

An Overview of Thermoelectric Sample Testing Methodologies

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Sincerely,
Shrikanth Venkata Tamirisa

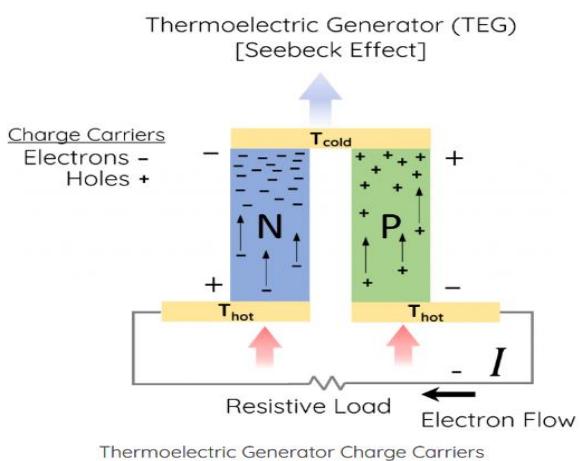
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Abstract and Introduction

The present-day woes of energy crisis conveys that we cannot afford to waste energy, especially those modes which are derived from non-renewable sources like fossil fuels. According to Yale School of Environment, a whopping 70 percent of all the energy produced by humanity gets chucked as waste heat. The knight in shining armor in this scenario is the thermoelectric technology.

Thermoelectric modules do the job of converting waste heat into useful electric energy. Reliable and robust with no moving parts, these semiconductor devices utilize Seebeck effect. The Seebeck effect involves an energy conversion of heat into potential difference. It occurs due to the movement of charge carriers within the semiconductor material. Charge carriers diffuse away from the hot side of the device. This diffusion leads to a buildup of charge carriers at one end. This accumulation of charge creates a potential difference that is directly proportional to the temperature difference across the device.



The efficiency of such a thermoelectric device is given by

$$\eta = \frac{P}{Q}$$

Where,

$\eta \rightarrow$ Heat to electricity conversion efficiency

$P \rightarrow$ Electric power generated

$Q \rightarrow$ Heat given as input by establishing temperature gradient.

Since efficiency is subject to a lot of factors and variables, another dimensionless term, the figure of merit zT is used to judge the usability of a semiconductor material as a thermoelectric objectively.

$$zT = \frac{S^2 \sigma T}{\kappa}$$

Where,

$S \rightarrow$ Seebeck Coefficient

$\sigma \rightarrow$ Electrical conductivity

$T \rightarrow$ Temperature

$\kappa \rightarrow$ Thermal conductivity

$$\eta = \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + T_c/T_h}$$

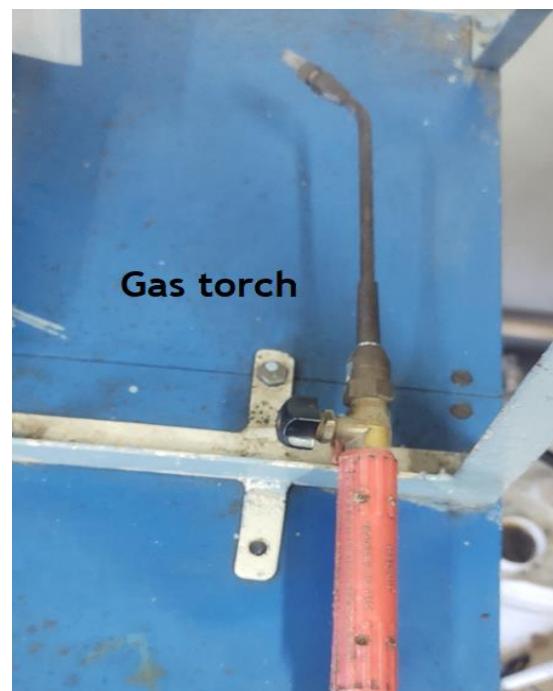
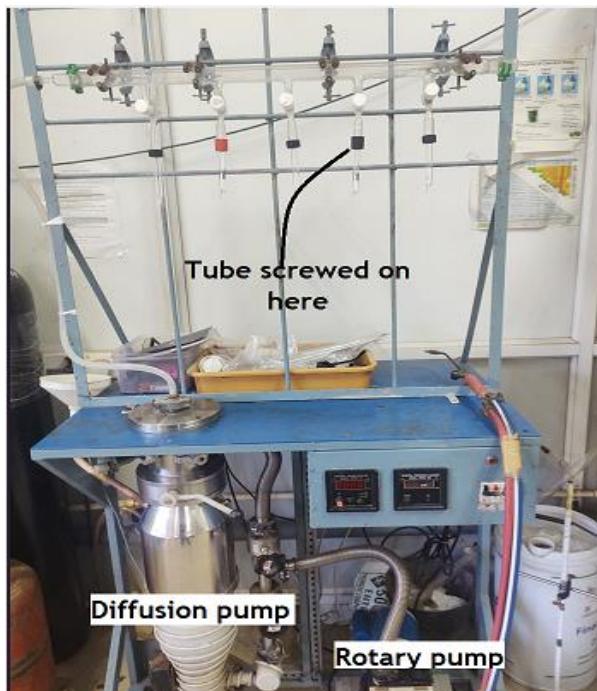
As can be seen, optimization of figure of merit leads to optimization of efficiency.

But, optimization of figure of merit is not a straight task. While high S is a semiconductor like property, a high σ is a metallic property, and a low κ is an insulator like property. More often than not all these factors are “coupled”, such as a high electrical conductivity (which leads to a high zT) leading to a higher thermal conductivity (which leads to a low zT) due to electronic contribution to thermal conductivity being proportional to conductivity (Wiedemann-Franz Law).

This makes the quest for thermoelectric materials enigmatic and an area of active research. Chemistry techniques such as doping, atomic ordering, multiscale hierarchical architecture, nano structuring, etc. are employed to make samples of thermoelectric materials. This project describes the various methodologies using which these samples are prepared and tested at laboratories as observed by me.

Sealing and quenching of thermoelectric samples

A sample of thermoelectric is prepared by mixing the required semiconductors and dopants in stoichiometric ratio in a quartz tube, creating a vacuum in it and sealing it off. This is done in a sealing line apparatus. This apparatus consists of two pumps, a rotary pump and a diffusion pump. While the rotary pump acts as a backing pump and takes vacuum down to 10^{-3} torr, the diffusion pump furthers the vacuum to 10^{-5} torr. The tube is screwed onto a glass tube which extends vacuum into it, and then using a gas torch the mouth of the tube is sealed shut by melting the glass inwards.



This tube is then heated in a furnace for appropriate reactions to take place. After this, the sample needs to be brought down to room temperature. This can be achieved in two ways: slow cooling or quenching.

Sometimes slow cooling is not an option as it may lead to formation of impurities. This may be revealed by X-ray diffraction (XRD) of the cooled sample. In such cases, one should go with quenching.

Quenching involves rapid cooling of the sample, within seconds.

This is achieved by putting the sample tube into a beaker of liquid nitrogen immediately after removing it from the furnace.



The furnace at our lab

The tube is removed from the furnace at 650 °C using tongs.



The tube is then quickly dropped into liquid nitrogen:





After a few minutes, the tube is removed from the beaker and is allowed to warm up to ambient temperature, and is marked up for identification and further processing.

X - Ray diffraction analysis of thermoelectric samples

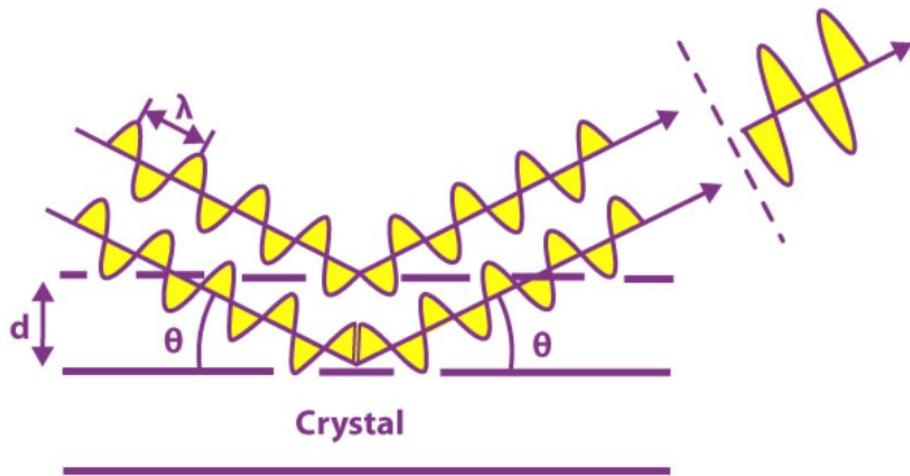
For further analysis of the crystallographic properties of the thermoelectric sample and for processes such as Bridgman synthesis, XRD analysis of the sample is essential. We use Rigaku SmartLab device at our lab for XRD analysis.



Working Principle:

This device works on the basis of Braggs' Law. When a crystal is bombarded with X-rays of a fixed wavelength (similar to spacing of the atomic-scale crystal lattice planes) and at certain incident angles, intense reflected X-rays are produced when the wavelengths of the scattered X-rays interfere constructively. In order for the waves to

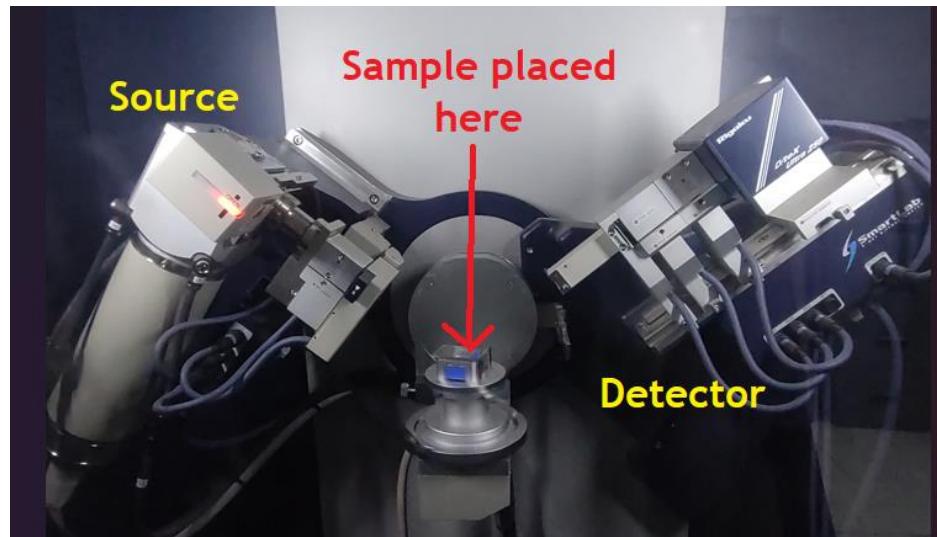
interfere constructively, the differences in the travel path must be equal to integer multiples of the wavelength. When this constructive interference occurs, a diffracted beam of X-rays will leave the crystal at an angle equal to that of the incident beam.



$$n\lambda = 2dsin\theta$$

Hence the device measures the angle θ at which constructive interference (peak in intensity) is observed, and the corresponding d is calculated. This d is the inter-planar spacing or d -spacing of a crystal which is used for characterization and identification purposes.

The device consists of two arms. One shoots X-rays at the sample, while another acts as the receiver and detects the resultant intensity of the X-rays diffracted from the sample. The angle at which X-rays are incident on the sample can be changed. Once all angles have been analyzed, the device draws a graph of 2θ vs intensity recorded. The angles at which peaks are noted help in characterization of the crystallographic structure of the sample, with the XRD pattern acting as a fingerprint of it, uniquely identifying its structure.

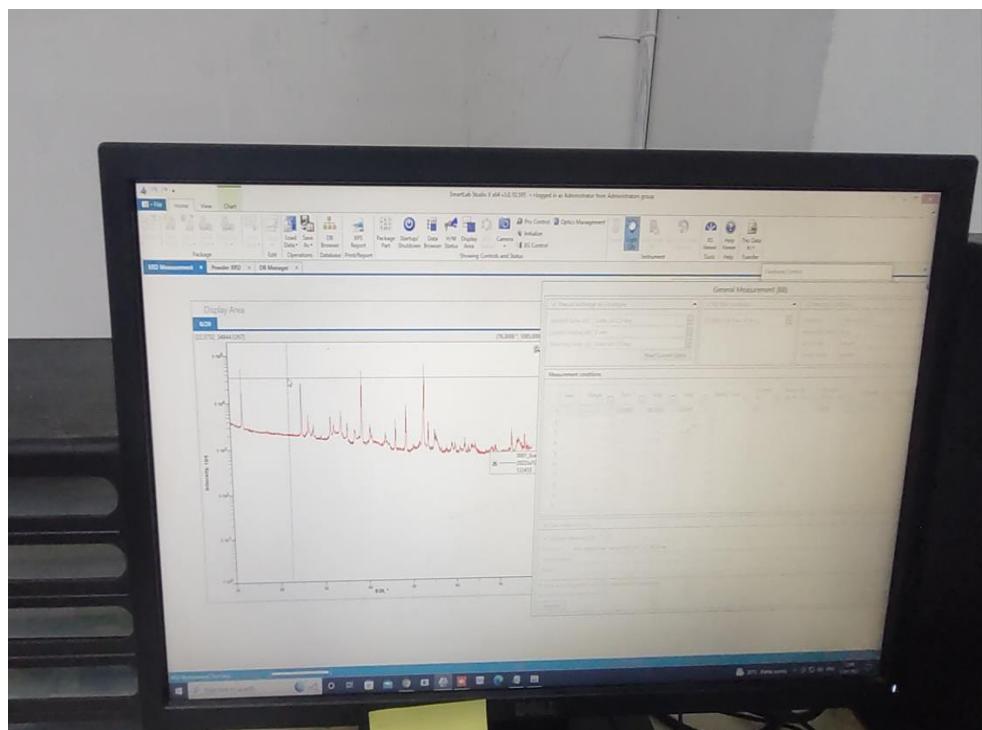


Operating Procedure:

1. A glass slide is taken and is thoroughly cleaned with acetone. The sample in powdered form is deposited on the slide as a thin layer, which is then entrapped by placing another glass slide on it.
2. Once the door lock sign is off, this setup is placed on the stage inside the device. The door is then locked subsequently.

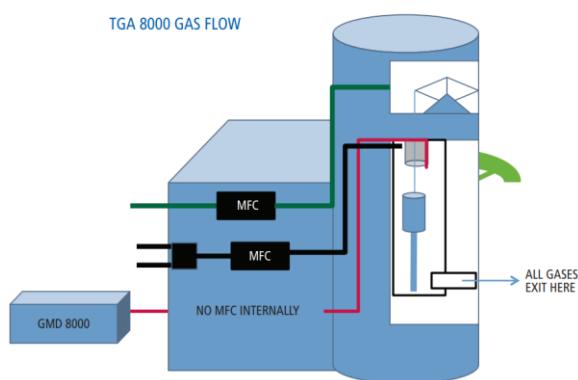


3. On the RAS software, specifications are set, which includes setting incident slit width as $2/3$, the speed of rotation (20 rotations/min in our case), start angle (10°), stop angle (80°), step size (0.02), etc.
4. After completion of measurements at all the specified angles, the door is unlocked and the sample setup is taken out. The XRD pattern is drawn by the data acquisition software.



Thermogravimetric Analysis of Thermoelectric Samples

The Thermogravimetric Analyzer (TGA) is an essential laboratory tool used for material characterization. It is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. A TGA consists of a sample pan that is supported by a precision balance of sensitivity 10^{-6} g . That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment. This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust.



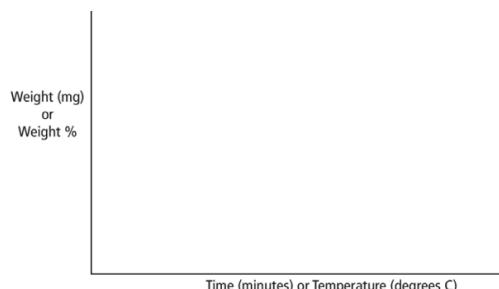
We are using Perkin Elmer TGA 8000 in our lab.



Balance Type	Hangdown Pan
Standard Furnace	Temperature Range: Subambient to 1200 °C
Balance Precision	0.001%
Balance Capacity	1300 mg

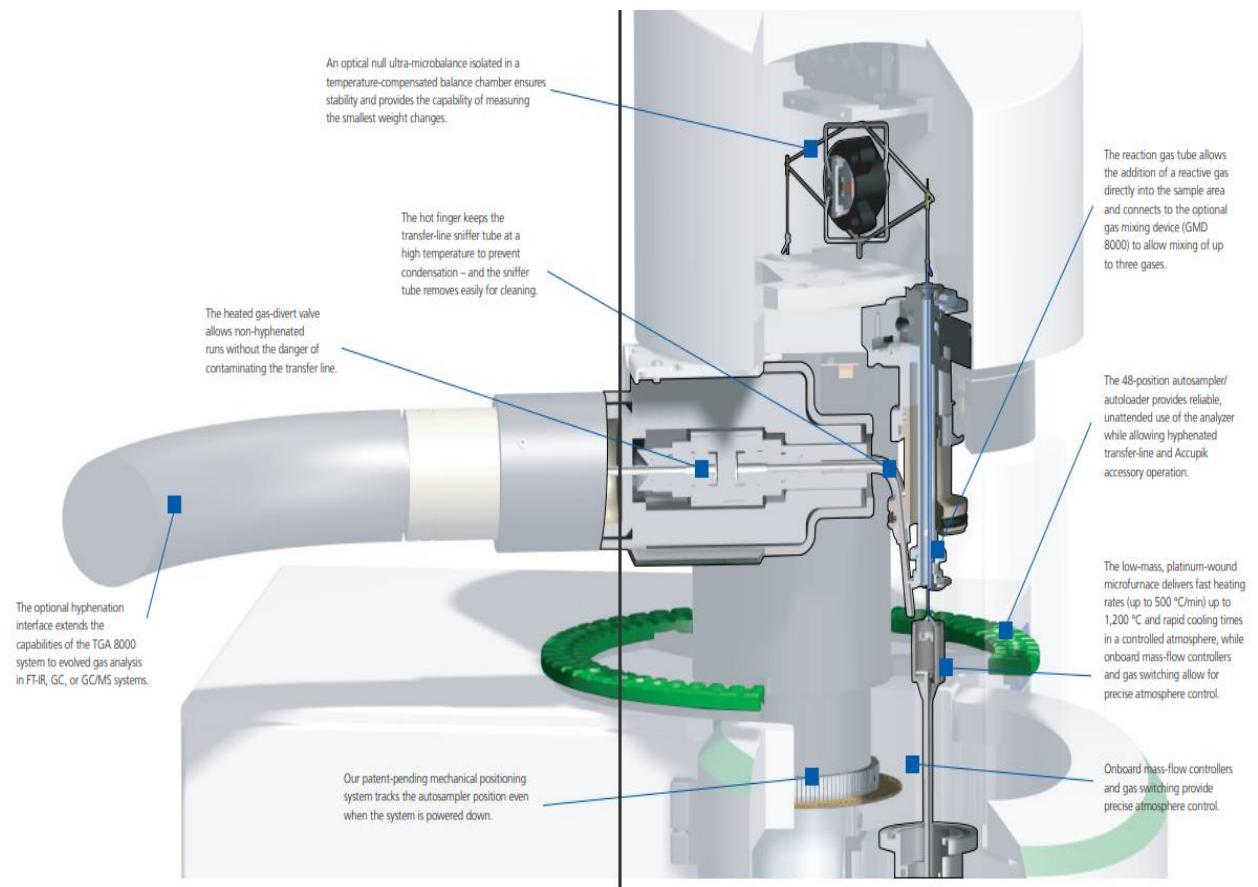
The system delivers heating rates from 0.1 °C to 500 °C/minute.

In a TGA curve, the abscissa (X-axis) can be displayed as time or temperature and the ordinate (Y-axis) can be displayed as weight (mg) or weight percent (%).



For reproducibility, 6 variables should be kept in mind while using TGA:

- Calibration
- Furnace cleanliness
- Sample preparation
- Temperature range
- Temperature scanning rate
- Sample atmosphere





The TGA Kit with sample pans, etc.

Procedure:

1. The sample pan comes in two variants, ceramic and platinum. We used the ceramic (alumina) variant in our analysis.
2. The pan has to be first coated with a thin layer of alumina powder. This is to prevent the sample powder or its residue from sticking to the pan, in order to ensure reusability. Alumina is also having excellent thermal conductivity; hence it doesn't interfere in the heating operation done on the sample.



3. Next, the sample has to be poured into the pan. The sample size should be between 2 and 50 mg. Many small pieces of sample are better than one large chunk. It is better to have a large surface area exposed to the sample purge. Hence, powdered form of sample was used. This pan now has to be loaded onto the autosampler for insertion into the furnace.
4. Next, the autosampler and furnace temperature control has to be programmed using Pyris software. The equipment has a 48 position autosampler. It is a disc with vacancies meant for accommodating the sample pans. It rotates with a precise motion control, such that each sample is positioned over the furnace to be picked up by a hook (attached to the precision balance); and then after the heating and cooling operation is complete, the disc positions itself in such a way that the sample pan is unloaded into the same numbered position in which it was residing prior to the analysis. Then, it again positions the next sample over the furnace, and the cycle continues. In our case though, we were analyzing only one sample. The sample pan was placed over position 10 of autosampler. In the software, this information was fed to the device:

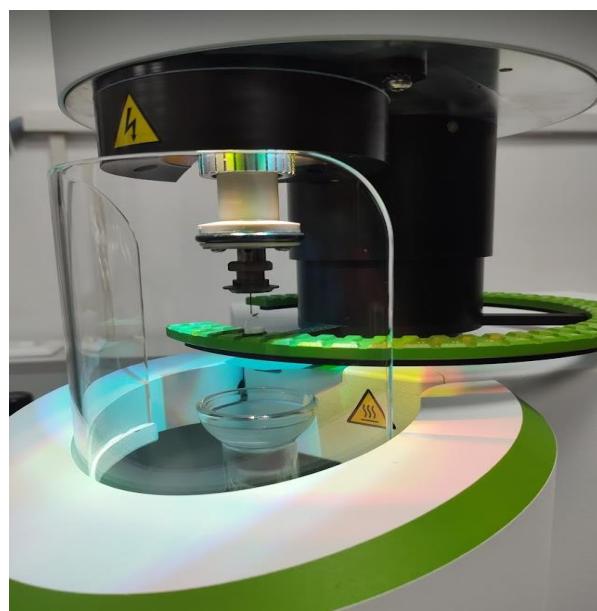
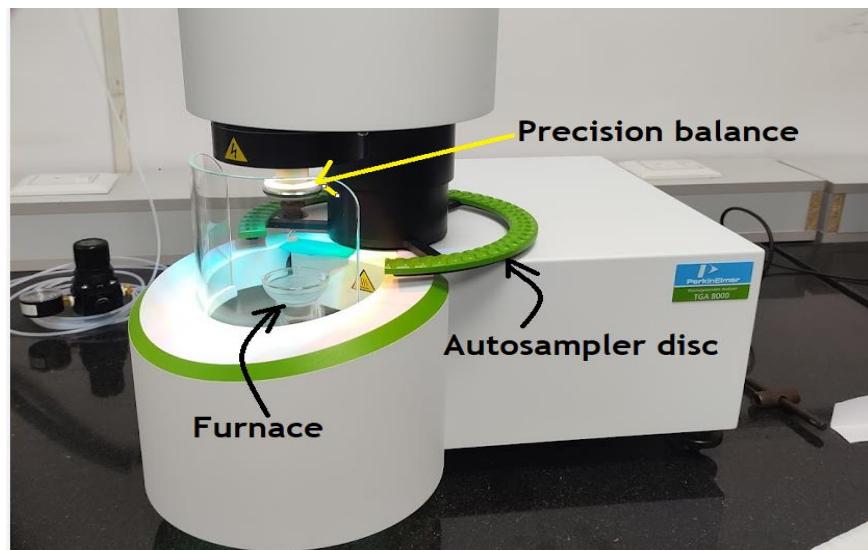
Autosampler Control → Carousel location → 10 → Load

Next, the temperature settings have to be given. For our analysis, the settings were:

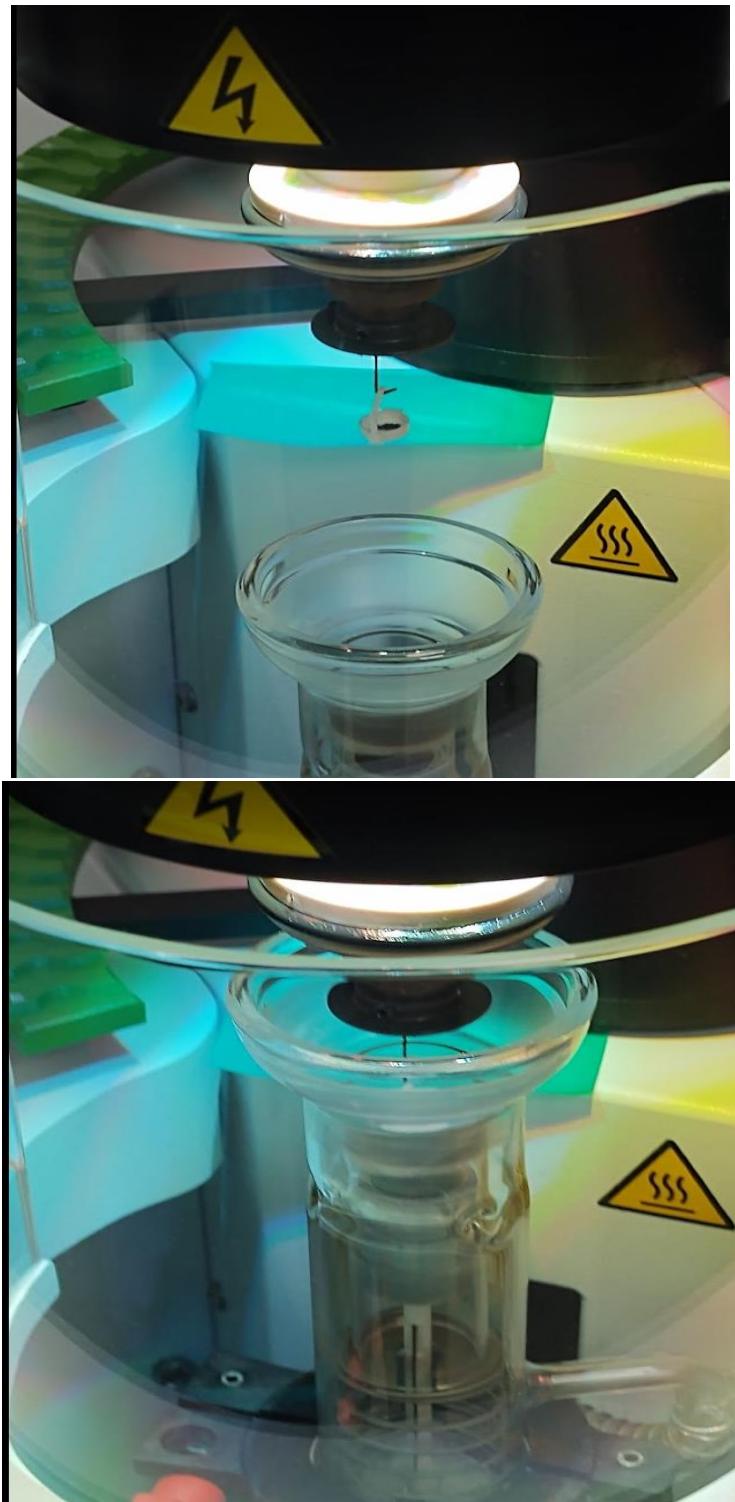
To: 800 °C

Rate: 20 °C/min

This means the temperature of the sample will be raised from ambient temperature to 800 °C at a rate of 20 °C/min, all the while measuring the weight of the sample. For better resolution of the weight vs temperature curve, the sample should be heated at a slower rate, around 10 °C/min.



Hook grabbing the sample pan from autosampler

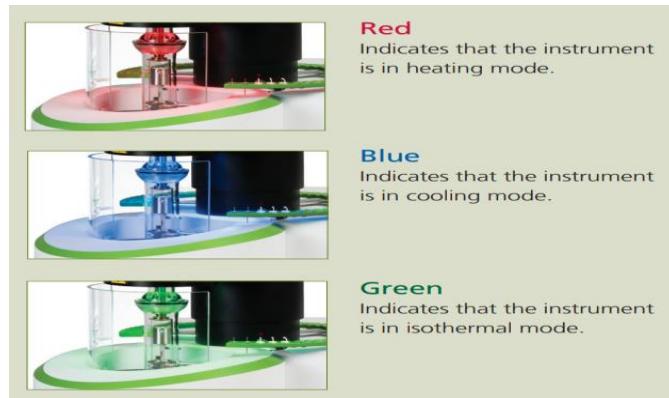


The furnace is hoisted up and now encompasses the sample

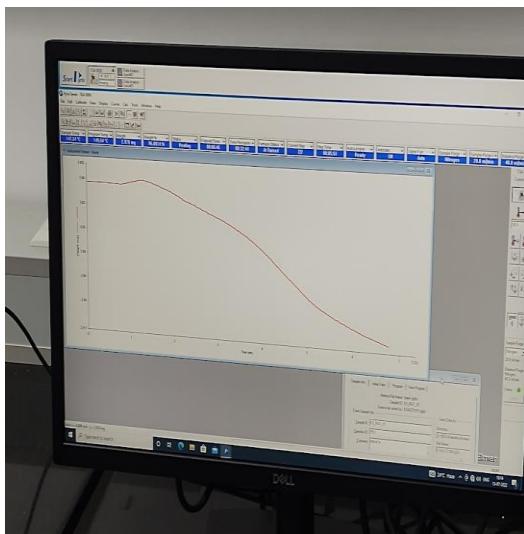
5. Next, the sample atmosphere has to be set. We use nitrogen as the purge gas in our lab. The purge rate is set up to 20 ml/min.
6. After this, the furnace raises to encompass the sample pan hanging from the balance, and begins heating it as per the

temperature profile set by us. The readings are translated into the weight (mg) vs temperature (°C) graph by the software.

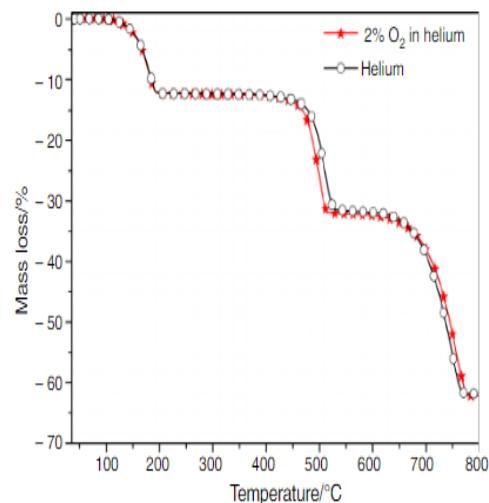
7. The equipment has a light indicator as follows:



8. After this, the sample has to be unloaded, which is again done by the autosampler using a procedure similar to the one done in loading.
9. The residual powder is discarded, and the pan is cleaned with acetone and stored away.
10. The furnace is allowed to cool down to ambient temperature, and then is shut down.



The TGA curve processed by the system



TGA curve of Calcium Oxalate

Measuring Band Gap of Thermoelectric Samples

The optimal bandgap of thermoelectric materials should be in the ballpark of 0.5 eV, and most certainly below 1 eV. To measure the bandgap of thermoelectric samples, we use the Bruker IFS 66 v/s device at our lab.



Working Principle:

This device works on the basis of Kubelka-Munk theory, and more specifically Tauc plot. The Tauc relation is given by:

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where,

$\alpha \rightarrow$ linear absorption coefficient

$h \rightarrow$ Planck's constant

$\nu \rightarrow$ light frequency

$A \rightarrow$ proportionality constant

$E_g \rightarrow$ Band gap of sample

$n \rightarrow$ For direct band gap materials, $\frac{1}{2}$.

Kubelka Munk relation is given by:

$$\frac{\alpha}{S} = \frac{(1 - R^2)}{2R}$$

Where,

$S \rightarrow$ Scattering coefficient

$R \rightarrow$ Reflectance

The band gap is calculated by plotting the graph of the square product of the absorption coefficient and energy $(\alpha E)^2$ versus energy E , $((\alpha E)^2 \text{ vs } E)$. The band gap can be obtained by extending a straight line from the straight segment of the graph such that it touches the E axis. This intercept gives the bandgap of the sample.

The sample is exposed to infrared radiation, and the wavelength of the incident and transmitted light is measured by the spectrometer for the purpose of plotting the Tauc plot.

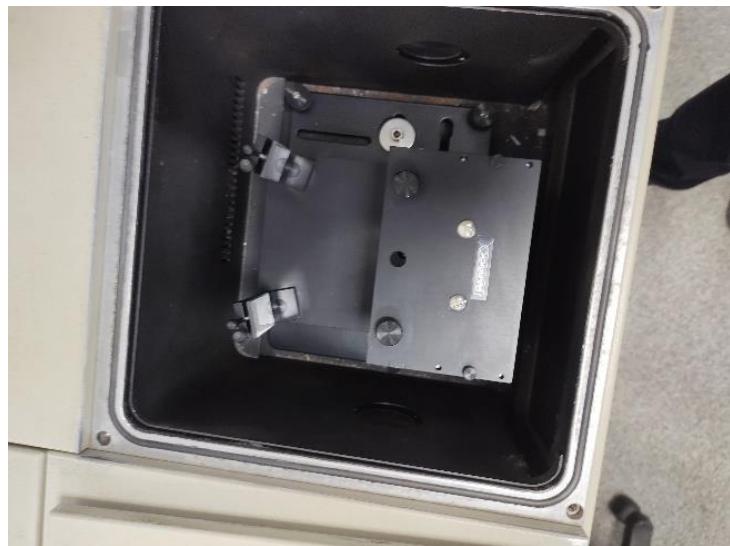
Operating Procedure:

1. The sample in powdered form is first filled into a special vessel up to the brim.



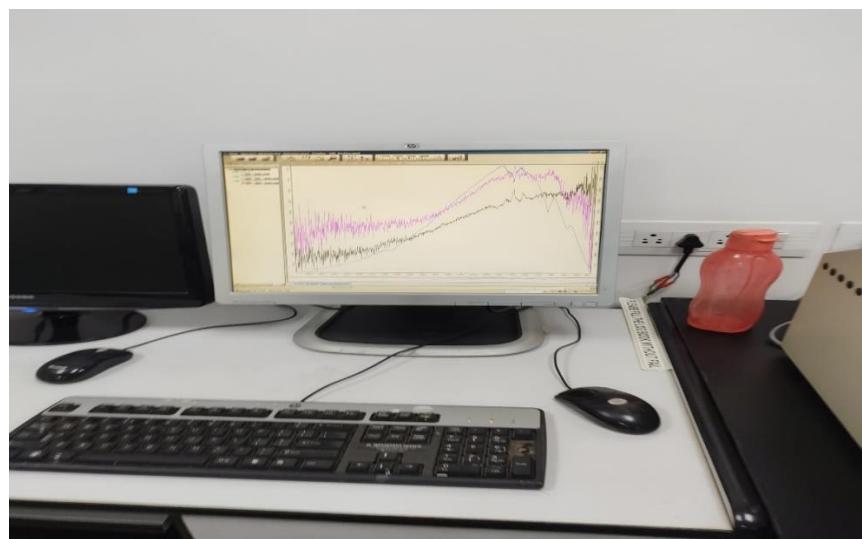
2. The vessel is placed in the sample chamber of the device and then it is closed with a lid. The sample chamber is then purged.





The insides of the chamber

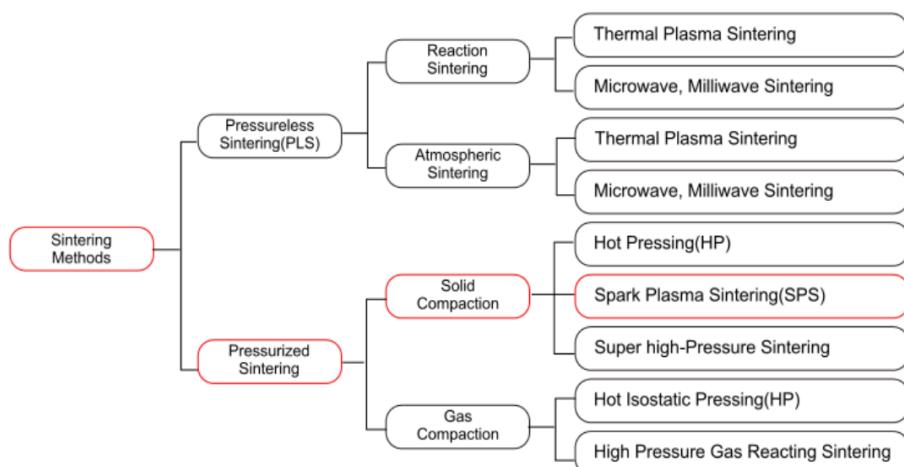
3. Specifications such as resolution and wavelength range (200-3500 nm in our case) are set in the software.
4. The Tauc plot is plotted by the software. The linear region of the curve is extrapolated and the X-axis intersection of the extrapolated line gives the band gap of the sample.



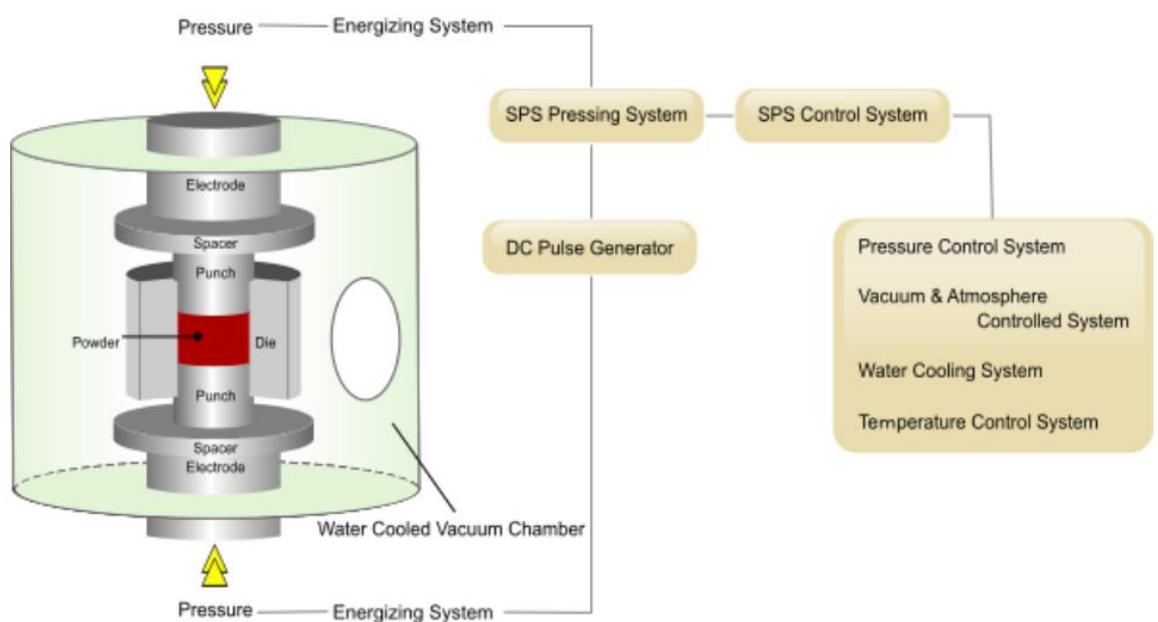
Spark Plasma Sintering of Thermoelectric Samples

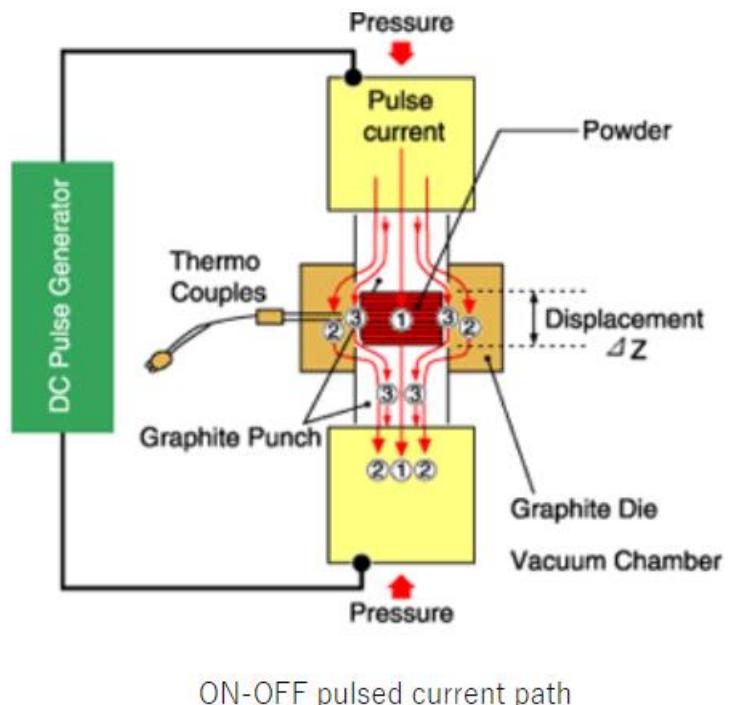
Thermoelectric materials are synthesized in powder form in labs. For analysis of its efficiency, figure of merit, etc. this powder has to be converted into pellets. This can be achieved by either cold pressing or hot pressing. Cold pressing, being a quick and easy process on one hand, is not capable of achieving more than 90% of ideal density of sample. Hot pressing, on the other hand, though efficient, is a lengthy process, and takes up to 8 hours for a single sample sintering.

Spark plasma sintering was thus formulated, which gives the benefits of hot pressing in a short duration. Hot pressing involves a procedure of heating up the entire furnace chamber, which is guilty of making the process time consuming. SPS heats up only the sample. It employs Joule heating for this purpose, by driving an electric current through the sample which heats it up while pressing. The SPS process is based on the electrical spark discharge phenomenon: a high energy, low voltage spark pulse current momentarily generates spark plasma at high localized temperatures. An achieved density of 99% of ideal density has been reported at our SPS lab in the past.



Source: FUJI ELECTRONIC INDUSTRIAL CO., LTD





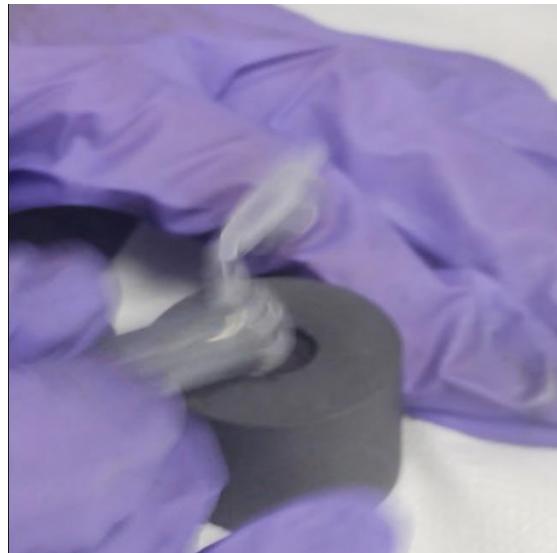
Source: FUJI ELECTRONIC INDUSTRIAL CO., LTD

Procedure and Working:

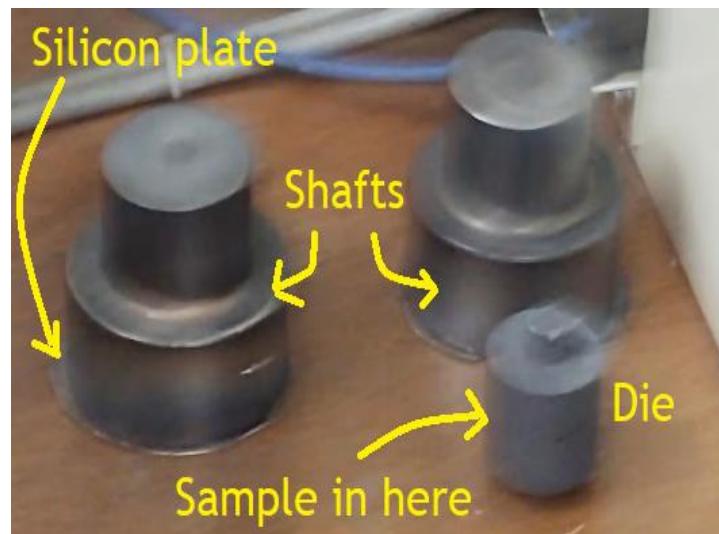
1. The sample has to be first analyzed using a Thermogravimetric Analyzer (TGA) to get the temperature at which the sample begins decomposing. The temperature at which sintering is done should always be below this temperature. For our sample, TGA revealed that it starts decomposing at 200 °C, hence we sintered it at 150 °C. The maximum temperature that could be achieved during sintering in this device is 1200 °C.
2. The plungers have to be first cleaned using IPA or acetone, and then sprayed with Boron Nitride. Boron Nitride is easily available in a can, and is used to prevent the powdered sample from sticking to the graphite die during sintering operation.



3. The chiller has to be switched on, which is responsible in shielding the electronics of the system from high temperatures inside the sintering chamber. It operates using water circulation mechanism.
4. Vacuum inside the chamber has to be eliminated first in order to open it. This is done by opening the air bleed valve. Once the pressure has increased to atmospheric pressure, the window to the chamber can be opened.
5. The sample powder is poured in the die container, on top of one plunger, up to the brim as shown. Then, it is pressed with another plunger such that the powder is trapped between two plungers inside the die.



6. The next step is to position the die setup inside the chamber. Two silicon plates are placed above and below two big shafts, between which the die setup is sandwiched. This entire setup is placed inside the chamber. The silicon plates are used to homogenize the current incoming through a point source, intended to pass through the die and then the sample while under compression. This current will be used to create Joule heating in the sample. The sintering chamber has two pressing plates. The one on top moves downward during sintering, applying pressure on the shafts and then eventually the plungers. After positioning the die and silicon plates setup, the pressing plate is brought down using the manual control panel such that the setup gets trapped in between the pressing plates in a snug fit. The maximum displacement possible of the top pressing plate using this control is about 2.77 mm.



7. The die has a hole in it. This is to fit the thermocouple inside it, for temperature readings of the setup.



8. The chamber has to be sealed, and a vacuum has to be created. A rotary pump, coupled with a Pirani Gauge, is used for this purpose. We need to wait till the pressure inside the chamber is below 5 Pa.



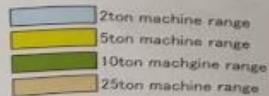
9. Next step is to program the temperature and pressure profiles using the control panels. For our process, we programmed the temperature as increasing from ambient to 150 °C in one minute, then staying at that temperature for 10 minutes and coming back to room temp. The pressure profile had been programmed to increase to 3.93 kN in one minute, stay at that pressure for 10 minutes and then come back to normal in one minute. We had used a 10 mm punch diameter die, and thus 3.93 kN translates to 50 MPa of pressure (inferred from conversion table below).

Pressure-Diameter Conversion Chart (Sample diameter base)

Pressure MPa	Punch Dia. • Sample Dia.(mm)							
	10	15	20	30	40	50	80	100
5	0.39	0.88	1.57	3.53	6.28	9.81	25.12	39.25
10	0.79	1.77	3.14	7.07	12.56	19.63	50.24	78.50
15	1.18	2.65	4.71	10.60	18.84	29.44	75.36	117.8
20	1.57	3.53	6.28	14.13	25.12	39.25	100.5	157.0
25	1.96	4.42	7.85	17.66	31.40	49.06	125.6	196.3
30	2.36	5.30	9.42	21.20	37.68	58.88	150.7	235.5
35	2.75	6.18	10.99	24.73	43.96	68.69	175.8	274.8
40	3.14	7.07	12.56	28.26	50.24	78.50	201.0	314.0
45	3.53	7.95	14.13	31.79	56.52	88.31	226.1	353.3
50	3.93	8.83	15.70	35.33	62.80	98.13	251.2	392.5
55	4.32	9.71	17.27	38.86	69.08	107.9	276.3	431.8
60	4.71	10.60	18.84	42.39	75.36	117.8	301.4	471.0
65	5.10	11.48	20.41	45.92	81.64	127.6	326.6	510.3
70	5.50	12.36	21.98	49.46	87.92	137.4	351.7	549.5
75	5.89	13.25	23.55	52.99	94.20	147.2	376.8	588.8
80	6.28	14.13	25.12	56.52	100.5	157.0	401.9	628.0
85	6.67	15.01	26.69	60.05	106.8	166.8	427.0	667.3
90	7.07	15.90	28.26	63.59	113.0	176.6	452.2	706.5
95	7.46	16.78	29.83	67.12	119.3	186.4	477.3	745.8
100	7.85	17.66	31.40	70.65	125.6	196.3	502.4	785.0

(Unit: kN)

- 1) Suitable pressure with standard type graphite tool should be between 30MPa and 50MPa.
- 2) Suitable pressure with high strength type graphite tool should be up to 90MPa.



$$F[N] = P[Pa] \times m^2$$

$$F[N] = P[MPa] \times mm^2$$

$$F[kN] = P[Mpa] \times r^2 \pi [cm^2] \times 1/10$$

T $f = kN/9.8$

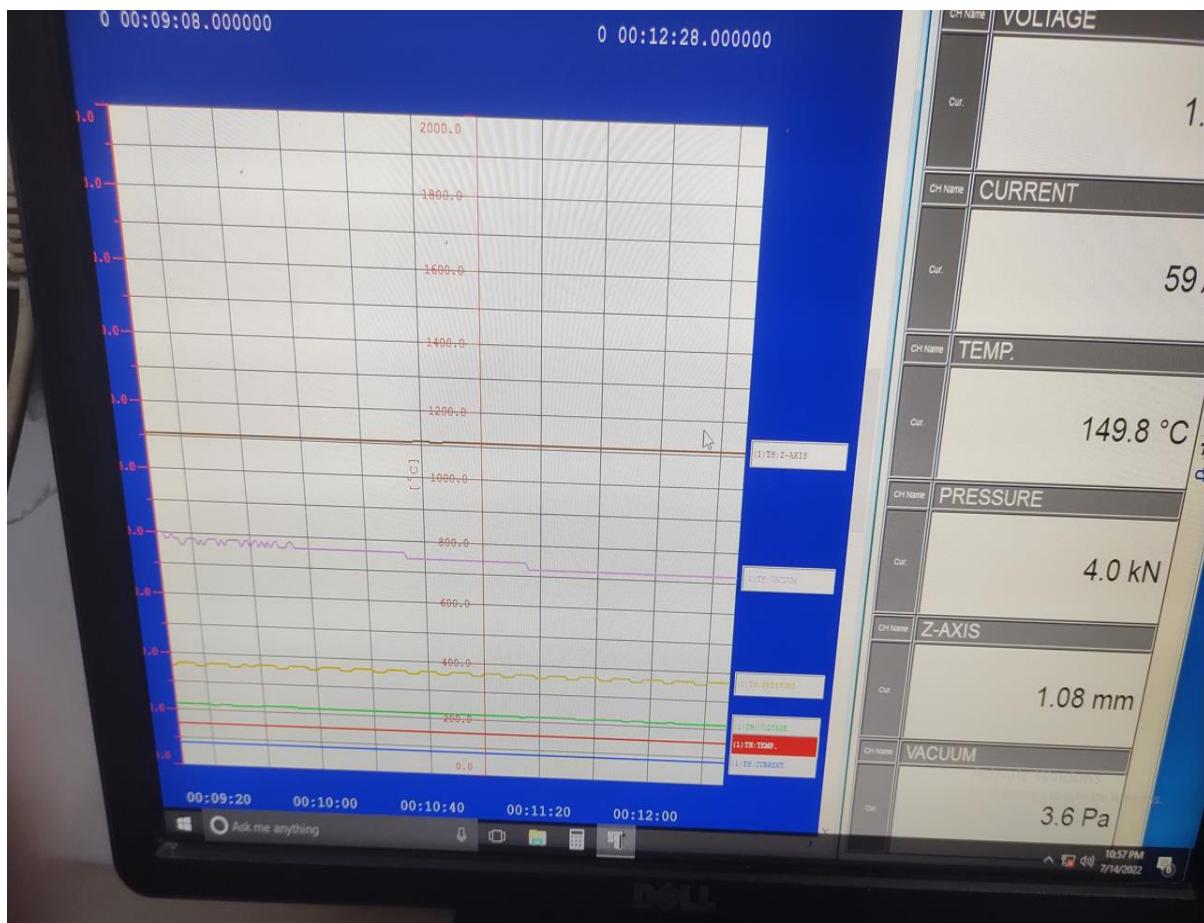
10. The temperature and pressure panels are split into two parts. The one on top displays the actual pressure and temperature respectively of the system. And the one on bottom is the programmed pressure and temperature, decided by the rate of increase in these parameters which we have set.



11. Also present on the control panel is a Z axis motion display which indicates whether the pressing plate is moving up or down; and a voltmeter and ammeter. When the programmed temperature, starting from 0, starts increasing to reach the target sintering temperature, and breaches the room temperature or the actual temperature, the voltage and current start getting produced to raise the actual temperature in order to match the programmed temperature.

12. DAS (Data Acquisition Software) is used to plot the various parameters associated with the SPS process: the vacuum level, pressure being applied, temperature, voltage, current, z

axis displacement; all varying with time. Any sudden fluctuations in these values could be due to some system failure, in which case we need to press the Emergency Stop button. In our case, there was a slight increase in gaseous pressure of the sintering chamber due to release of fumes on heating of the sample in initial stages. It was later stabilized.



13. After the process ends and the temperature returns to ambient, air has to be pumped in to decimate the vacuum so as to open the chamber and remove the die setup.

14. The insides of the chamber are not made of stainless steel, hence is prone to rusting if exposed to atmosphere. Hence at the end of the process, the chamber has to be shut after flushing out

the air and creating a vacuum. After this, the device power supply as to be shut down, including that of the chiller.

15. The next step is to extract the pellet from the die setup. For this we need to employ a 10-ton press. The press is used to push the plunger out of the die setup along with the pellet. The die setup is placed on a metal block with a hole in its centre such that the protruding plunger is on top of the hole. Then, the top plunger is pushed down by the press as shown till the two plungers with the pellet in between them fall out of the die.



16. The obtained pellet will have a layer of Boron Nitride on either side. This has to be removed by polishing the surfaces of the pellet.



Measuring thermal properties of thermoelectric samples

The thermoelectric conversion efficiency is limited by the dimensionless figure of merit zT ,

$$zT = \sigma S^2 T / (\kappa_{el} + \kappa_{lat})$$

where, σ , S , T , κ_{el} and κ_{lat} are electrical conductivity, Seebeck coefficient, absolute temperature, electrical thermal conductivity, and lattice thermal conductivity, respectively. Hence, to characterize and study figure of merit of a sample, we need to measure its thermal properties like thermal conductivity and diffusivity.

The lower the thermal conductivity is, the greater is the zT and ultimately the efficiency of the device.

The Netzsch MicroFlash LFA (Laser Flash Apparatus) 457 is a measurement device used in our lab to analyze and measure thermal properties of thermoelectric semiconductor samples.



Operating Principle:

The most widely used method for determining thermal conductivity (κ) is to measure the thermal diffusivity (a), specific heat (C_p) and density (ρ) as a function of temperature, and then to calculate the thermal conductivity from these data:

$$\kappa(T) = a(T) \cdot C_p(T) \cdot \rho(T)$$

It has been estimated that 80% of thermal diffusivity measurements conducted worldwide use Laser Flash Apparatus.

Advantages compared to direct measurement of thermal conductivity:

1. Simple test piece configuration
2. Small test piece size
3. Applicability over a wide range of diffusivity values
4. Great accuracy, reproducibility
5. Short testing duration: wide range of temperatures can be covered in a few hours

The front face of a cylindrically shaped test piece is homogeneously heated by an unfocussed laser pulse. On the rear face of the test piece the temperature increase is measured as a function of time with the help of an infrared InSb sensor. The mathematical analysis of this temperature/time function allows the determination of the thermal diffusivity a .

For adiabatic conditions, a is determined by the equation:

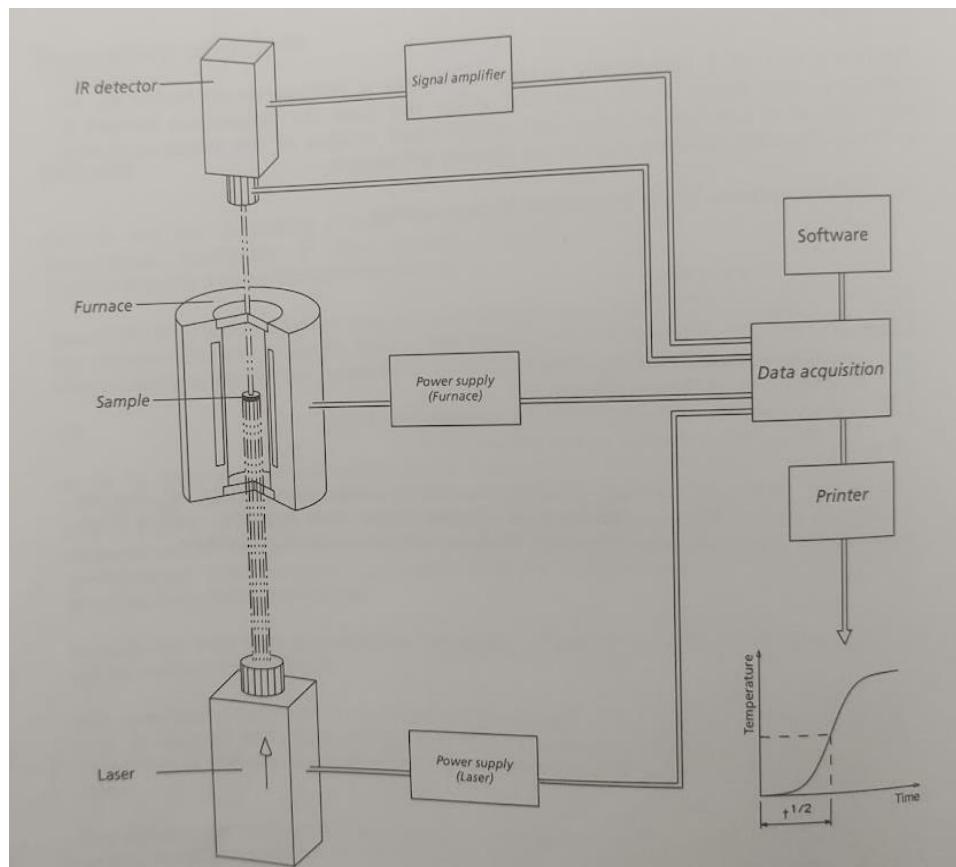
$$a = 0.1388 \cdot \frac{l^2}{t_{0.5}}$$

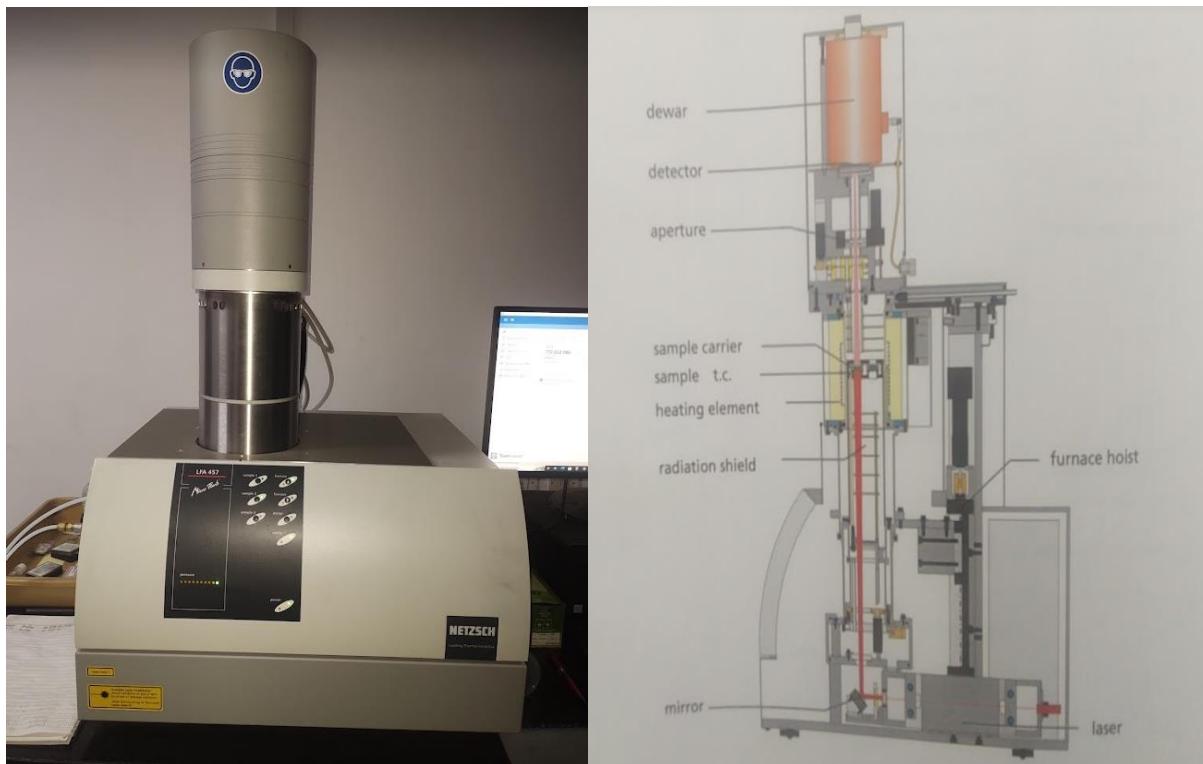
Where:

a → temperature diffusivity in cm^2/s

l → thickness of the test piece in cm

$t_{0.5}$ → time at 50% of the temperature increase, measured at the rear of test piece in s by the device.



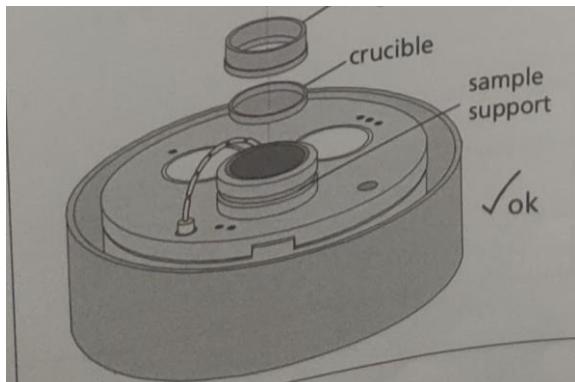


Working procedure:

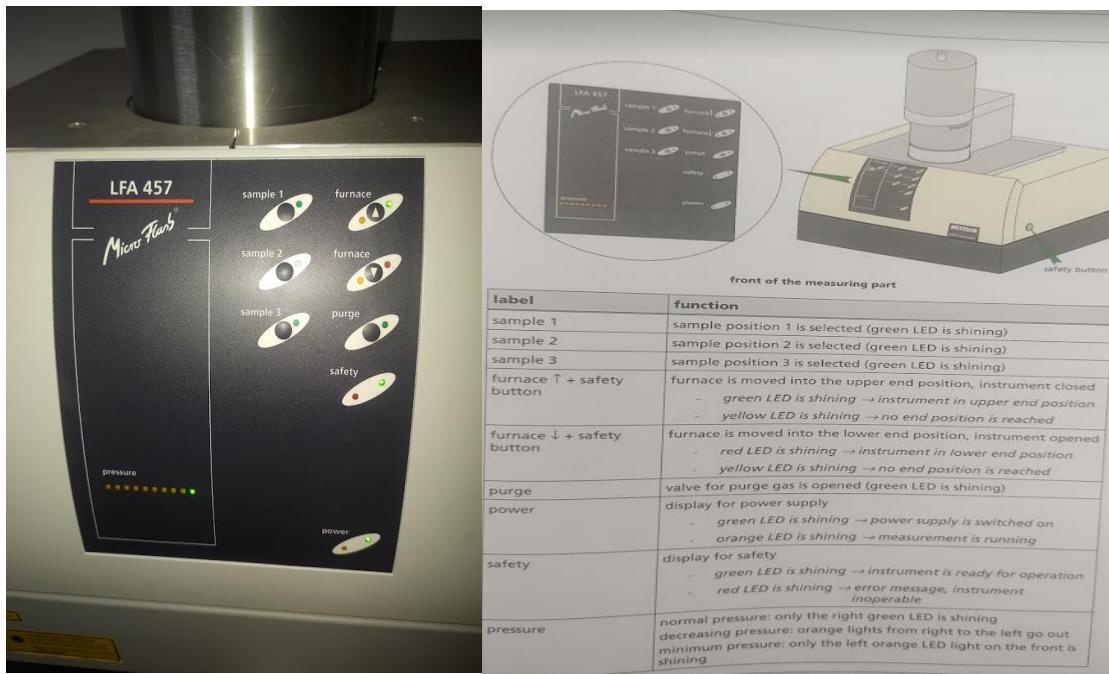
1. Sample preparation: The sample tray of the device can accommodate up to three samples at a time. One of the samples inserted is Pyro Ceram, a reference sample with known thermal properties. The other two could be the samples meant to undergo testing. All three are sprayed with a thin layer of graphite on both sides, and are allowed to dry. This is to enhance the absorption of laser energy and the emission of IR radiation to the detector. The graphite coating significantly increases the resulting signal to noise ratio. The coating thickness should be approximately $5 \mu\text{m}$.

Ideal Sample Thickness	
therm. diffusivity range	possible sample thickness / mm
Low diffusivity e.g. polymers (0.01 – 1 mm ² /s)	0.05 to 3
Medium diffusivity e.g. ceramics (1 – 50 mm ² /s)	0.5 to 5
High diffusivity e.g. copper (50 – 1200 mm ² /s)	1 to 5

2. The furnace is lowered by pressing the safety button and the furnace button together. Each sample is placed in a SiC holder. These holders are placed in slots on the furnace sample tray. Each slot is numbered (1,2 and 3) and this number is noted against each sample. Then, the furnace is hoisted up and the device is shut.



3. The next step is purging. The measurements are carried out in an atmosphere of nitrogen. For this, a three-time purge is carried out to ensure that a pure nitrogen environment is created in the sample chamber. This involves creating a vacuum in the chamber, and filling it with nitrogen gas by opening a manual valve, and repeating the process again. Each purge is followed by a 15–30-minute wait. At the end of the third purge, the auto purge valve is opened. The software of the device automatically and periodically fills the chamber with nitrogen to maintain a uniform environment.



4. Next step is to fill in the physical attributes of the sample into the software application of the device. This includes the thickness of the samples and their densities, details which are useful in calculating the thermal diffusivities and C_p of the samples. Also, we need to select the reference sample as Pyro Ceram, and set the purge specifications.
5. The next step is to setup the temperature profile. We need to input the temperature steps at which measurements are to be taken. The number of “shots” or measurements the device takes at each temperature is also set up here. We had set it as 5.
6. With the help of a funnel, liquid nitrogen is poured through an inlet into the infrared temperature sensor chamber so as to prevent damage due to high temperatures to the delicate electronics.
7. The device can take up to 12 hours to take the readings and draw conclusions.
8. After the readings are complete, the furnace is again hoisted down and the samples are extracted.

This procedure can provide us with κ . The next step is to use the Wiedemann–Franz Law to get κ_{el} .

$$\kappa_{el} = \sigma \cdot L \cdot T$$

Where:

κ_{el} → electronic thermal conductivity (electrical contribution from electron/hole transport to thermal conductivity)

σ → electrical conductivity

L → Lorenz number

T → temperature

Once κ_{el} is obtained, κ_{lat} can be easily obtained by:

$$\kappa_{lat} = \kappa - \kappa_{el}$$

It is κ_{lat} , or lattice contribution from phonon transport to thermal conductivity, in which we are primarily interested in case of thermoelectric materials. This is because as shown in the Wiedemann–Franz Law, κ_{el} is directly proportional to σ . For a good zT , we need to increase σ on one hand and decrease κ on the other. Since κ_{el} increases with σ , it all comes down to decreasing κ_{lat} .

Measuring Seebeck coefficient and electrical conductivity of thermoelectric samples

The next parameters to be determined to fully characterize the figure of merit zT of a thermoelectric sample are the Seebeck coefficient and the electrical conductivity of it. This is done with the help of Ulvac ZEM-3 at our lab.



Working Principle:

This measurement device utilizes a 4-probe technique to quantize these parameters. The thermoelectric sample block is heated on the lower side and a temperature gradient is generated, and the corresponding potential difference generated is measured using a voltmeter across probes A and B. The Seebeck coefficient is calculated by the ratio of the potential difference generated and the temperature gradient applied.

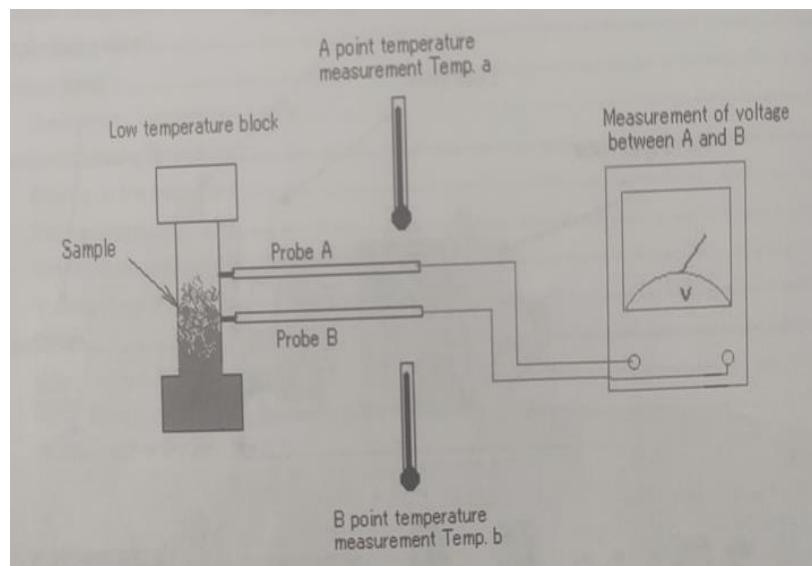
$$S = \frac{\Delta V_{th}}{\Delta T}$$

Where,

$S \rightarrow$ Seebeck coefficient

$\Delta V_{th} \rightarrow$ EMF generated due to thermoelectric effect

$\Delta T \rightarrow$ Temperature gradient applied, (temp at B – temp at A)



Using two other probes along the vertical direction, a constant current is passed through the sample. The generated potential difference across the sample is again measured, and the thermoelectric emf measured before is subtracted from it to get the actual voltage drop across the sample due to the current through it. The ratio of this voltage drop and the constant current gives us the resistance of the block by Ohm's Law.

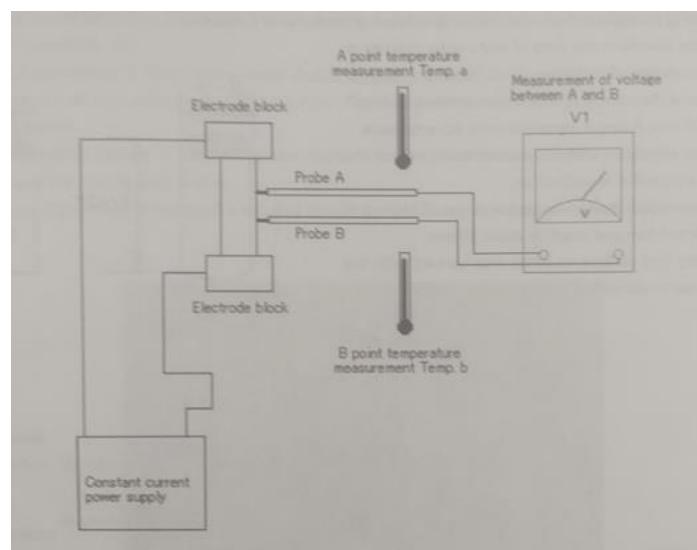
$$R = \frac{\Delta V - \Delta V_{th}}{I}$$

Where,

R → Resistance of the sample

ΔV → Potential difference measured across the sample when current is passed through it

I → Constant current passed through sample



After obtaining R, the electrical conductivity of the sample can be easily obtained by

$$\sigma = \frac{L}{A \cdot R}$$

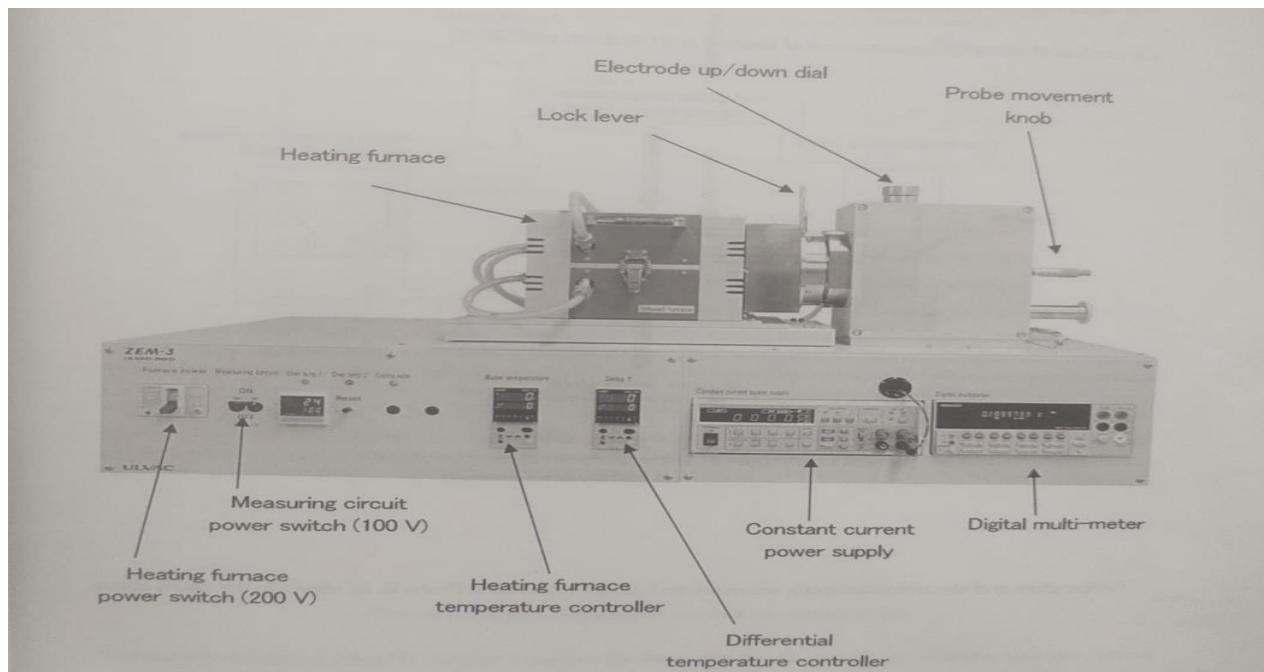
Where,

σ → electrical conductivity of sample

L → length of sample block

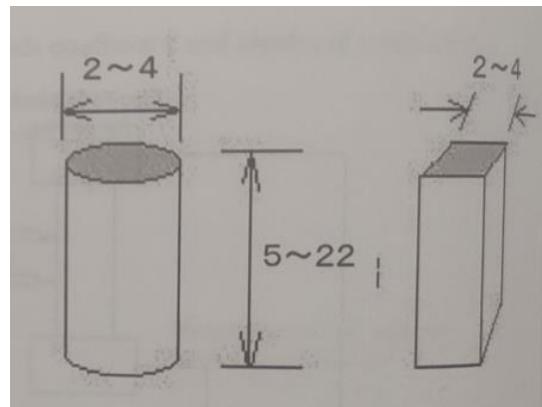
A → cross section of sample block

Operating Procedure:

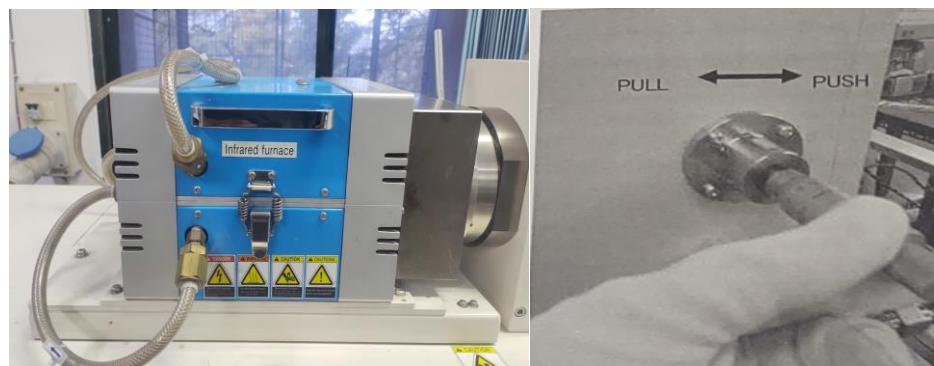


1. Sample preparation: The sample should be in form of a prism or circular cylinder of one side or diameter about 2-4 mm and length 5-22 mm. Both ends should be parallel to each other and

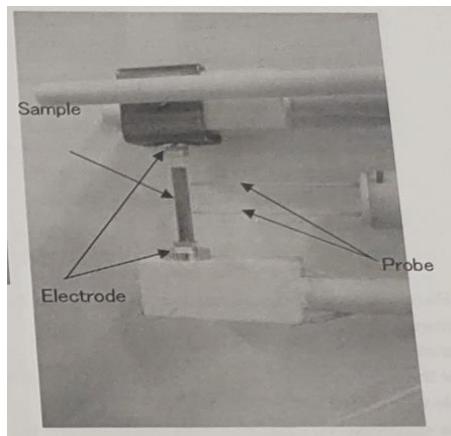
should be polished for good electrical contact with electrodes. Recommended sample is a square prism of side 2-4 mm and length 20 mm.



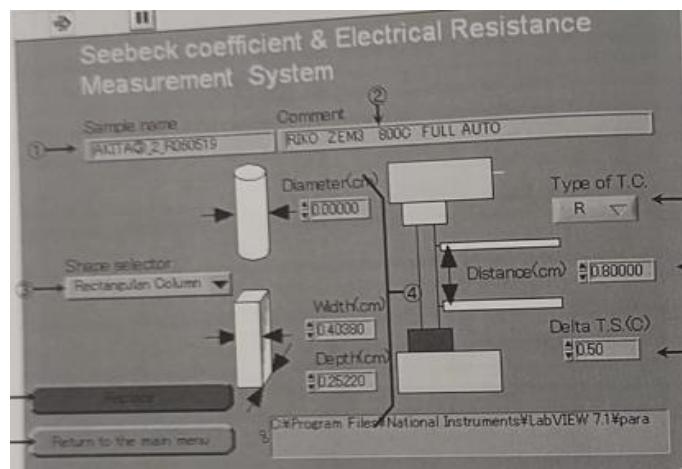
2. Turn ON the cooling water pump, measuring circuit, constant current power supply, digital multimeter, and data processing unit in order.
3. Bring chamber pressure to atmosphere pressure, loosen the lock lever, move heating furnace to left and open the sample assembly. Turn the probe moving knob counterclockwise to retract the probe.



4. Turn the electrode elevating dial clockwise to secure a space in which the sample can be caught between the top and bottom electrodes. Place the sample on the bottom electrode, and bring down the top electrode until the sample is held firmly in its place.

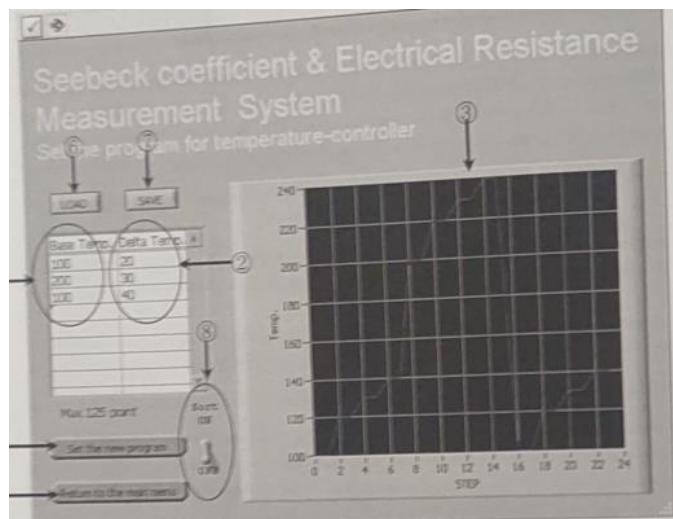


5. Push the probes back into contact with the sample. Move back the heating furnace and fix it with lock lever.
6. The measurements have to be carried out in low pressure helium environment; hence the chamber atmosphere has to be purged thrice as a standard operating procedure. This is done with the help of a rotary pump. First, the chamber atmosphere is evacuated for 20 minutes, and then helium is filled. This process is repeated thrice. At the end, the chamber should have an atmosphere of about 0.09 MPa Helium.
7. Now, on the software, input the sample parameters, specifically the sample name, shape, diameter (if shape is cylinder), width and depth (if rectangular column) and distance between probes.

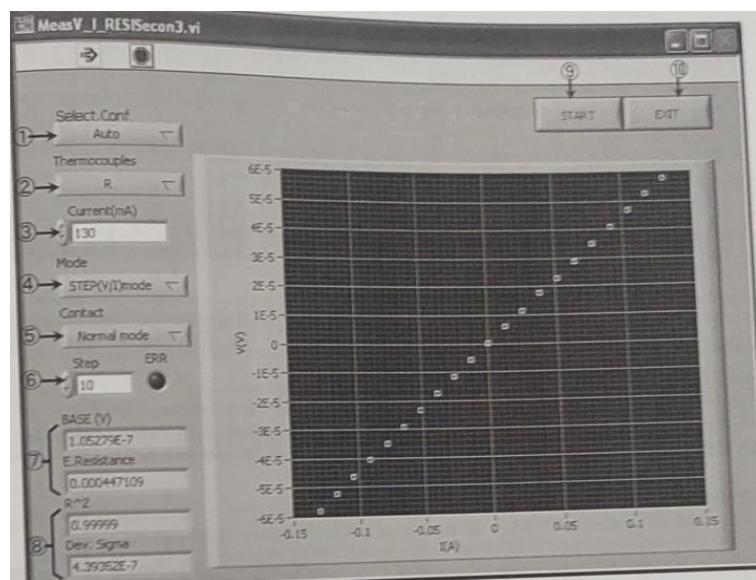


8. Next step is to input temperature program. A list of temperatures and delta temp is given at which measurements are

to be carried out. After this, measurement reading could be started.

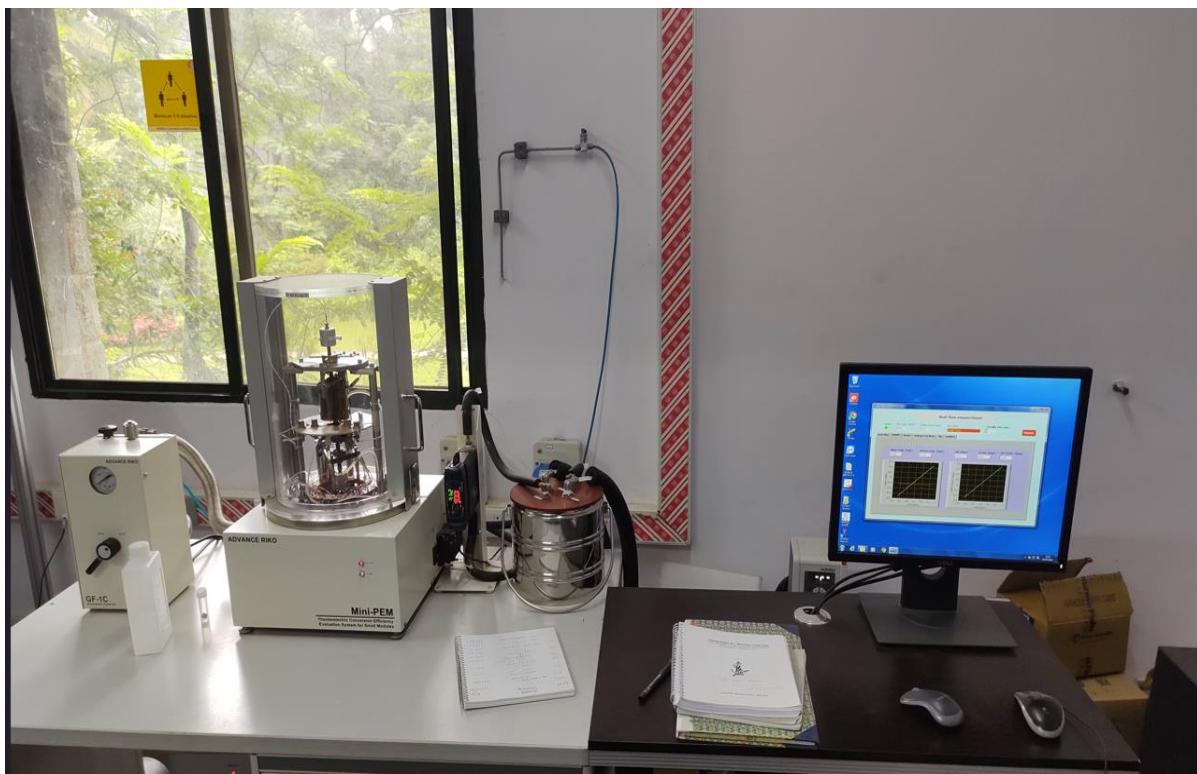


9. A V-I graph will be plotted by the system to calculate the resistance of the sample.



Measuring Conversion Efficiency of Thermoelectric Modules

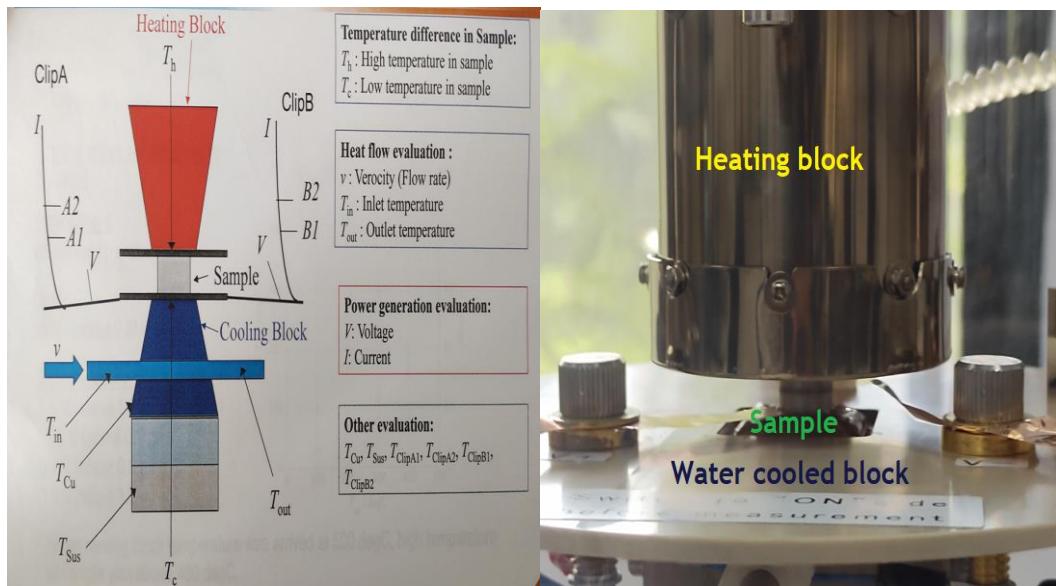
The final step of analyzing thermoelectric samples is measuring the efficiency of modules made of those samples. At our lab we use Mini PEM (Advance Riko) device which obtains the efficiency of single leg thermoelectric devices.



Working Principle:

The thermoelectric module would be placed in between two blocks. The upper block consists of a heating element, and the lower block is

water cooled. A temperature gradient is set up across the module using these two. Two copper strips are used as probes to measure the current and potential difference generated as a result of the temperature difference. The heat which is passed on to the lower water-cooled block through the thermoelectric device is calculated using a water calorimeter. Subsequently, efficiency is calculated.



$$\eta = \frac{P}{Q_h} = \frac{P}{P + Q_c}$$

Where,

$\eta \rightarrow$ heat to electricity energy conversion efficiency

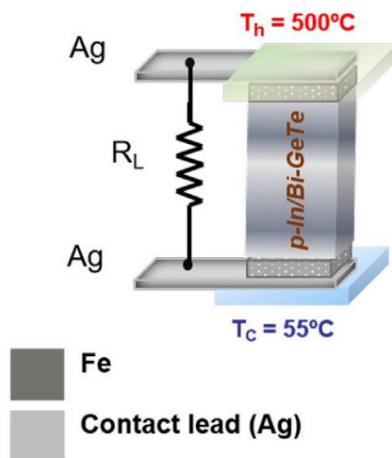
$P \rightarrow$ output electric power generated by module, given by product of voltage and current produced

$Q_h \rightarrow$ input heat absorbed

$Q_c \rightarrow$ heat released into water, measured by water calorimeter

Operating Procedure:

1. First, the single leg thermoelectric module is prepared, using the previously discussed Spark Plasma Sintering method. A layer of copper powder, iron powder, sample, iron powder and again copper powder in order is deposited in the die setup and SPS process is carried out, so as to deposit layers of Fe and Cu above and below the thermoelectric sample cylinder. These layers act as diffusion barrier layer, which provide negligible extra resistance at contact and prevent chemical diffusion. Diffusion barriers could also be made of layers of Fe and Ag, or SnTe and Ag.



2. The next step is to prepare the copper strip probes. Two copper strips of appropriate length are taken, and alumina paste is applied to one of their ends. Thin strips of graphite of appropriate size are then stuck there. These ends would be in contact with the diffusion barrier of our modules. The copper probes would be so placed that graphite strip would be in contact with the heating and cooling blocks of Mini PEM, and the copper would be in contact with the module, with alumina in between. The purpose of this setup is to prevent any reaction between copper and the blocks at high temperatures. Also, alumina is good conductor of heat but a bad one for electricity,

ensuring that the module is electrically separated from the device, but not thermally. Electrical separation ensures the device doesn't lose its microvolt sensitivity.



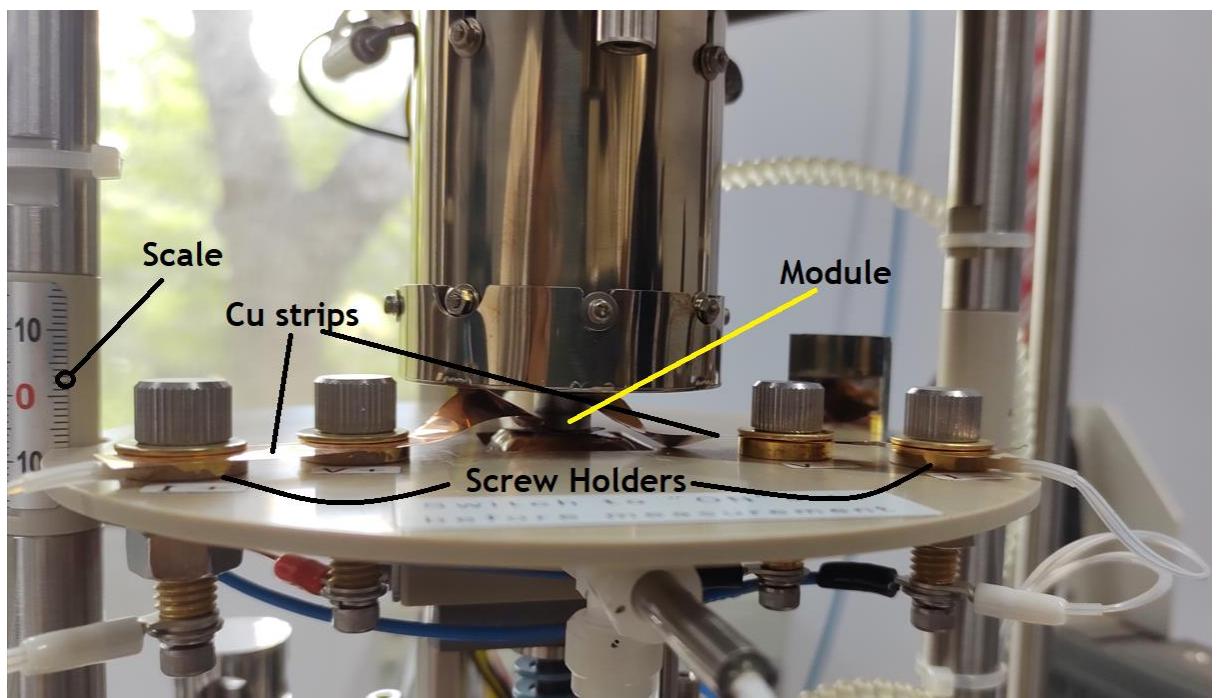
Cutting graphite and copper strips



Applying alumina paste on copper strip for sticking graphite strip

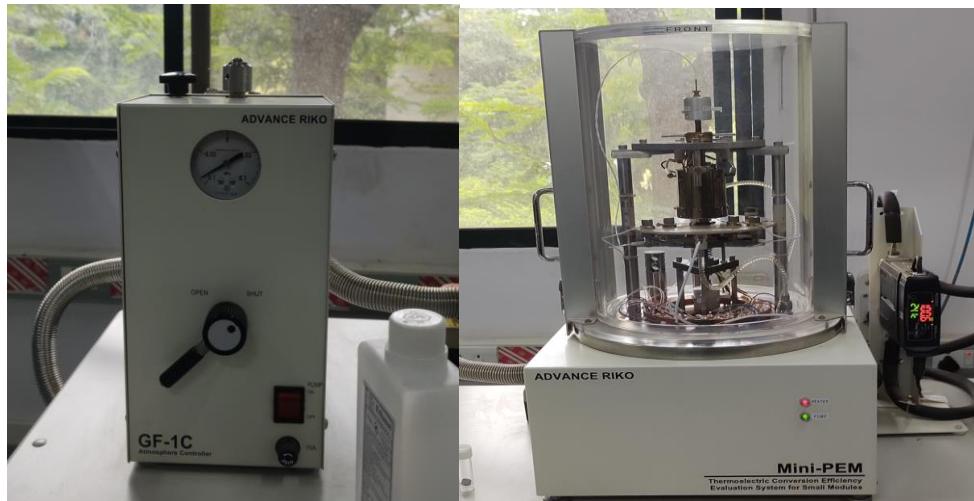


- The above-mentioned arrangement of module along with probes is placed in between the two blocks as shown. The heating block is then lowered till its plate reaches 8 mm on the adjacent vertical scale. This implies we are pressing the arrangement into a snug fit with a load of 80 N, since Load (N) = 10*thrusting quantity (in mm). The copper probes are inserted into the screw holders. The bottom strip was connected to V^+, I^+ screw holders and the top one to V^-, I^- , since it was a p-type module.



- The thermocouple switches associated with the top and bottom blocks are pushed into on state. This allows for temperature measurements. Also, the water pump and water calorimeter are switched on.
- On the software Mini PEM Meas 211.exe, in “device check” section of “maintenance”, the Seebeck and resistance is measured in a dry run. If both turn out to be positive, we proceed with the actual measurement. Else, we reconfigure the setup of copper strips and module.

- After completion of this setup, the glass shield is again placed enclosing the entire setup. The chamber atmosphere is purged thrice with the help of a vacuum pump, followed by filling it up with helium. The final measurement is taken in vacuum.



- Next, we go into “Settings” of Meas software, and in Temperature Settings, we list out the temperatures of the top block at which we intend to perform the measurements. On the next page, we set the maximum temperature. In this way, we set the “recipe” for the measurements.
- After the recipe is set, we proceed for final measurements. The MiniPEM ana 203.exe is the software used for analysis of the acquired data.



9. An EMO button is provided for emergency stop of the device.



Device Specifications of Mini PEM:

- Weight: 150 kg
- Temperature range of heating block: 50°C – 550°C. Sheath heater is used for the block.
- Temperature control sensor: K type thermocouple
- Temperature measurement sensor: E type thermocouple
- Calorimeter: platinum resistance thermometer (0-100°C)
- Flowmeter: 0-200 ml/min
- Vacuum control: GF-1C
- Water circulation system: Julabo Corio CD

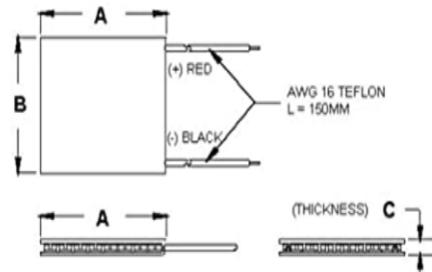


Water calorimeter and pump

DISADVANTAGE: Mini-PEM system does not provide a proper shield to suppress the radiative heat loss, hence the heat flow through the device is overestimated. In the ideal scenario, only the heat which is passed on to the water conducted through the module should be accounted, but in case of Mini PEM, the heat which is radiated by the heating block to the cooling block is also counted in, thus the estimation of Q_c is not perfectly accurate, leading to calculation of an efficiency lower than the actual.

Insides of a commercial thermoelectric module

At the lab, a non-functional commercial thermoelectric Peltier cooler module was ripped open to observe its construction.



Ceramic Material: Alumina (Al_2O_3)
Solder Construction: 138°C, Bismuth Tin (BiSn)

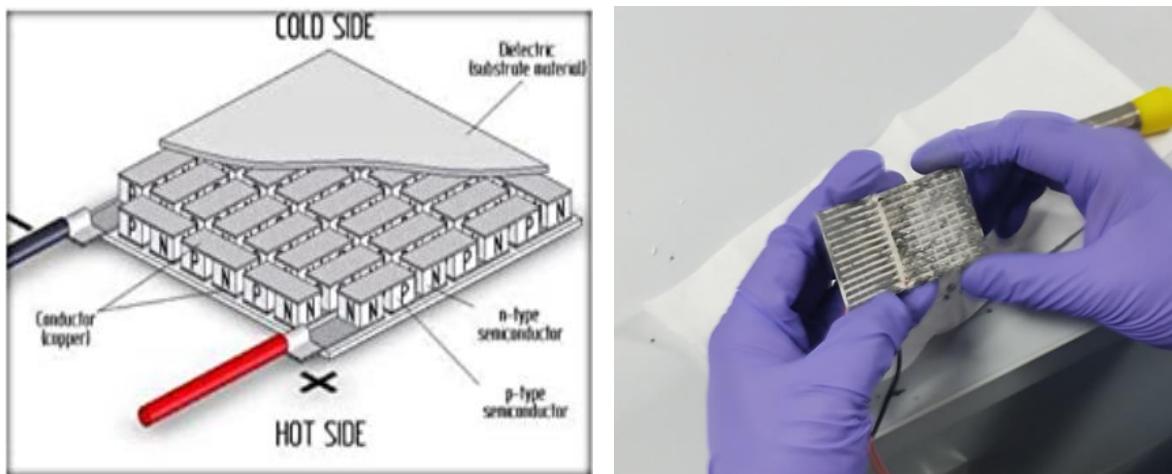
Size table:

A	B	C			
40	40	3.9			

Using a SYJ-160 low speed Diamond Saw and later a knife, the ceramic (alumina) padding of the device was split open.



The diamond saw was operated at a speed of 345 rpm. It would be difficult to handle the cutting if the speed was to be increased, hence a knife was later used to complete the process.



Thermoelectric legs on the copper plates

As observed above, a commercial module is made by depositing n and p type thermoelectric material on to copper contacts embedded on alumina sheets. These sheets are then stuck together so as to envelope the thermoelectric legs.

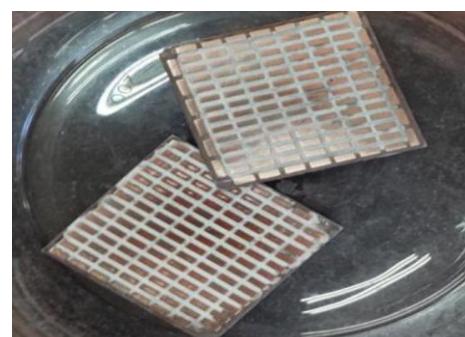
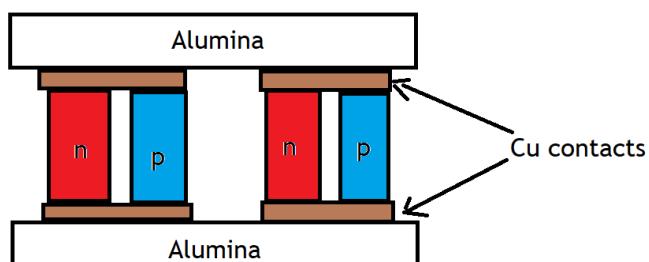
Making of a 4-leg thermoelectric device

A process of making a 4-leg thermoelectric generator device was initiated at our lab during my fellowship tenure. The aim is to replicate a commercial module, but instead of regular compounds, lab synthesized thermoelectric semiconductor material will be utilised.

The jacket of the module will be made of alumina sheets. Copper strips will be suitably placed on these and will be held in place with the help of alumina paste. This setup ensures high thermal conductivity and at the same time will ensure electrical isolation of the thermoelectric legs.

Silver paint will be applied on the copper strips so as to use it as electrical contacts. This can work till 200 °C.

This was an ongoing process at the time of writing this report.



Sectional front view of proposed module

Alumina jacket (with copper contacts) prototype

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