# Thermoelectric materials and generators: modeling and fabrication

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**ABSTRACT**

With current focus on clean energy options toward the goal of reducing pollution and climate change, thermoelectric materials are seeing a renewed interest. While the operating principles are easy to understand and apply experimentally at the undergraduate level, increasing the efficiency of thermoelectric materials remains a challenge at all levels of research. The work presented here is a complete module of thermoelectric undergraduate study, from modeling in Comsol Multiphysics to fabrication and thermal characterization. The Comsol model of a thermoelectric 3 component generator successfully mimics the experimental prototype and can be used for further optimization of the thermoelectric system. The preliminary fabrication data show that mechanical grinding leads to a stable compound of Bismuth and Tellurium with the same melting point as a compound fabricated at high temperatures.

## I. INTRODUCTION

From medical devices to photonics and mechanics, Comsol Multiphysics software is used extensively in education, and R&D to model, test and refine prototypes. Its ability to accurately model multiple physical systems and record various measurements—such as voltage, surface temperature, pressure, etc—was the reason for its selection for this project, where Comsol Multiphysics was applied to the reemerging study of thermoelectric generators. Due to the increasing global demand for energy, climate change and a need for sustainable energy solution, thermoelectric generators are a very appealing, clean option. Despite their relatively low efficiency of about 7%[1-5], recent developments in nanotechnology prove that their response can be improved. Therefore, a resurgence of research projects has been dedicated to increasing their thermopower while reducing the thermal conductivity and increasing the Seebeck coefficient and electric conductivity of the electrical contacts. The thermoelectric (TE) effect was discovered by German scientist Thomas Johann Seebeck in 1821. Over years of study, Seebeck proved that two different materials with junctions held at different temperatures deflect a compass needle. The temperature difference produces a current. Real devices work under large temperature difference so for a real thermoelectric material working in open-circuit conditions and temperatures $T_{hot}$ and $T_{cold}$, an "effective" Seebeck coefficient is defined as[2]:

$$S_{eff} = -\frac{\Delta V}{\Delta T} = \frac{\int_{Tcold}^{Thot} S(T)dT}{\Delta T} \qquad (1)$$

The reverse is also true. A voltage difference applied to a junction of two different materials led to the temperature difference (the Peltier effect) currently used in Peltier coolers. In 1854, Lord Kelvin (formerly William Thomson) explained the phenomenon and the relationship between the coefficients using the principles of thermodynamics. He also predicted the Thomson effect—namely, the heat absorbed or released along the length of a material that has the ends at different temperatures is proportional to the electric current and the temperature gradient through the Thomson coefficient of proportionality, τ.

The Seebeck coefficient at a junction of two materials has been found to be large for junctions between p-type and n-type semiconductors due to a several physical parameters discussed below. The efficiency of a TE material is defined by the figure of merit quantity, zT, defined as[1]:

$$zT = \frac{\sigma T S^2}{k} \qquad (2)$$

where σ is the electrical conductivity, S is the Seebeck coefficient, k is the thermal conductivity and T is the absolute temperature. Let us briefly analyze the most important factors affecting the values of S, σ and k.

1. Carrier concentration

The relationship between carrier concentration and the Seebeck coefficient for metals or semiconductors can be derived from simple models of electron transport[3]:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T (\frac{\pi}{3n})^{2/3} \qquad (3)$$

where $k_B$ is the Boltzmann constant, m* is the density-of-states effective mass of the carrier, n is the carrier concentration, T is the absolute temperature, e is the charge of the electron and h is Planck's constant. The carrier concentration n is related to the electrical conductivity σ through the relation σ = neμ, where μ is the carrier mobility and e is the charge of the electron. Therefore, in order to achieve a high S value, the material should have one type of carrier, high electrical conductivity and an optimal value of the carrier concentration that maximizes S and σ at the same time. Eq.3 suggests that the effective mass m* should be high, however, since m* is related to the inertial effective mass, a high value of m* would reduce mobility so a balance between the two effects must be found.

2. Thermal conductivity

A good thermoelectric material has low thermal conductivity. Thermal conductivity is the sum of two components, one from the electrons and holes transporting heat, $k_e$ and another from the phonons traveling through the lattice, $k_l$. $k_e$ is defined as

$$k_e = L\sigma T \qquad (4)$$

where L is the Lorentz factor, $\sigma$ is the electrical conductivity and T is the absolute temperature.[4] $k_l$ is usually measured by subtracting $k_e$ from the measured value of k. L depends on the carrier concentration so a good estimate of L is essential for an accurate estimate of $k_l$. Lattice thermal conductivity is very low in glasses but glasses have lower carrier mobility and lower effective masses. Therefore, for thermoelectric applications, a good material has "glass-like" behavior for phonon scattering and "crystal-like" behavior for electron transport.[3]

Semiconductors with crystalline structure have been the most efficient TE materials so far and therefore, are the most studied. A simple n-p pair of semiconductors of Bismuth Telluride connected in series is shown in Fig. 1 left. The blocks are connected via an electrical contact plate—such as copper—at the top and maintained at the hot temperature $T_{hot}$ via an electrically insulating plate, such as graphite. The bottoms of the blocks are placed on conducting plates and the overall system is placed on a cold temperature source via a second graphite plate. When heat flows into the system from the hot source (Fig. 1 left), the electrons and holes move toward the cold face and a current I flows through the two blocks connected in a series, as indicated by the blue set of arrows.

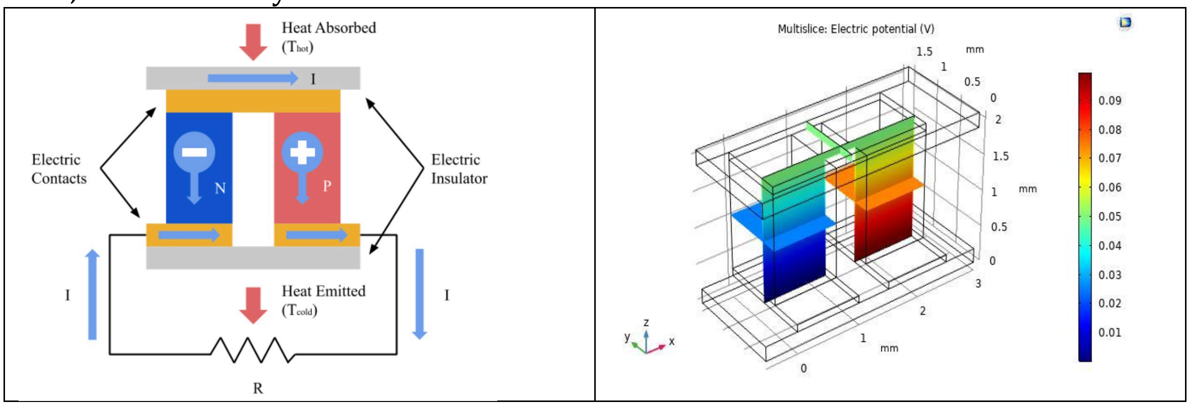


FIG. 1 Left: A model of electric and thermal conduction in a pair of $Bi_2Te_3$. semiconductor blocks electrically connected in series and in parallel thermally. Right: A Comsol model for the Seebeck effect for an n-p pair of $Bi_2Te_3$.

More semiconductor block pairs can be added to increase the voltage V. Since the tops and bottoms of the blocks are maintained at the constant temperatures, $T_{hot}$ and $T_{cold}$, the blocks conduct heat in only one direction, similar to a parallel connection of resistors. Fig. 1 right shows a Comsol model for a pair of n-p blocks connected electrically in series and thermally in parallel, similar to the model shown in Fig. 1 left.

Numerous fabrication efforts have been dedicated to developing high zT materials over the past few decades.[5] For a while, the most effective common material was the p- and n-type Bismuth Telluride, $Bi_2Te_3$, with a zT value of about 1. Various doping procedures and fabrication methods have been employed to increase the zT factor[6,7] Values from 1 to 1.5—were reported and reproduced by several groups using fabrication methods, such as spin-melting followed by Spark Plasma Sintering,[7] mechanical alloying,[8] etc. High zT values were reported for skutterudites[2, 3, 9] although the fabrication is much more elaborate and expensive. A superior zT material that works at high temperature, Silicon Germanium alloy, was used on recent US space missions.[3] Fitted with special electrical contacts and under vacuum conditions, this thermoelectric generator reached 8% efficiency between 300 and 1000$^0$C. Finally, an exciting development in photonic topology showed that new thermal metamaterials can control the emission of a hot object by enhancing a certain portion of the spectrum and reducing the rest.[10] With such material interfaces, the spectrum emitted by a hot surface can be tailored to match the energy gap of the thermoelectric material. This promotes more charge carriers to the conduction band and reduces heat waste. The efficiency of a TEG can also be significantly improved by adding a cooling system that carries away heat from the cold face. In addition to a fluid cooler, a heat sink offers additional cooling. A combination of both is often employed when commercial TEGs are developed. Various versions of these systems have been commercially developed for car engines, outdoor activities and space missions.[3] Given the need for alternative sources of energy, students need to be educated on the physics and fabrication challenges of thermoelectrics[11]. Recent developments in computer modeling and 3D printing allows for low cost testing of these prototypes. The low financial costs—paired with the high experimental freedom of both the physical and virtual systems—creates a perfect learning environment for students to familiarize themselves with fundamental thermal laws, as well as perform cutting-edge research in a re-emerging field.

**The goals of the work presented here are:**

a. To obtain experimental data from a commercial thermoelectric generator and measure the voltage/current generated for a variety of temperature gradient values and cooling conditions. The data collected was used to set up boundary conditions in the Comsol model.

b. To develop Comsol Multiphysics computer models to simulate the commercial model and test the agreement between the model and the experimental data

c. To investigate whether grinding powders of Bismuth and Tellurium powders with a planetary ball mill down to 100nm size particles leads to the formation of a stable alloy with similar thermal properties as an alloy fabricated by high temperature melting followed by grinding and cold pressing.

The work was done by two undergraduate students and two faculty members over the course of one academic year. All modules developed have been integrated in the undergraduate physics curriculum and undergraduate research at Ramapo College of New Jersey.

## II. THE EXPERIMENT

**a.** A cooled TEG system is composed of three main components, as shown in Fig. 2 below: a) the TEG array of semiconductor blocks with electric contacts and electrical insulator plates, b) a cooling system, such as a water cooler, and c) a heat sink such as a large plate of aluminum placed on the cold face. The TEG side was placed on a hot plate at various temperatures. The voltage, current and temperature set of the data was collected via LoggerPro software using thermocouples, voltage and current sensors from Vernier. Inc. The water cooler was fed from the sink with an inlet water temperature T = 288K. The voltage generated was recorded as a function of the temperature difference between the faces of the TEG and plotted in Fig. 5.

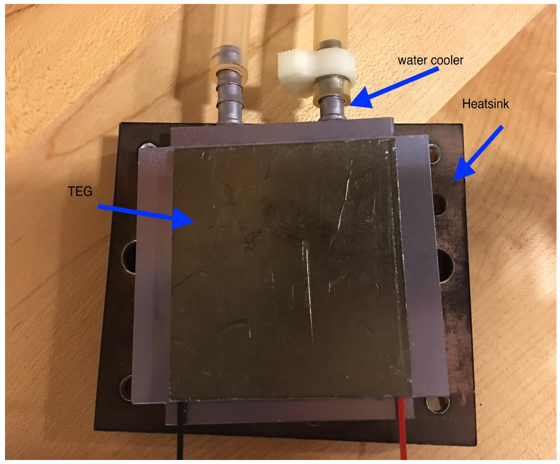


Fig. 2 The three main components of a cooled TEG system: the TEG, a water cooler and a heat sink.

**b. Comsol multiphysics software models**

The software used for modeling is the Comsol Heat Transfer interface. We developed a Comsol model for the themoelectric chip, the heat sink and the water cooler and then put them together as a three-component system. The details of each step are presented below.

**Component one: Seebeck, Peltier and Thomson effects in the thermoelectric material**

The unit of the TEG is pair of n- and p-type $Bi_2Te_3$ semiconductor legs connected in series through a thin layer of electrical contacts as shown in Fig. 1a and 1b.[11] The block pair is sandwiched between two plates of an electric insulator such as graphite. An array of 16x16 of these pairs was developed in order to model a commercial TEG. For the Seebeck effect, a temperature gradient of $100^0$C above room temperature has been imposed between the plates and the electrical contact corresponding to the cold plate is grounded. Comsol Multiphysics solves the double coupling between current and temperature due to Joule heating. The model uses only heat transfer by conduction. The equations solved are the thermoelectric effect and electromagnetic heating for the thermoelectric material, the electromagnetic heating for electrical contacts and the heat transfer for the material of the faces[11-12]:

$$J = -\sigma(T)(\nabla V + S\nabla T) \qquad (5)$$

$$\rho C_P \frac{\partial T}{\partial t} + \nabla \cdot q = Q \qquad (6)$$

$$q = -k\nabla T + PJ \qquad (7)$$

where J is the current density, V is the electric potential, T is the absolute temperature, q is the heat flux, Q is the heat source, k is the temperature dependent thermal conductivity, σ is the temperature dependent electrical conductivity, $C_P$ is the specific heat at constant pressure and ρ is the physical density.

**Component two: Cooled heat sink. Heat conduction/convection and nonisothermal air flow**

Further analysis of heat transfer by conduction and convection is performed on a model of a heat sink used in our experimental set-up. The aluminum heat sink is shown in Fig. 3 left. The model includes a heat source as the hot plate of silica glass generating a constant power $P_0$ = 1Watt and is enclosed in a large rectangular box filled with air moving with a velocity $v_0$ = 0.05m/s along the negative y-axis while the heat influx points along the negative x-axis. The program solves the nonisothermal flow of air by coupling heat transfer (conduction and convection) and laminar (or turbulent) flow and solves for heat transfer by conduction in the heatsink and silica glass plate using the Navier-Stokes equations[11-12]. The Navier-Stokes and continuity equations for a weakly compressible fluid are given below:

$$\rho(\boldsymbol{u}\cdot\nabla)\boldsymbol{u} = \nabla\cdot[-p\boldsymbol{I} + \mu(\nabla\boldsymbol{u} + \boldsymbol{u}^T) - \frac{2}{3}\mu(\nabla\cdot\boldsymbol{u})\boldsymbol{I} + \boldsymbol{F} \qquad (8)$$

$$\nabla\cdot\boldsymbol{u} = 0 \qquad (9)$$

where **u** is the fluid velocity, ρ is the fluid density, μ is the fluid dynamic viscosity, **F** represents the external forces, p is the pressure and **I** is the identity matrix. The temperature distribution is shown in Fig. 3 left.

**Component three: Water cooler model. Cooling by Heat Conduction and Laminar Flow.**

The model developed below is a Comsol model of a commercial rectangular box alumina watercooler with one inlet and one outlet (TEGpro). The Comsol program solves the Navier-Stokers and continuity equations for the fluid (water) and the heat transfer equations for conduction and convection. The program can calculate the temperature at any boundary as a function of the water inlet T and velocity. The heat transfer in the heat sink is shown in Fig. 3 left while the slice velocity data for the water cooler is shown in Fig. 3 right.

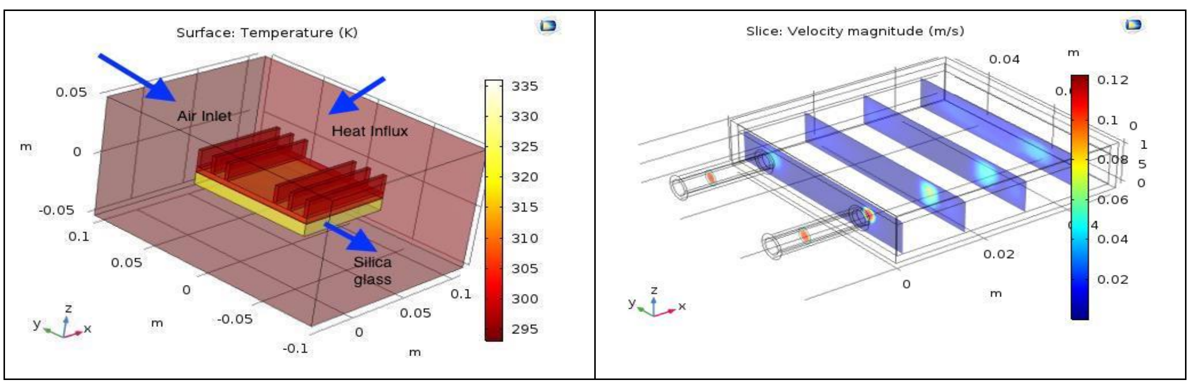


FIG. 3 Left) Temperature distribution for a Comsol model for an aluminum heat sink with silica glass heat source of power P = 0.1 watt. Right) Slice velocity for a water cooler placed on top of a hot surface.

Using the three independent component models discussed above, the students assembled the system in Comsol as shown in Fig. 4 and calculated the voltage induced by the temperature gradients, inlet water velocity and temperatures at all surfaces measured experimentally on the TEG prototype shown in Fig. 2.

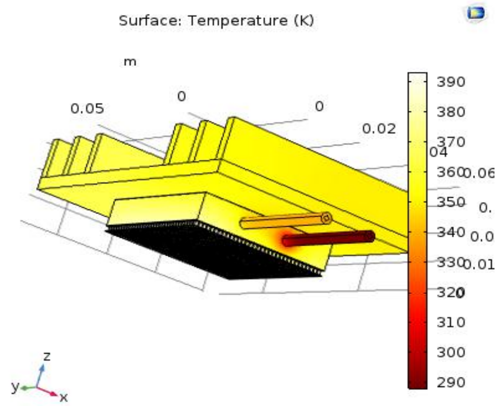


FIG. 4 Three-component Comsol model of a thermoelectric generator cooled by water and a heatsink.

**c. Fabrication of $Bi_2Te_3$ alloys by grinding with a planetary ball mill. Thermal characterization using a differential scanning calorimeter**

Research[13] shows that during the grinding, pressing, and sintering processes in the preparation of cold-pressed thermoelectric materials of Bi and Te alloys changes in the thermoelectric properties of these materials take place primarily due to presence of "several kinds of point defects (anion and cation vacancies and antisite defects) and their interaction". In the fabrication method presented[13], grinding, pressing, and sintering take place after the alloy of Bi, Te and various small doping with Sb is done at high temperatures. We decided to investigate whether extended time grinding at high speed with a planetary ball mill creates sufficiently high temperatures and low pressures to initiate the formation of a stable alloy between Bi and Te. High purity Bi and Te powders were mixed in stoechiometric ratio of 2 to 3 and grinded for 9 hours to a particle size of approximately 100nm. The powder obtained was encapsulated in an alumina pan and analyzed using a Perkin-Elmer DSC 7 differential scanning calorimeter (DSC). A heating ($40^0$C/min) and a cooling cycle ($5^0$C/min) were conducted on our samples as well as a commercial sample fabricated by hot alloying. The heating and cooling cycles were compared for melting and fusing points as well as other effects as discussed in the next section.

## III. DATA PRESENTATION AND INTERPRETATION OF RESULTS

**Experiment versus model:** The computer model was tested against the experimental data and the comparison results plotted in Fig. 5 below show excellent agreement between the model data and the experimental data. Fig. 5 shows that the model is an excellent computer model for the physical set-up. It can be used to test a variety of physical parameters such as the dependence of the voltage generated on the thermoelectric leg physical parameters, geometry of the set-up, semiconductor materials, cooling water flow rate, etc. It can also be used to calculate the efficiency of the TEG under a variety of testing conditions.

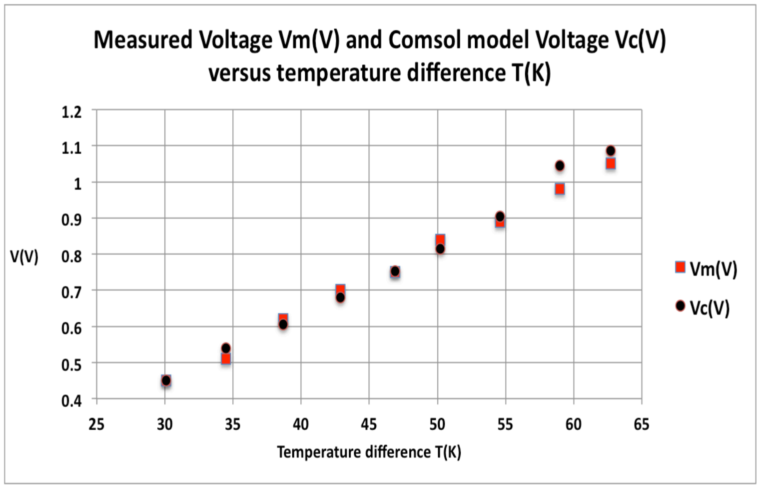


Fig. 5 Voltage measured, $V_m$ and Voltage calculated on Comsol model, $V_c$ versus temperature difference

**Fabrication results**: The commercial alloy fabricated at high temperatures is labeled “hot alloy” and is represented by the red line in Fig. 6. The alloy fabricated by extended grinding is labeled “cold alloy” and is represented by the blue line in Fig. 6. The cold and hot alloys show very close melting point temperatures. Since the cold alloy does not show individual melting peaks for Bi and Te during heating it is clear that the process of mechanical grinding with a High Speed Planetary Ball Mill (AcrossInternational, Inc) leads to a stable alloy. A small peak of re-crystallization is seen in the heating spectrum of the cold alloy as well as small individual melting peaks for Bi and Te. These temperature values are close to their elemental melting temperatures of 265$^0$C and 435$^0$C indicating that not all Bi and Te is bonded. Additionally, the cold alloy shows a small re-crystallization peak at 370$^0$C not present in the hot alloy heating cycle. While the initial results are encouraging more investigations need to be conducted on understanding the structure and properties of the compound formed by grinding.

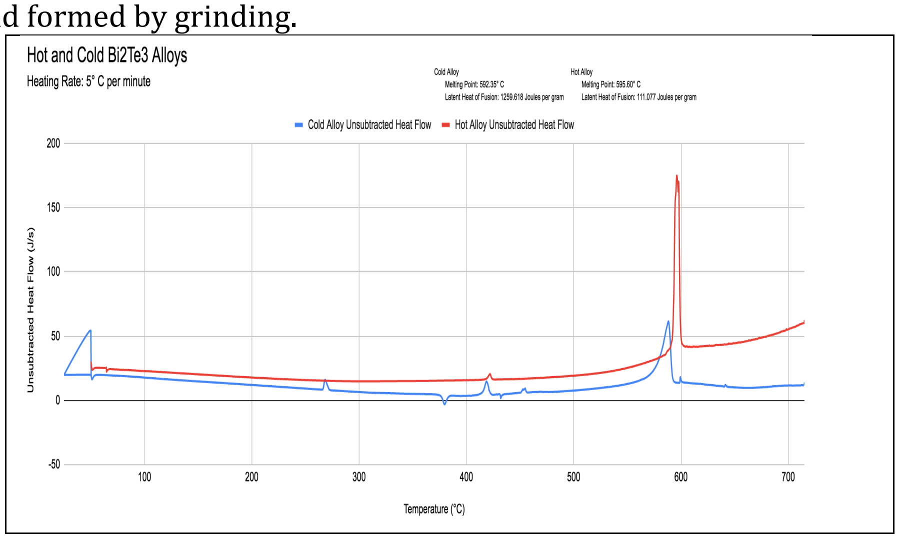


Fig.6a Heating DSC curves for a commercial hot alloy and a cold alloy fabricated by extended grinding.

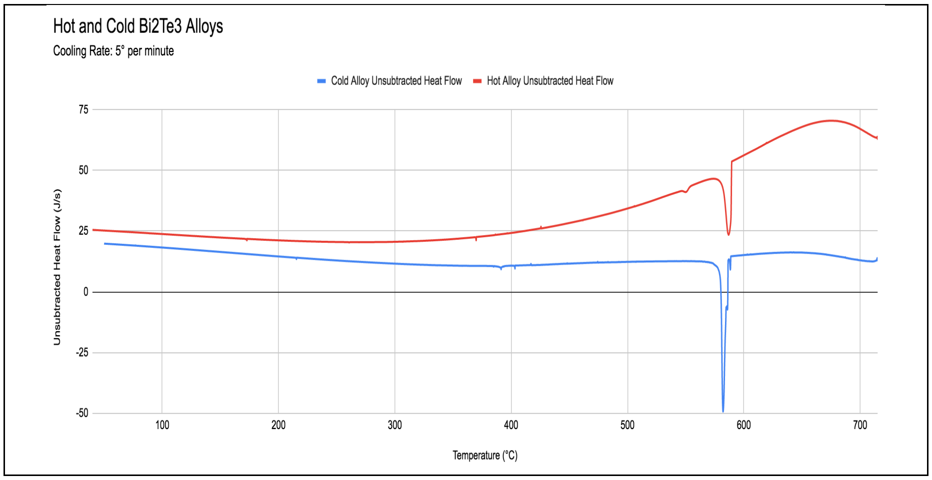

Fig.6b Heating DSC curves for a commercial hot alloy and a cold alloy fabricated by extended grinding.

## IV. CONCLUSIONS

Comsol Multiphysics can play a major role in designing and developing prototypes and getting students interested in thermoelectrics. Under similar temperature conditions, the three-component Comsol model calculates a voltage within 6.6% of the experimental voltage values measured, therefore proving to be a reliable software model for the physical system. Further investigations will be conducted on increasing the cooling efficiency of the cooler by investigating various cooling geometries. The theory and modeling of thermoelectric generators can be understood at the undergraduate physics level while certain forms of fabrication can also be tested within an undergraduate materials science laboratory. Comsol Multiphysics has recently launched its database of examples and applications under the Knowledge Base center online[10] which can be used as a self-learning and teaching tool for undergraduate education. An undergraduate materials science laboratory allows the students to understand material properties and undertake fabrication projects.

## Acknowledgements

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