2}Sb_{1.6}Te_{3.2}$	$5.8x10^{-3}$	$Bi_{0.4}Sb_{1.6}Te_3$ Wang et.al, (2018)	$1.3x10^{-3}$
E	$Pb_{1.1}Te_{0.7}Se_{0.2}$	33.8	$PbTe_xSe_{1-x}$ (x = 0.2, 0.3, 0.5, 0.85 and 1.0) Pure PbTe Li et. al, (2011) Unuma et al. (1998)	$(2.8– 9.5)$ $x10^{-3}$ ~ 6.8 $x10^{-3}$ 167
F	$Pb_{0.5}Te_{1.1}Se_{0.4}$	2.7		
G	$Pb_{0.7}Sn_{0.2}Te_{1.1}$	$1.8x10^{-4}$	$Pb_{0.8}Sn_{0.2}Te$ Zhu et. al, (2002)	$(0.51-0.25)$ x 10^{-3}
H	$Pb_{0.2}Sn_{0.7}Te_{1.1}$	$1.8x10^{-3}$		

4.5 Conclusions

All samples have been successfully constructed using a hot press machine. Based on the elemental compositions of samples analyzed from FESEM, the atomic mass method used in determining the mass of powders for each ratio was better than the ratio method. Although the samples from the ratio method used higher pressure than the atomic mass method, the FESEM shows that the ratio of constructed samples (atomic mass method) was nearly close to the expected ratio. Therefore, the atomic mass method can be used in calculating the powder needed for certain samples in hot press techniques so that materials wasted can be avoided. In addition, for fabrication using HP techniques using mould available in USIM the optimum pressure, temperature and holding time to fabricate Bi_2Te_3 based alloy are 13 MPa, 473 K and 17 – 30 minutes respectively. Meanwhile for samples PbTe based on thermoelectric, to fabricate the samples, the suitable pressure, temperature and holding time were 13 MPa, 493 K and 17 minutes respectively.

The thermoelectric performance such as the Seebeck coefficient (α) of all fabricated samples was successfully measured under sΔT and lΔT. According to the measured α results, n-type Bi_2Te_3 based thermoelectric materials (sample A) measured under sΔT lower than the reported values (literature). However, the pattern of the measured values was similar between sΔT and lΔT. Surprisingly, the α of PbTe based thermoelectric materials (sample E) under sΔT has a higher value than the reported α value at room temperature. The behaviour of measured α was almost the same between sΔT and lΔT.

On the other hand, the electrical resistivity has successfully measured using 4-point probe equipment. It can be concluded that samples A, B, G and H have electrical resistivity within the range of the reported value. Meanwhile, for samples, C, D, E and F, the electrical resistivity was higher than the reported values. The samples fabricated in UKM (B, D, F and H) have a lower error difference from the reported electrical resistivity value. This is because of the higher pressure used (20 MPa) during the fabrication samples. This causes the space between the grains to be closer to each other. Meanwhile, the high electrical resistivity is affected by the space between grains as well as the oxidation layer on the surface. Thus, improvement in modifying the interface between grains can be done to reduce the electrical resistivity of all samples. All in all, high pressure can reduce the interface between grains which can produce low electrical resistivity.