Development and experimental study of copper selenide based thermo-electric material by the method of powder metallurgy

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ABSTRACT

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Copper Selenide is one of the promising single crystal thermoelectric material for power generation in low temperature range 300 - 360 K. Universal testing machine is used for pressing the Nano powder to obtain the Nano bulk samples. By using X-ray diffraction (XRD) and scanning electronic microscope (SEM) identified the structure and phase composition. This study shown that 150 kN pressing force in sample without carbon nano tubes showed ZT=1.2 at a temperature of 322K. It is also shown that thermal conductivity and power factor is mainly influencing the value of thermoelectric efficiency of the studied materials.

1. Introduction

In recent years, an increasing concern of environmental issues of emissions, in particular global warming and the limitations of energy resources has resulted in extensive research into novel technologies of generating electrical power. Electrical energy has become more important for modern day living. However, due to the insufficient production of electricity leads to the frequent power cut offs at many areas. Nowadays, due to the frequent power cut offs the electrical power in remote areas is generated primarily by gasoline motor-generators. But, most people believe these generators are too noisy, require too much maintenance, and have high fuel costs. Currently, the electrical-power demand is increasing which prompts the need to build new Power Plants. Thermoelectric power generators have emerged as a promising alternative green technology due to their distinct advantages such as the can potentially be integrated into existing technologies to boost efficiency and reduces environmental impact by producing usable power from waste heat.

The thermoelectric materials can be used for various engineering applications depending on intensity of heat source the voltage and current obtained from the material. Few of the applications are waste heat energy utilization. Auxiliary power supply to charge the battery. Also used in satellites, where proper power supply of solar energy doesn't reach.

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The conversion efficiency of thermoelectric materials is related to quantity – called the Figure of merit (ZT)[1] which is defined as follows:

$$ZT = \frac{s^2\sigma}{k}T$$

See - beck coefficient S, thermal conductivity k, electrical conductivity σ and absolute temperature T.

However current available thermoelectric devices are not in common use, partly due to their lower efficiency relatively to mechanical cycles and engineer challenges related to using thermoelectric devices for general applications [2] The best thermoelectric materials so far as Bi_2Te_3, PbTe, and SiGe have shown a maximum ZT valve about 1, which restricts the large scale application of thermoelectric technology. A few remarkable progress have been made to improve the thermoelectric properties, especially recent achievements to create nano-structured materials, such as super lattices, quantum wires, and nanocomposites.

A brief literature review on Nano- bio-materials is presented in the following. To start with, the metallic and metallurgical nano-structure of materials for thermoelectric applications has been studied.

Giovanni Pennelli [1] have review on nanostructured devices for thermoelectric applications in the particular emphasis on Nano structured silicon, which represents a valid compromise between good thermoelectric properties on one side on material availability, sustainability, technological feasibility on the other side. The most important bottom up and top down Nano fabrication techniques for large area silicon Nanowire arrays, to be used for high efficiency thermoelectric devices.

Zhi-Gang Chen et al., [2] have studied the Nanostructured thermoelectric materials: Current research and future challenge. In this field of thermoelectrics has long been recognized as a potentially transformative power generation technology and the field is now growing steadily due to their ability to convert heat directly into electricity and to develop cost-effective, pollution-free forms of energy conversion of various types of thermoelectric materials, Nano structured materials have shown the most promise for commercial use because of their extraordinary thermoelectric performances.

Yufei Liu et al., [3] have investigated towards higher thermoelectric performance of Bi_2Te_3 via defect engineering. In this, no thermoelectric material would have attained its best performance without defects. The electrical resistivity, Seebeck coefficient and thermal conductivity in their totality are manifestations of charge flow, phonon flow, and their interplay mediated by defects.

Stephen Dongmin Kang et al., [4] have studied on the enhanced stability and thermoelectric figure-of-merit in Copper Selenide by lithium doping. In the investigation process the maximum ZT> 1.4 from $Li_{0.09}Cu_{1.9}Se$. The high temperature effective weighted mobility of the doped sample is found higher than $Cu_{2-x}Se$, while the lattice thermal conductivity remains similar. The results show signatures of suppressed bipolar conduction due to an enlarged band gap and set forth a possible route for tuning the stability of superionic thermoelectric materials.

Ivanova. et. al. [5] have investigated on the Copper Selenide by the Methods of Powder Metallurgy in this the Copper Selenide is a promising material for power generation in a medium-temperature range 600–1000 K. A number of features of the Cu–Se system, namely, the existence of phase transition in a Cu_2Se compound, the high speed of the diffusion of Cu ions, and the high vapor pressure of Se at elevated temperatures, make it necessary to carry out a series of experimental investigations to develop and optimize the methodology for obtaining the bulk material based on Copper Selenide. The methods of Hot Pressing (HP) and Spark Plasma Synthesis (SPS) are used to obtain the bulk samples. The investigation of the structure and phase composition is performed by the X-ray diffraction and scanning electron microscopy. It is shown that increasing the duration of the mechanochemical synthesis up to 5 h leads to the depletion of copper in powders and to the formation of non-stoichiometric β-phase $Cu_{1.83}Se$, which persists after SPS. A comparison of the structure and properties of the material obtained by SPS and HP showed that the material obtained by HP has a greater degree of grain defects. The highest thermoelectric efficiency ZT = 1.8 at a temperature of 600°C is achieved for the material obtained by SPS. It is shown that low thermal conductivity is the main factor affecting the value of the thermoelectric efficiency ZT of the studied materials. The difference in the values of thermal conductivity of the materials obtained by different methods is related to the electronic component of thermal conductivity.

Saniya LeBlanc et al., [6] have review on thermo electric generators: Linking material properties and systems engineering for waste heat recovery applications. This review discusses these challenges and indicates ways system-level performance relies on more factors than traditional thermoelectric material performance metrics alone. Relevant thermo mechanical and chemical material properties, system components such as thermal interface materials and heat exchangers, and system form factors are examined. Manufacturing processes and total system cost components are evaluated to provide product development and commercial feasibility contexts.

Jin-Cheng Zheng [7] has studied the recent advances on thermoelectric materials reviewed the efforts on improving thermoelectric efficiency. Particularly, several novel proof-of-principle approaches such as phonon disorder in phonon glass electron crystals, low dimensionality in nanostructured materials and charge-spin-orbital degeneracy in strongly correlated systems on thermoelectric performance will be discussed.

The copper, silver nanoparticles are the important part of nanomaterial, with the potential for broad range of electronic, optical and communication application. Therefore the copper, Silver Nano particles were paid wide Attention on its application field in the recent years. Similarly, oxides of copper and silver find a variety of applications such as Nano particulate film fabrication. The synthesis of copper, silver Nano particles is Solution combustion method has emerged as potential technique of preparing nanomaterial.

2. Materials and Methods for Nanoparticles Preparation and Characterization

The approach used to synthesis the Copper/ Silver Nano particles is bottom up approach i.e. green synthesis method is used to synthesis the Copper /Silver Nano particles.

The pure chemical Copper nitrate/Silver nitrate obtained from LABORATORY TRADERS for the synthesis. $[Cu(NO_3)_2.3H_2O.]$/ $[Ag(NO_3)_2]$ used as an oxidizer and plant leaf extract powder used as reduction agent. After synthesis the Copper/Silver Nano particles are collected in the container and tested for the size using the SEM.

By the SEM analysis the size of the Copper Nano particles were about 40nm – 60nm Silver Nano particles were about 25nm to 60nm, from the above obtained images by the SEM analysis

The three other materials selected for the samples to be prepared are difficult to be found in nitrate or oxide form, due to this restrictions the three materials Carbon Nano tube (CNT) (Multi-walled), Graphene and Selenium were purchased from The Energy Resources Institute (TERI), the Nano particle of selenium powder SEM-EDX images are shown in Fig 1 and 2.

3. Specimen Preparation Methods and Characterization

The preparation of the specimen by using the Nano powders was done by powder metallurgy technique. This composition and mass of Nano powders are taken and mixed properly and then compressed in the die with the help of Universal Testing Machine. The load is given in such a way that a proper compaction of the material and load should not exceed the compression force of the material, else it would lead to the formation of crack in the specimen. The total volume of the specimen is = 5089.3 mm^3. The specimen prepared by using the Nano powders is having three different compositions of samples are shown in the Table – 1, for each sample 5 specimens prepared.

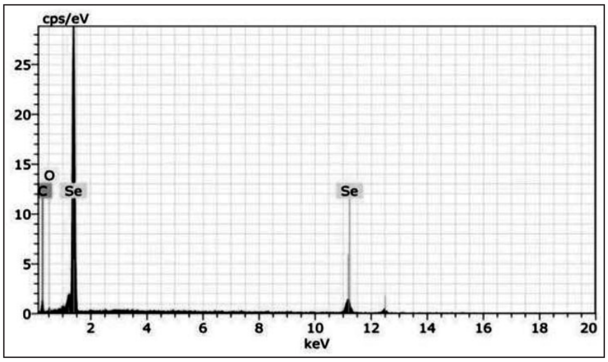

Fig. 1. The SEM-EDX analysis results for Selenium powder.

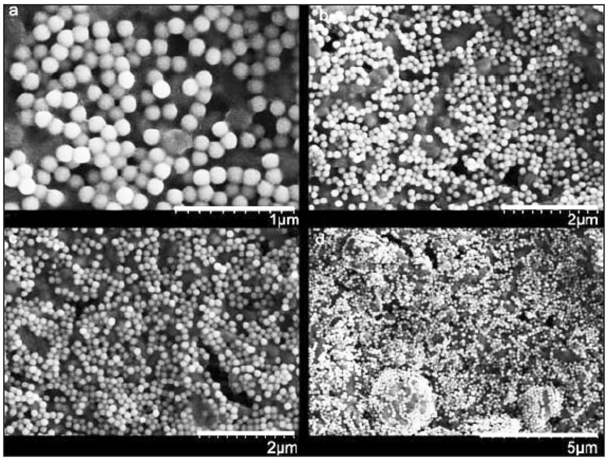

Fig. 2. SEM image of Selenium size (20 nm to 40 nm).

3.1 Specimen preparation method

From green synthesis method Copper, Silver nano powders obtained and Selenium, Graphite, CNT obtained from TERI (Research Institute). All the required amount of powder for specimen preparation was calculated and mixed properly. Then the die is fastened to each other. The powder is then filled inside the hole layer by layer by appling less pressure on powder. Once the material is filled completely the die is kept in the UTM and plunger is placed applied load, preparing the specimen the force applied was around 150 kN. All the process done at room temperature cold pressing.

Table 1
Composition of elements considering.

Elements	Density g/cm³	Sample-1	Sample-2	Sample-3
Copper	8.96	40% (45.51 grams)	50% (45.51 grams)	50% (45.51 grams)
Selenium	4.819	40% (24.48 grams)	30% (24.48 grams)	30% (24.48 grams)
Graphene	2.267	16.7%(11.51 grams)	15% (11.51 grams)	10% (11.51 grams)
Silver	10.5	3.3% (53.34 grams)	-	-
CNT		-	5% (4.128 grams)	10% (8.128 grams)
Total mass		31.624 grams	36.8 grams	32.0618 grams

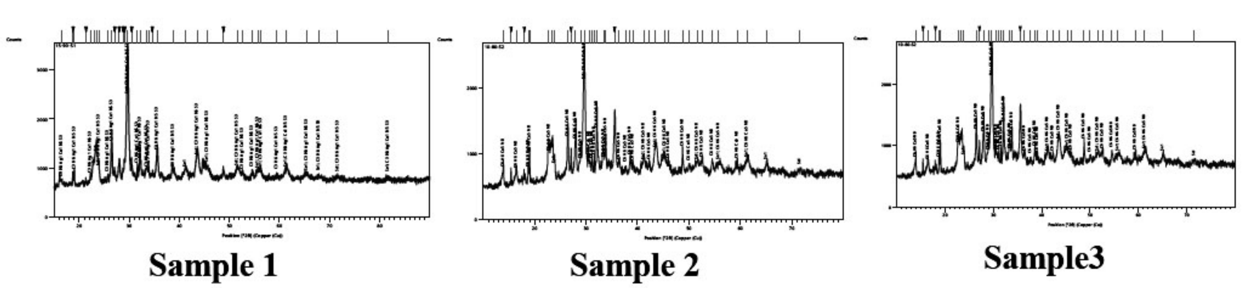

Fig. 3. XRD patterns of Nano Sample (1) Nano $GrCuAg_2Se$, (2) CGr Cu_2Se, (3) $CGrCu_2Se$.

Table 2

	Specimen-1	Specimen-2	Specimen-3	Specimen-4	Specimen-5
Sample-1	1.7	1.6	1.7	1.6	1.7
Sample-2	1.4	1.5	1.4	1.5	1.4
Sample-3	1.3	1.4	1.2	1.3	1.3

4. Results and Discussions

X-Ray diffraction of samples as shown in fig 3.

XRD pattern of sample 1 shows that it has two main phases at room temperature, a mono clinic alpha-Cu_2Se and the orthorhombic CuAgSe. Similar phases were reported in stoichiometric CuAg Se compounds.

4.1 Thermal conductivity test analysis

The table 2 shows the thermal conductivity values in W/mK for the prepared specimens at various temperature ranges are tested by C-THERM. In all samples 5 specimens are prepared and tested.

4.2 Electrical properties

The electrical properties of specimens were obtained by using the 4 probe method and the results are as tabulated as shown in table-3,4,5.

4.3 Seebeck-coefficient

The table - 6 shows the Seebeck-coefficient valves in V/K

Figure of merit ZT for sample 1 =

$$\frac{S^2\sigma\ \mathrm{T}}{K} = \frac{(5.8x10^{-3})^2 x\ 172.24\mathrm{x}355}{1.7} = 1.256$$

Table 3
Electrical properties for sample 1.

Specimen no	Resistance (Ω)	Resistivity (Ωm)	Electrical conductivity (S/m)
1	0.723	$6.33*10^{-3}$	157.91
2	0.536	$5.67*10^{-3}$	176.28
3	0.632	$5.67*10^{-3}$	165.28
4	0.712	$5.67*10^{-3}$	162.28
5	0.523	$5.67*10^{-3}$	165.1

Table 4
Electrical properties for sample 2.

Specimen no	Resistance (Ω)	Resistivity (Ωm)	Electrical Conductivity (S/m)
1	1.2	0.0107	93.33
2	0.96	$7.865*10^{-3}$	127.13
3	0.92	$7.725*10^{-3}$	128.13
4	0.96	$7.865*10^{-3}$	127.13
5	0.95	$7.865*10^{-3}$	127.13

Table 5
Electrical properties for sample 3.

Specimen no	Resistance (Ω)	Resistivity (Ωm)	Electrical Conductivity (S/m)
1	1.2	0.0107	93.33
2	0.96	$7.865*10^{-3}$	127.13
3	0.92	.00728	125.12
4	0.96	$7.865*10^{-3}$	127.13
5	0.95	$7.865*10^{-3}$	126.13

Figure of merit ZT for sample 2 =

$$\frac{S^2\sigma\ \mathrm{T}}{K} = \frac{(6.509\mathrm{x}10^{-3})^2 x\ 93.33\mathrm{x}322}{1.4} = 0.98$$

Figure of merit ZT for sample 3 =

$$\frac{S^2\sigma\ \mathrm{T}}{K} = \frac{(6.509\mathrm{x}10^{-3})^2 x\ 93.33\mathrm{x}322}{1.4} = 0.965$$

5. Conclusions

Cu-Ag Nano particles have been synthesised. Structural characterization performed via XRD and SEM analysis. High temperature transport properties, based on the measurement of the electrical conductivity, thermal conductivity, and the See beck coefficient, were carried over range 300-360 K. Three material properties, Seebeck coefficient S, electrical conductivity σ, and thermal conductivity k, are vital to the thermoelectric generation, and ZT = S2σT/κ is employed to evaluate the thermoelectric performance of materials, where T is the absolute temperature.

In conclusion remarks of this work the material compacted by sequential process. This compaction process resulted in a high porosity in the specimen, due to this the specimen had to be handled carefully, the thermal conductivity decreased. To increase mechanical strength, to avoid porosity in the specimen the die used for compaction must be 4-5 times longer than the original length of the specimen. By adding CNT thermal conductivity increased. As a result, ZT value of 1.25 at 322 K achieved for Cu_2Se compound without CNT.

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Table 6
Seebeck-coefficient for samples at different temperature differences in V/K.

	Specimen-1	Specimen-2	Specimen-3	Specimen-4	Specimen-5
Sample-1 at 49^{0}C	$5.8\mathrm{x}10^{-3}$	$5.8\mathrm{x}10^{-3}$	$5.8\mathrm{x}10^{-3}$	$5.8\mathrm{x}10^{-3}$	$5.8\mathrm{x}10^{-3}$
Sample-2 at 49^{0}C	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$
Sample-3 at 49^{0}C	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$	$6.509\mathrm{x}10^{-3}$

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