Fabrication and Characterization of PbSnTe Crystals for Thermoelectric Applications

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***Abstract*—PbSnTe crystals were grown using the horizontal vapor phase growth (HVPG) method with growth temperature of 1000 °C and 1200 °C and growth time of four and eight hours where its surface morphology and elemental compositions were analyzed using the Phenom ProX Desktop SEM with EDS. The effect of the interaction term between growth temperature and growth time with respect to the figure of merit ZT was analyzed using the Design of Expert software, where the p-values obtained was significant. At room temperature, the high figure of merit was approximately 0.084, which can be correlated from the formation of the cubic crystals that was grown at 1200 °C for four hours.**

***Index Terms*—Crystal structure, HVPG, PbSnTe, Thermoelectrics material.**

I. Introduction

$Pb_{1-x}Sn_xTe$ is known as a good material for thermoelectric (TE) application because of its crystal cubic (rock- salt) structure [1] which enhances phonon scattering that leads to a maximum figure of merit (ZT) [2] where ZT is known as a parameter for characterizing the performance of a thermoelectric material. An ideal material should be able to provide ZT higher than 1 to provide conversion efficiency of the thermoelectric device from 10% to 15% [3], [4]. ZT has a function of Seebeck coefficient (S), thermal conductivity (κ), electrical conductivity (σ), and temperature [5], [6].

According to previous studies, at room temperature measurement, ZTs of PbSnTe nanowires were approximately 0.035 and 0.018 which is higher than that of PbTe nanowires at 0.0054 while the ZT of bulk structure PbSnTe is less than 0.01 [7]. At x = 0.67, the nanostructure of Pb1-xSnxTe has a small energy gap of 0.28 eV [8] where high ZT can be found [9].

In this study, the growth temperature of 1000 °C and 1200 °C was explored with a growth time of four hours and eight hours, respectively, using horizontal vapor phase method (HVPG) while the statistical design was used to analyze and correlate the ZT of the grown material with the growth temperature and growth time.

II. Material and Method

A. *Preparation of Raw Material*

An amount of 50 milligrams of Pb shot, Sn, and Te powder with a purity of 99% were used to fabricate the grown materials via HVPG technique. $Pb_{1-x}Sn_xTe$ was set to x = 0.67. Two growth times, four and eight hours, and growth temperature, 1000 °C and 1200 °C, were the parameters used in this study. The mixture was placed in a quartz tube with 8.5 mm inner diameter, 11.5 mm outer diameter, and 304.8 mm length.

B. *Design of Experiment*

The 2^k factorial design was used to analyze the effect of two factors, namely growth temperature (A: 1000 °C, 1200 °C) and growth time (B: four hours, eight hours). The result was the figure of merit (ZT) of the grown material with two replications for each run.

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C. *Fabrication of Thermoelectric Material*

The quartz tube with the source materials inside was attached to a high vacuum system with pressure to 10^{-6}torr. A blowtorch was used to seal the other end of the quartz tube. It was later placed in a Thermolyne programmable horizontal tube furnace with half-length exposed outside at room temperature. The furnace was programmed to control the growth time and growth temperature.

D. *Characterization ZT and Structure of Thermoelectric Material*

The characterization of ZT was obtained using the Harman method [10], [11], [12] which is calculated using the formula ZT = (Rdc - Rac)/Rac, where Rdc and Rac are the resistance generated from the sample. A DC and AC power supply was set to 5mA current input and square waveform. The figure of merit was measured at room temperature.

After obtaining the ZT values, normal distribution was used to analyze the error from the measurement, which was performed by Mintab software where the measured value was close to the true value. SEM with EDS was used to analyze the formed crystals.

E. *Statistical Analysis*

The 2^k full factorial design with two replications was used to correlate the effect of growth time and growth temperature on ZT, which was calculated using the Design of Expert software. From the results of the analysis of variance (ANOVA), the p- values obtained was smaller than 0.05 where it indicates that the growth temperature and growth time has a significant ZT response [13].

III. RESULT AND DISCUSSION

A. *Effect of Growth Time and Growth Temperature on ZT*

In this study, ZT was computed by obtaining the value of the voltage and current using a Fluke digital multimeter. The AC resistance (Rac) and DC resistance (Rdc) were calculated using the value of the voltage from the sample divided by the current supplied. Using the Harman method, ZT can be calculated by taking the difference between Rdc and Rac divided by Rac.

After applying normal distribution, a maximum of two outliers were found in sample number 3 from 15 measurements (N=15). This means that for the other 13 measured data of sample, number 3 was normally distributed. Moreover, a minimum of one outlier was obtained in sample numbers 1, 4, 6, and 7. This indicated that the remaining 14 measured data of these samples were normally distributed. Moreover, all 15 measured data of sample numbers 2, 5, and 8 were normally distributed. Fig. 1 shows normally distributed spreading around the straight line.

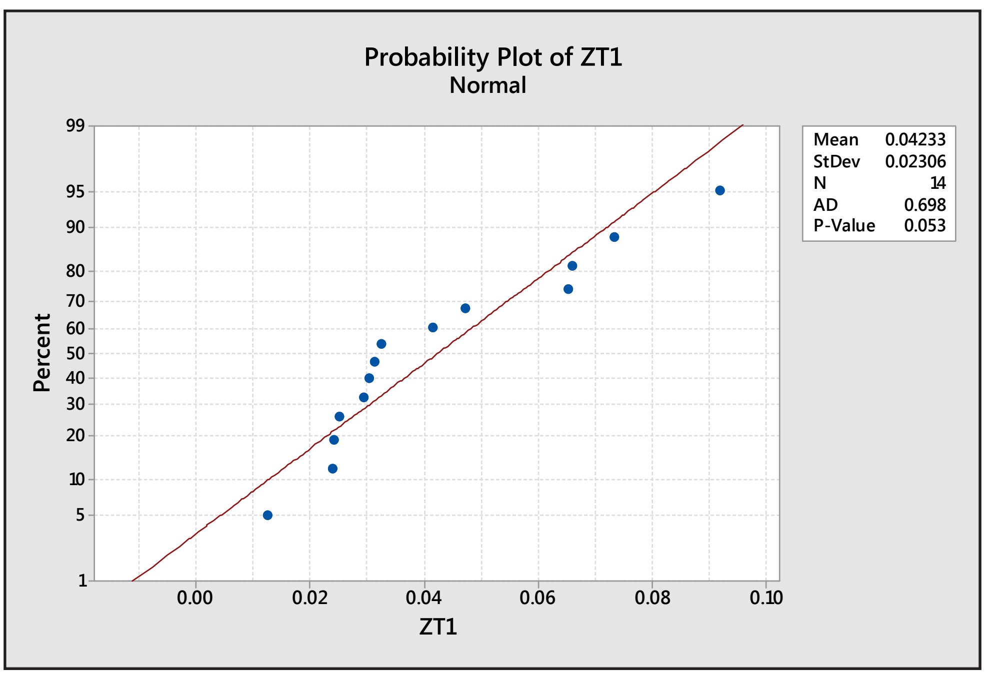


Fig. 1. Probability plot for ZT of sample number 1 after removing an outlier..

The summary of ZT's mean for all samples is shown in Table 1. The highest ZTs were 0.084 and 0.067, which were samples 3 and 4 at a growth temperature of 1200 ^{o}C and growth time of four hours. However, the minimum ZT was 0.036 from samples 2 and 8. This indicated that when the growth temperature was high and growth time was low, the maximum ZT can be achieved.

Table 2 shows the table of ANOVA of ZT. The result of the model is significant. Thus, it can be concluded that the effect of AB is significant at 95% level of confidence. The effect of the interaction term can be seen in Fig. 2. At growth time of four hours and growth temperature from 1000 ^{o}C to 1200 ^{o}C, the ZT significantly increased. However, with a growth time of eight hours and growth temperature from 1000 ^{o}C to 1200 ^{o}C, the ZT decreased. The final equation in terms of actual factors was generated as below:

$$ZT = (-0.3465) + 3.775 \times 10^{-4}\,\text{Temp} + 0.05075\,\text{Time} - 4.875 \times 10^{-5}\,\text{Temp*Time}$$

TABLE I
Experimental Result of Mean ZT Values of the Synthesized material

Std/ Sample	Run	Factor A: Growth Temp [^{o}C]	Factor B: Growth Time [hour]	Response Y: Mean ZT
2	1	1000	4	0.036
4	2	1200	4	0.067
8	3	1200	8	0.036
7	4	1200	8	0.053
6	5	1000	8	0.045
5	6	1000	8	0.049
1	7	1000	4	0.042
3	8	1200	4	0.084

TABLE II
ANOVA of ZT

Source	Sum of Square	df	Mean Square	F Value	P-value Prob > F	
Model	1.60E-03	3	5.34E-04	6.79	0.0477	significant
A-Temperature	5.78E-04	1	5.78E-04	7.34	0.0536	not significant
B-Time	2.65E-04	1	2.65E-04	3.36	0.1408	not significant
AB	7.61E-04	1	7.61E-04	9.66	0.036	significant
Pure Error	3.15E-04	4	7.88E-05			
Cor Total	1.92E-03	7				

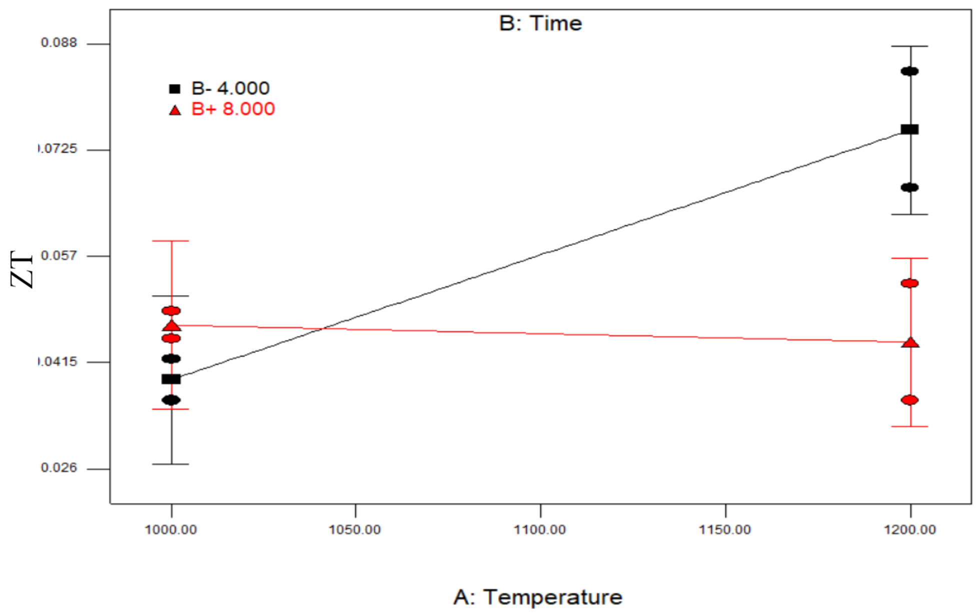


Fig. 2. Interaction plot of growth temperature vs. growth time.

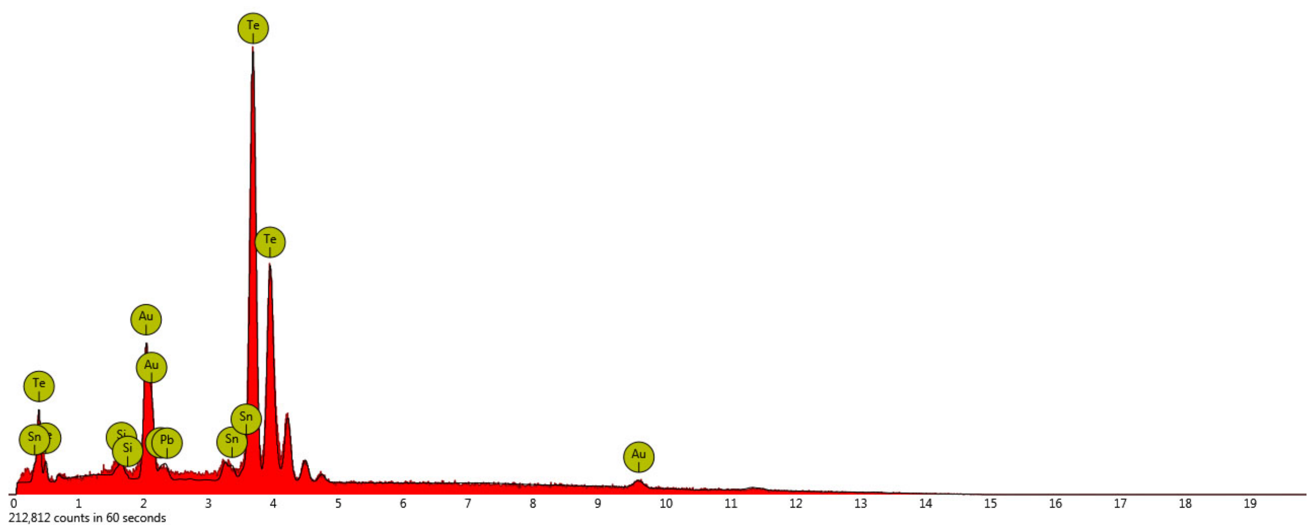
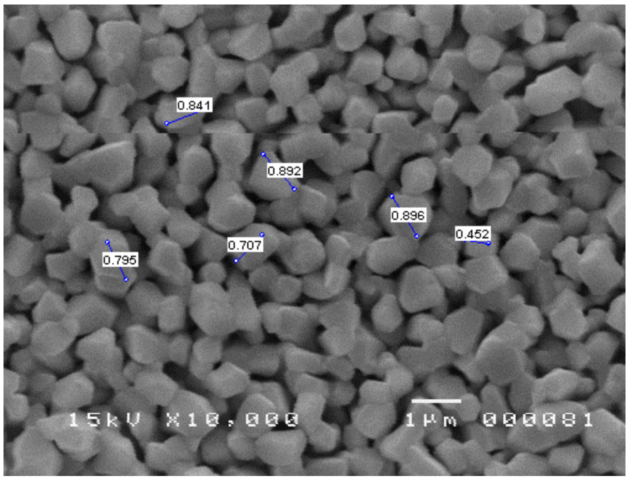


Fig. 3. (a). SEM of sample 3 (b) sample 4 with the same growth temperature of 1200 ^{o}C and growth time of four hours magnified at 10,000x.

B. *Crystal Formation of Material*

The maximum ZTs were found in samples number 3 and 4, while the minimum ZTs were samples number 2 and 8. The maximum ZT can be correlated to the formation of cubic rock-salt structure having lengths less than 1 μm compared to the other samples as shown in Fig. 3(a). The rock-salt structure, according to literature, leads to enhanced phonon scattering for the improvement of ZT. Although the lengths of crystal formed in sample 4 were similar to that of sample 2 and 8, sample 4 has a higher ZT value. This is due to the distribution of the grown material of sample 4, which is completely uniform as shown in Fig. 3(b). The same explanation for samples number 3 and 4 since they have a high ZT value of 0.084 and 0.067, respectively.

However, as shown in Fig. 4, sample number 2, has artifacts and was synthesized both at minimum growth temperature and time. Fig. 5 shows that the distribution of grown material of sample 8 is not uniform. The voids can be attributed to the minimum ZT values. Wire structures were also observed in sample 8 grown both at high temperature and time. The result of the EDX spectrum is shown in Fig. 6, where the materials of interest were Pb, Sn, and Te, respectively.



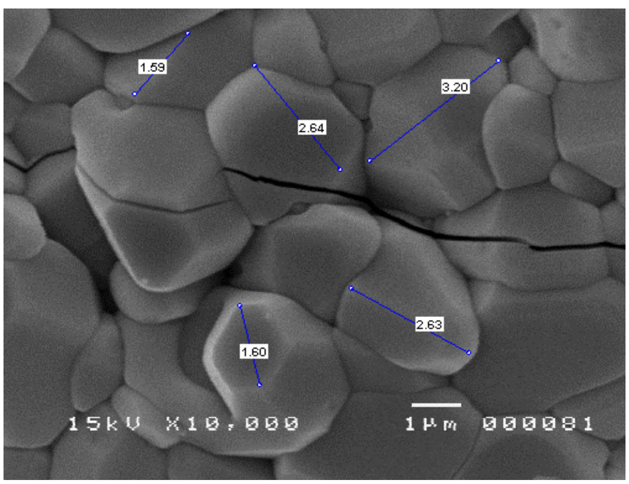
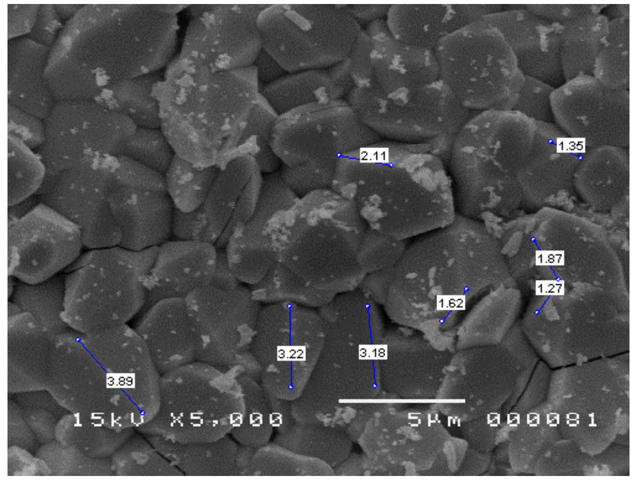


Fig. 4. SEM of sample 2 with growth temperature of 1000 °C and growth time of 4 hours magnified at 5,000x.



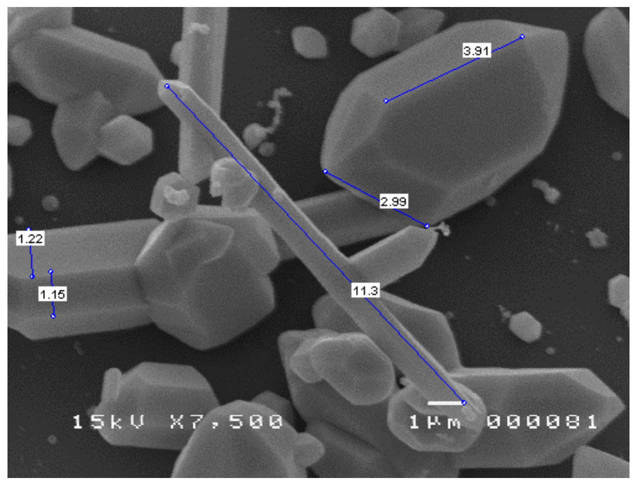


Fig. 5. SEM of sample 8 with growth temperature of 1200 °C and growth time of 8 hours magnified at 7,500x.

V. Conclusion

PbSnTe thermoelectric materials were successfully synthesized using HVPG technique with growth temperature of 1000 °C and 1200 °C and growth times of four and eight hours. Based on the results of ANOVA, the growth parameters were significant. At low growth time of four hours, ZT significantly increased as growth temperature increased from 1000 °C to 1200 °C, however, with the growth time of eight hours, the ZT value decreased. Significantly, the highest figure of merit was approximately 0.084 with cubic crystal formation grown at 1200 °C for four hours.

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