



# Performance Evaluation of Thermoelectric Materials: A Case Study of Orthorhombic Tin Sulphide ( $S_nS$ )

Emeruwa, C.<sup>1</sup> and Okoro, R.C.<sup>2</sup>

<sup>1</sup>Department of Physics, Federal University Otuoke, Nigeria.

<sup>2</sup>Department of Physics, University of Calabar, Nigeria.

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## ABSTRACT

This work studies the experimental approach employed in performance investigation of thermoelectric materials using Orthorhombic Tin Sulphide ( $S_nS$ ) crystals as a case study. The sample material was joined with Lead Telluride ( $PbTe$ ) to form a closed couple in the module. The two junctions of the couples were held at different sets of temperature causing varying sets of temperature gradients with  $30^\circ\text{C}/\text{m}$  difference between each set. The result obtained reveals that  $SnS$  and  $PbTe$  module has a high thermoelectric conversion efficiency which ranges from 1.92% to 4.84% for the range of temperature gradient of  $60^\circ\text{C}/\text{m}$  to  $180^\circ\text{C}/\text{m}$ . These ranges of thermoelectric conversion efficiency are better than those of commercial thermoelectric modules which has efficiencies of between 0.5% to 1%. It is also seen that  $SnS$  module can operate as both low and high temperature thermoelectric material.

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## I. Introduction

The conversion of thermal energy into electrical energy, occasioned by the dissimilarity in temperature is done using a device called thermoelectric generator (TEG). This device is usually in a solid state, and utilizes Seebeck effect which may equally be generally referred to as an effect due to temperature gradient. Charge carriers (electrons/holes) are the working flux in this device, which obeys the fundamental laws of thermodynamics. Thermoelectric generators typically are made up of fixed, immovable and highly reliable components that require little or no maintenance. Their suitability for equipments with low power needs located at inaccessible places that are devoid of public power supply (such as vacuum or space, mountain tops, etc.), is emphasized by their high durability rate and long lifespan which sets them apart from other devices. The major challenge of TEG is to find materials with high conversion efficiency in order to boost its output level.

## II. Objectives Of The Study

This research, which focuses on the experimental analysis of the conversion efficiencies of Orthorhombic Tin Sulphide ( $S_nS$ ) as a thermoelectric material, was guided by the following objectives:

1. to identify if the thermoelectric materials is reliable in terms of its time of steady-state operation;
2. to identify if it can operate at very high temperatures;
3. to identify if it can operate at both low and high temperatures;
4. to identify the rate at which electrical energy changes with variations in temperature.

## III. Experimental Overview

When a thermoelectric module is operated as a generating device the key parameters that are controlled in

order to vary performance output values are the junction temperatures and attached load resistance. Since all performances are evaluated at steady state conditions these temperatures must be constant to signify that the rate of heat transfer is at a net value and is not varying with time. The hot side is usually equipped with a heat source that can take various forms. The most common practice is surface to surface solid heating using plate or flat heaters [1]. Cartridge heaters or resistance wire are sometimes embedded into metallic blocks of high thermal conductivity instead of using prefabricated heaters. These heaters are insulated at all surfaces other than the one in contact with the module. The heat source is powered by a stable source (such as a DC power source) to ensure continuous and constant power so that steady state conditions can be achieved. Heat has to be constantly rejected at the cold side of the module otherwise both junctions of the module would eventually reach thermal equilibrium and there would be no power generation. Heat dissipation on the cold side is usually achieved using forced fluid convection cooling. Liquids such as ethylene glycol mixtures are used to achieve cooling water temperatures below freezing [2]. Constant flow rates of these cooling fluids are crucial to achieving and maintaining steady state conditions. Forced air convection flow rates can be easily varied or maintained at a constant value by manipulating the input power to the fans. Liquid cooling is primarily achieved through a secondary heat exchange processes where the absorbed heat from the intermediary fluid is dissipated to the ambient using a heat pumping or refrigeration process. Recirculating chillers or bath temperature controllers are employed to achieve such conditions. These devices are electronically configured and controlled either by using internal or external control systems that usually employ a

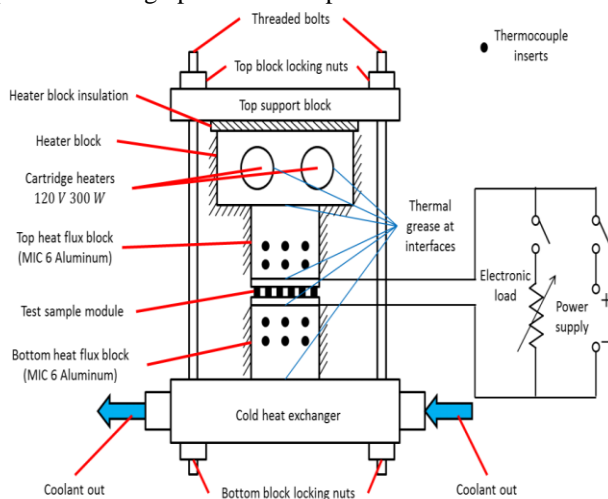
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E-mail address: [chibuzo45@yahoo.com](mailto:chibuzo45@yahoo.com)

form of proportional-integral-derivative (PID) control [3]. This ensures that the circulating fluid is maintained at a desired temperature. Variable speed or positive displacement pumps are used to supply flow of liquid. When using positive displacement pumps bypass lines with adjustable valves are used to control the fluid flow rate [4]. The load resistance value attached to the TEG modules can be manipulated by using electronic loads. Electronic loads are primarily used to test power supplies, fuel cells and power generating devices. The electronic load, when attached to a power producing device, draws either a constant amount of voltage or current.

#### IV. Experimental Setup

The setup used for this study was designed to evaluate the performances of Tin Sulphide module. The test stand accommodates modules with areas of  $30 \times 30 \text{mm}^2$ . Figure 1 shows the setup of the test stand connected to a switchable circuit that consists of an electronic load and a power supply. The electronic load used is a BK8500 Precision model that is capable of testing up to 300W of power from a source.



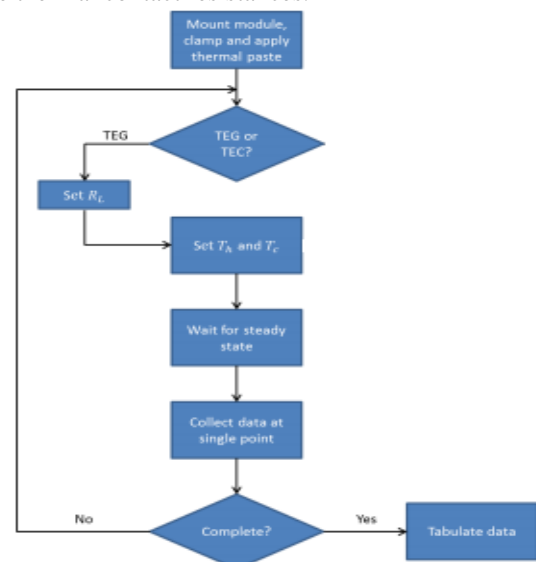
**Fig.1. Schematic of Experimental Setup.**

The heat was supplied by a heater block that consists of two cartridge heaters embedded within. The cylindrical cartridge heaters have dimensions of 15.8mm in diameter and 88.9mm in length. Each cartridge heater is rated to have up to  $0.078 \text{W/mm}^2$  of power density, with a total of 300W at a maximum voltage of 120V. The resistance coils were embedded within a rust resistant sheath with a maximum temperature of  $567^\circ\text{C}$ , which was far beyond the requirements of this study. Stainless steel sheaths were not required since the cartridge heaters would not be exposed to any ionized or corrosive fluids. The power supply connected to the cartridge heaters was a TDK-Lambda EMS80-60 model (refer to Appendix A) with an output of up to 80V and 60A of DC power for a maximum of about 5kW of power. The heat dissipation of the module was achieved using a Thermo Scientific NESLAB RTE 7 recirculating chiller. The chiller consisted of a refrigeration system, circulating pump and a microprocessor temperature controller. The unit employed was capable of a temperature range between  $-25^\circ\text{C}$  and  $150^\circ\text{C}$ . The pump had a capacity of 15liters/min at  $0^\circ\text{C}$ . The operating fluid used was 50:50 glycerin/water with freezing and boiling temperatures of  $-22.8^\circ\text{C}$  and  $106^\circ\text{C}$ , respectively. An internal 800W heater was used alongside an embedded PID control to maintain the recirculating fluid at a desired working temperature (set point). The working fluid absorbed the heat liberated from the module via a one-pass, rectangular channel heat sink. Both the heater and cold side heat sink sandwiched the test sample with respective heat flux blocks

in between. These heat flux blocks were machined from MIC 6 aluminum alloy with an approximate thermal conductivity of  $142 \text{Wm}^{-1}\text{K}^{-1}$ . Each block had a contact surface area of  $30 \times 30 \text{mm}^2$  and height of 20mm. There were six thermocouple inserts in each block with three slots on one horizontal level and another three on another horizontal level with a perpendicular distance of 5mm between each row (center to center). These inserts were fitted with K-type thermocouples clad in standard stainless steel sheathing. Each insert had a diameter of 2mm and a depth of 20mm. The heat flux blocks were insulated at all surfaces other than those in contact with either the cold or hot sources and the module's surfaces using fiberglass held together by reflective tape. These heat flux blocks had two purposes. The first was to measure the heat flux that occurred at the particular junctions of the module and the second was to measure the junction temperature of the modules through a linear method of extrapolation. It was possible to set values by manipulating the voltage output of the power supply connected to the heater and the temperature set point of the chiller. The control loop was able to maintain the junction temperatures within  $\pm 0.1^\circ\text{C}$  of the desired values. Simple proportional gain (determined through a series of trial and error) was used since the settling time of the system was not crucial.

#### V. Experimental Procedure

Here the steps involved when obtaining performance data on a module being tested is looked into. Figure 3 below illustrates the processes followed in obtaining various data points that would be tabulated or graphed to show the performance of the module. The first step in the process was to mount the Tin Sulphide module between the heat flux blocks (refer to Figure 1). Since the surfaces of the heat flux blocks had micro cracks and surface imperfections, highly conductive thermal paste was applied onto such regions to reduce thermal contact resistances.



**Fig.2. Process Flowchart of Experimental Performance Evaluation.**

The test stand was then bolted down with the locking nuts using a torque wrench to ensure that all bolts applied equal pressure.

#### VI. Results

The geometrical information regarding the thermoelectric elements (i.e. the number of couples and geometric ratio) were physically measured using a vernier caliper. The process of obtaining these values was done before assembling the modules.

**Table 1. Effective Parameters for Tin Sulphide Module.**

Criterion	Symbol (Unit)	Set I	Set II	Set III	Set IV	Set V
		$T_h = 230^\circ\text{C}$	$T_h = 200^\circ\text{C}$	$T_h = 170^\circ\text{C}$	$T_h = 140^\circ\text{C}$	$T_h = 110^\circ\text{C}$
		$T_c = 50^\circ\text{C}$	$T_c = 50^\circ\text{C}$	$T_c = 50^\circ\text{C}$	$T_c = 50^\circ\text{C}$	$T_c = 50^\circ\text{C}$
		$\Delta T = 180^\circ\text{C}$	$\Delta T = 150^\circ\text{C}$	$\Delta T = 120^\circ\text{C}$	$\Delta T = 90^\circ\text{C}$	$\Delta T = 60^\circ\text{C}$
Maximum Parameters	$W_{\max}$ (W)	3.50	3.05	2.60	0.93	0.63
	$V_{\max}$ (V)	7.58	7.03	6.53	2.67	2.08
	$I_{\max}$ (A)	1.66	1.63	1.60	0.76	0.72
	$\eta_{\max}$ (%)	4.84	4.70	4.56	2.09	1.92

It should be noted that the effective material properties were obtained for one couple on the assumption of similar materials and geometry between each thermoelectric element. TABLE 1 below summarizes the experimentally obtained parameters for Tin Sulphide TEG module. The tabular data was reported at five different hot junction temperatures but with the same base cold side temperature. Since the maximum outputs of a module are dependent on temperature, five separate cases of maximum efficiencies were computed based on generated maximum parameter information. The maximum parameters generated are Maximum Power ( $W_{\max}$ ), Maximum Voltage ( $V_{\max}$ ), Maximum Current ( $I_{\max}$ ) and Maximum Efficiency ( $\eta_{\max}$ ).

The five different hot junction temperatures used are  $230^\circ\text{C}$ ,  $200^\circ\text{C}$ ,  $170^\circ\text{C}$ ,  $140^\circ\text{C}$  and  $110^\circ\text{C}$  which corresponded to temperature differences of  $180^\circ\text{C}$ ,  $150^\circ\text{C}$ ,  $120^\circ\text{C}$ ,  $90^\circ\text{C}$  and  $60^\circ\text{C}$  respectively with uniformed base colds side temperature of  $50^\circ\text{C}$ .

Fig. 3 below, shows that the output power varied in a linear manner with the changes in temperature difference. At the temperature difference of  $180^\circ\text{C}$ , its value was  $3.50\text{W}$ . The value decreased progressively as the change in temperature was lowered. Its lowest value recorded was  $0.08\text{W}$  at a temperature difference of  $60^\circ\text{C}$ . This near linear relationship between the output power and changes in temperature difference is in agreement with the concept of thermoelectric properties being dependent on temperature. When compared side by side with manufacturer's provided performance data for commercial TG12-4-01L Thermoelectric module by Marlow Industries, it is seen that Tin Sulphide Module generated slightly lower values of output power at temperature difference of  $120^\circ\text{C}$  and above; and when compared with HZ-2 Thermoelectric module by Hi-Z, its output power is slightly better across all tested temperature differences. This above average values of output power generated will translate to modest conversion efficiency.

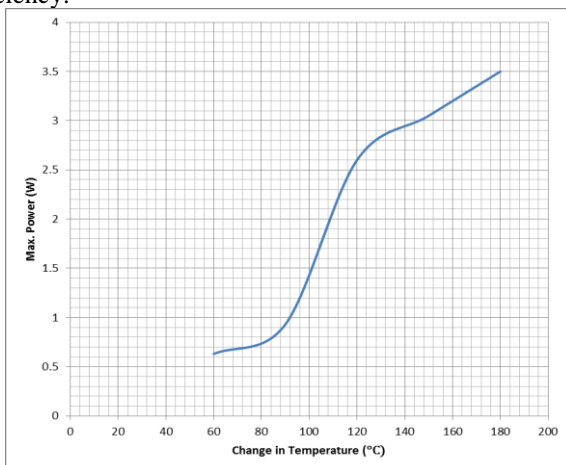
**Fig. 3. Max. Power Variation with Change in Temperature for Tin Sulphide.**

Fig. 4 shows the relationship between changes in temperature difference and output voltage. The maximum voltage value achieved is  $7.58\text{Volts}$  at a temperature difference of  $180^\circ\text{C}$ , which is a good fit. As anticipated, the output voltage decreased as the temperature difference decreased but it stood at  $2.08\text{Volts}$  at the temperature difference of  $60^\circ\text{C}$ , suggesting a sudden fall in output voltage at low temperatures. This figure also shows a near linear relationship but with a major appreciating partner from temperature difference of  $120^\circ\text{C}$  and above. When compared with values from commercial TEG modules (TG12-4-01L and HZ-2), it shows slight difference at same temperature difference all through the tested temperature differences. Its values are greater than that of HZ-2 but a bit less than that of TG12-4-01L.

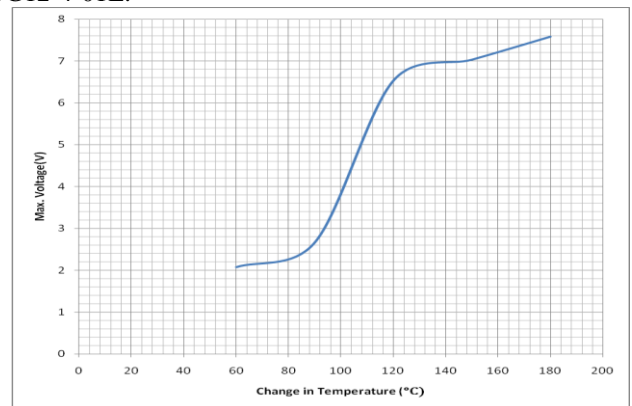
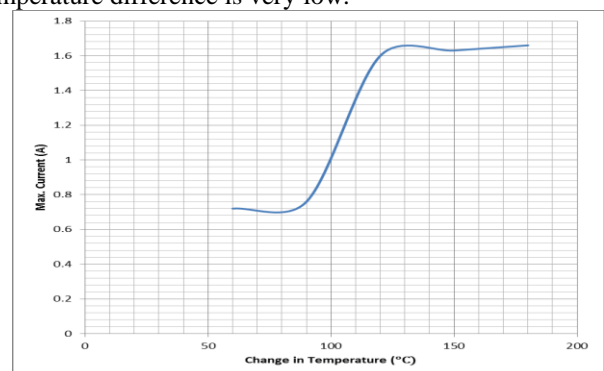
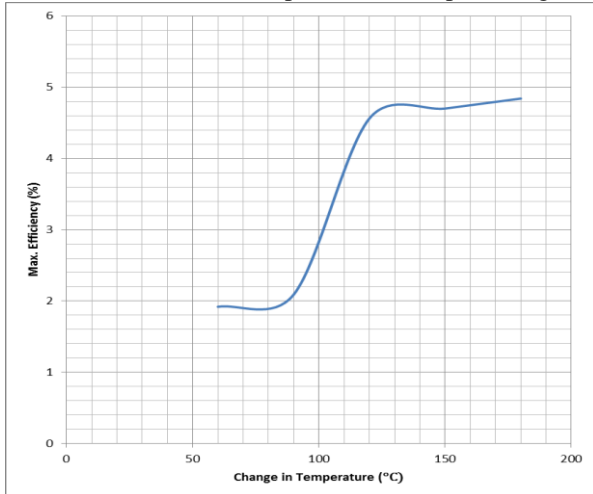
**Fig. 4. Max. Voltage Variation with Change in Temperature for Tin Sulphide Module.**

Fig. 5 is a plot showing the relationship between temperature changes and output current generated. It is similar in shape to figs. 4 and 3 which agree with ohm's law relationship between current and voltage. Here the maximum value is  $1.66\text{A}$  at the temperature difference of  $180^\circ\text{C}$ , it decreases linearly as the temperature difference is lowered, and the least measured value was  $0.72\text{A}$  at the temperature difference of  $60^\circ\text{C}$ . it can be clearly seen that the rate at which the output current decreases with change in temperature difference is very low.

**Fig. 5. Max. Current Variation with Change in Temperature for Tin Sulphide.**

The relationship between changes in temperature and efficiency is shown in fig. 6. Efficiency is a very important factor in choosing thermoelectric materials, in fact it is the underlining objective of most recent researches in thermoelectric materials including this very one. Low conversion efficiency has been a very big limiting factor for TEGs and has made them almost economically non viable except where there are no alternatives. The efficiency of this module ranged from 4.84% to 1.92% for change in temperature range from 180°C to 60°C. This conversion efficiency is attributed to high power factor ( $S^2\sigma$ ) along with fair thermal conductivity ( $\kappa_e + \kappa_l$ ) of Tin Sulphide [5]. As expected, the conversion efficiency decreases as the change in temperature is lowered though the rate of decrease is low. Evident of this is the low steep nature of the plot in fig. 6.



**Fig. 6: Max. Efficiency Variation with Change in Temperature for Tin Sulphide**

## VII. Discussion

This research which experimentally investigated the performance of orthorhombic Tin Sulphide thermoelectric module had its primary objective of assessing the instantaneous thermoelectric conversion efficiency.

This module displayed high conversion efficiency in line with the predictions of that orthorhombic IV-VI compounds are likely to produce high thermoelectric conversion efficiency due to their unusual high power factor [6]. The maximum conversion efficiency of this module was 4.84% at a temperature gradient of 180°C, generating an electric current of 1.66A and electric voltage of 7.58V. As the temperature gradient was reduced, this conversion efficiency dropped, with a very sharp drop between temperature gradient of 120°C and 90°C. At the least tested temperature gradient of 60°C, the conversion efficiency was 1.92%. This means that this module can be put into use most suitably at high temperature reference points. The rapid change in outputs between temperature gradient of 90°C and 120°C can be attributed to electron mobility and alloy composition fluctuations in the constituent materials [7]. Since this effect is related to temperature changes, it is suggested that the primary cause maybe the electron mobility because it is usually affected by temperature variation.

## VIII. Summary

One of the main objectives of this study was to provide designers aiming at implementing thermoelectric modules

into their designs, alternative materials with high conversion efficiency. The motivation behind this objective was the very poor and non competitive conversion efficiencies of commercial TEGs, which has made them almost irrelevant. A thermoelectric modules made from orthorhombic material have been investigated and it has been found to have a marvelous conversion efficiencies when compared to available commercial TEGs primarily due to the arrangement of its atoms and its electron mobility. It was discovered that Tin Sulphide module has good conversion efficiency at high temperature regions but poor conversion efficiency at low temperature regions. This module also shows a rapid increase in conversion efficiency between temperature gradient of 90°C to 120°C. This reveals that the constituent materials of this module have irregular electron mobility. The constituent materials are better suited for use as TEG materials at temperature reference points of 120°C and above.

## IX. Conclusion

It is shown from this study that orthorhombic solids have good thermoelectric conversion efficiency. This good conversion efficiency is attributed to their atomic arrangement and electron mobility which directly influence their power factor. The Tin Sulphide module is only appropriate for application in high temperature TEG. At low temperature reference points, it shows no much distinction from already available commercial TEGs. The sharp increase in conversion efficiency of this module between the temperature gradient of 90°C to 120°C deserve to be well investigated as this could lead to a breakthrough in thermoelectric material research should this effect be felt across all other temperature ranges.

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