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Thermoelectric Properties of Oxide Semiconductors

M. Ajaz Un Nabi, Adnan Ali, M. Imran Arshad, Sofia Akber, A. Manzoor, M. Sharif, Kashif Javaid, Nasir Amin, Nadeem Sabir, Khaalid Mahmood, S. Ikram, Sajad Hussain and H. Naeem Ur Rehman

Abstract

In this chapter, we have explored the potential of oxide semiconductors for thermoelectric power generation. Various oxides (Cu_2InO_4, $CuAlO_2$, and Zn_2GeO_4) were grown on Si substrate by thermal evaporation method using tube furnace. After the growth, a representative sample of each oxide was cut into pieces and was annealed at various temperatures from 600 to 800°C in oxygen environment for 1 h using a programmable furnace. The structure of all annealed sample was verified by performing X-ray powder diffraction (XRD) measurements. XRD data suggested that all oxide materials show crystalline behavior at annealing temperature 800°C. XRD results further confirmed that crystal structure of investigated samples improved significantly with annealing because the intensity of oxygen-sensitive (0 0 6) plane was found to be increased with annealing temperature. To investigate the thermoelectric properties of annealed samples, Seebeck effect and Hall effect measurements were performed in the temperature range 25–100°C. It was found that the value of Seebeck coefficient and power factor increased as the annealing temperature increases. Zn_2GeO_4 was found to be a potential thermoelectric material because it has the highest value of Seebeck coefficient and power factor. This highest value is related to the presence of secondary phases in this oxide.

Keywords: oxide semiconductors, thermal evaporation, XRD, Seebeck coefficient, power factor

1. Introduction

Energy has a fundamental importance in the human civilization. Conventional methods are used for the production of energy use oil, gas, and coal. The reservoirs of oil and gas in the world are decreasing, and the burning of oil and gas causes a threat to the environment; therefore, people are searching for cheap methods for the production of clean energy. These renewable energy production methods include photovoltaic, nuclear energy, biogas, wind energy, and thermoelectricity. All these methods have their advantages and disadvantages. For example, solar cells can produce energy during the daylight and also need high technology for the fabrication of solar cells. Nuclear energy production needs nuclear power plants which

not only require high cost but also a high risk for the community. Similarly, wind energy can only be produced in the strong windy areas. On the other hand, thermoelectricity is very cheap and an easy method for the clean energy production. Thermoelectricity is based on the very famous Seebeck effect which was invented by Seebeck in 1821 and is stated as.

An emf is induced when a temperature difference is created between two metal junctions. Thermoelectricity needs only temperature difference between two metals; therefore, it is supposed to be the cheapest form of clean energy. It is reported that that 60% of heat produced during cooking process, in industry and in running vehicles, is wasted, but we are able to convert this wasted heat into electricity using thermoelectric power generators; we can save huge amount of money. Furthermore, thermoelectricity has other advantages over other sources of energy such as it has no moving parts, it is environment friendly, no specialized technology is required, and it is less maintenance.

1.1 Physical interpretation

The thermoelectric devices convert thermal energy into electrical energy, and the principle is based on the Seebeck effect invented by Seebeck in 1821. It states that a voltage is induced between two points of metal/semiconductor having a difference of temperature as shown in **Figure 1**. The charge carriers on the hot side can have more energy than the cold side; therefore, they form a potential difference. Suppose dT is the temperature between hot and cold side of sample, therefore according to Seebeck effect.

$$dT = SV \tag{1}$$

where S is the Seebeck coefficient.

Another term frequently used in thermoelectric is the power factor which is defined as.

$$\text{Power factor} = S^2 \alpha \tag{2}$$

where α is electrical conductivity.

The performance of thermoelectric material strongly depends upon a unit less quantity called figure of merit:
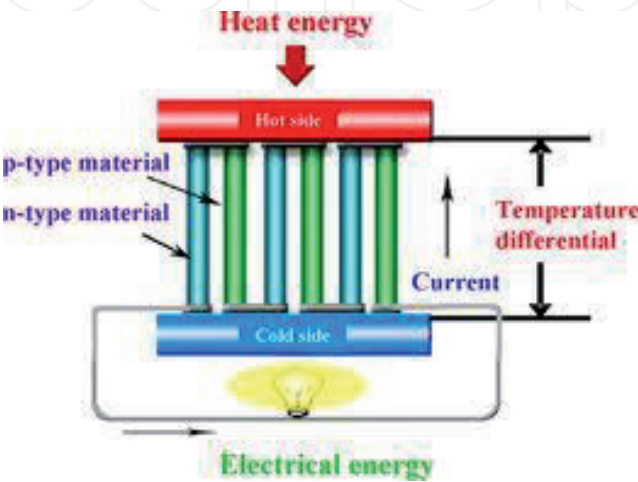
$$zT = \frac{S^2 \sigma T}{\kappa} \tag{3}$$

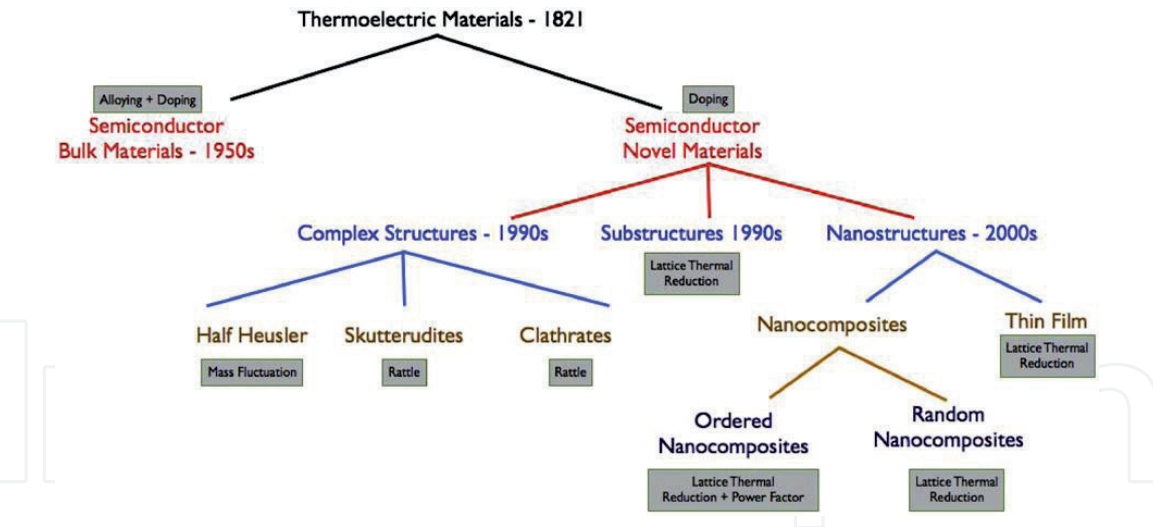**Figure 1.**
Schematic diagram of the Seebeck effect.

Figure 2.
A brief history of materials used for thermoelectric applications.

This equation shows that for a good thermoelectric material, high Seebeck coefficient, high electrical conductivity, and low thermal conductivity are essential.

The thermoelectric conversion efficiency depends upon a quantity called figure of merit and can be written as [1].

$$ZT = S^2\,\alpha/\sigma \qquad\qquad (4)$$

where S is the Seebeck coefficient, α is the electrical conductivity, and σ is the thermal conductivity.

The figure of merit for a material to be used for practical power generation system should be in the range of 2–3 [2]. But the best reported value of figure of merit for oxide semiconductor is not more than 0.1. **Figure 2** indicates the history of efforts to increase the figure of merit.

Different strategies have been employed to tune and alter the thermoelectric properties. The general techniques are as follows [3]:

1. Optimization using doping techniques

2. Substructuring

3. Nanostructuring

4. Compositing

But for the semiconductors the governing parameters includes the following:

1.2 Band gap

Band structure is a very important parameter to tune the thermoelectric properties of oxide semiconductors. One of the most important methods of band gap control is varying the carrier concentration by doping [4]. But the doping process itself required a high technology that increased the cost of thermoelectric devices very high. So if we tune the carrier concentration by controlling the density of intrinsic defects, this will cut short the cost of the final device. Interestingly, oxide semiconductors have rich the chemistry of intrinsic defects. Oxygen vacancy and zinc interstitials act as intrinsic shallow donors and form electronic states near the conduction band [5].

1.3 Mobility

The mobility of carriers in thermoelectric materials has played a vital role in the tuning of Seebeck coefficient and power factor. The power factor is strongly dependent on the conductivity which has strong dependence on mobility. Therefore, the modulation of mobility to achieve highest value of power factor is necessary. The mobility of the carrier can be controlled by the scattering mechanisms. Two scattering mechanisms, that is, lattice scattering and impurity scattering mechanisms, are very important in oxide semiconductors [6].

1.4 Carrier diffusion

Diffusion is a process of movement of particles from hot junction to cold junction in thermoelectric material. The diffusion of charge carriers has fundamental importance to tune the thermoelectric properties of oxide semiconductors. The diffusion in compound semiconductors is more complex than in elemental semiconductors because of the larger number of possible native point defects that can, in principle, mediate self-diffusion [7, 8]. Oxide semiconductors have high density of intrinsic defects, which in principal affect the diffusion of charge carriers. Therefore, for the effective use of oxide semiconductors for thermoelectric properties, the control of intrinsic defects has fundamental importance and should be studied further. Again, we propose that annealing will be a very effective method of studying the diffusion properties of carriers in oxide semiconductors.

1.5 Thermal expansion coefficient

Thermal expansion is critical, as the devices for high-temperature applications will be subjected to extreme temperature fluctuations. The CTE of TE materials is of critical importance because the shear stress is proportional to the temperature gradient, and the larger the heterogeneity in the thermal expansion coefficient of a material is, the larger is the shear stress that will result [9]. It is also reported that thermal expansion coefficient of semiconductor for low- and high-temperature region is almost the same but different for medium temperature. Therefore, a comprehensive study on the thermal expansion coefficient is still needed to completely understand the mechanism [10].

2. Experimental

In this study, experiment is held under thermal vapor deposition technique using single-stage horizontal glass tube furnace. In this experiment, 99.9% pure magnesium, Zinc, and Copper powders along with Ge, In, and Al powders are used under the ratio 1:1 as source material. This source material is being kept in the center of a glass tube in ceramic boat. The silicon substrate is placed at substrate holder, and the distance between source and the substrate is about 15 cm. The temperature of the furnace is tuned at 950°C for 30 min, whereas the oxygen flow is kept constant at 100 sccm. After the growth of thin film, the substrate of silicon is divided into different pieces for annealing purpose at different temperatures from 600 to 800°C for 30 min.

X-ray diffraction has been performed for the structural analysis of grown thin film. Raman spectroscopy has been also performed to study the rotational and vibrational modes of thin film. Surface morphology is being assessed by the scanning electron microscope (SEM). The most important characterization to calculate

Seebeck coefficient has been performed on the homemade Seebeck system which is based on the four-probe system. And the thickness of the thin film has been measured by the filmtronics technique and it is about.

3. Results and discussion

Figure 3(a–c) represents the XRD patterns of Cu_2InO_4, $CuAlO_2$, and Zn_2GeO_4 thin films annealed at different temperature from 600 to 800°C, respectively. The XRD graph of Cu_2InO_4 thin films in **Figure 3(a)** demonstrated that unannealed and low temperature (600°C) would not be able to make the grown material crystalline due to low thermal energy for bonding. But as we increased the temperature above 600°C, the sample is converted into crystalline structure with preferred orientation (006) at $2\theta = 33.086°$ [11, 12]. It is also observed that the intensity of this plane is increased as we further increase the annealing temperature, which suggested that carriers now get enough energy to sit down at a particular position in planes of the crystal. **Figure 3(b)** shows the XRD graph of $CuAlO_2$. The unannealed sample consists of one major phase at $2\theta = 32.05$ which belongs to $CuAlO_2$ (0 0 6) plane [13]. Annealing resulted in the development of new phases at $2\theta = 35.4, 42.4$, and 48.4 related to CuO (1 1 1) and $CuAlO_2$ (1 0 4) and (0 0 9) orientations, respectively. We have observed that (0 0 6) plane has the strongest intensity which is oxygen sensitive; therefore, enhancement of intensity of this plane with annealing temperature is understandable.

Figure 3(c) shows the XRD pattern of grown and annealed samples of Zn_2GeO_4 thin films at various temperatures. The unannealed and annealed samples consist of eight diffraction peaks which are related to Zn_2GeO_4, Si, Au, and ZnO, respectively. The diffraction peak at 25.8, 42.9, 44.7, 58.4, 58.9, and 65° are belonging to Zn_2GeO_4
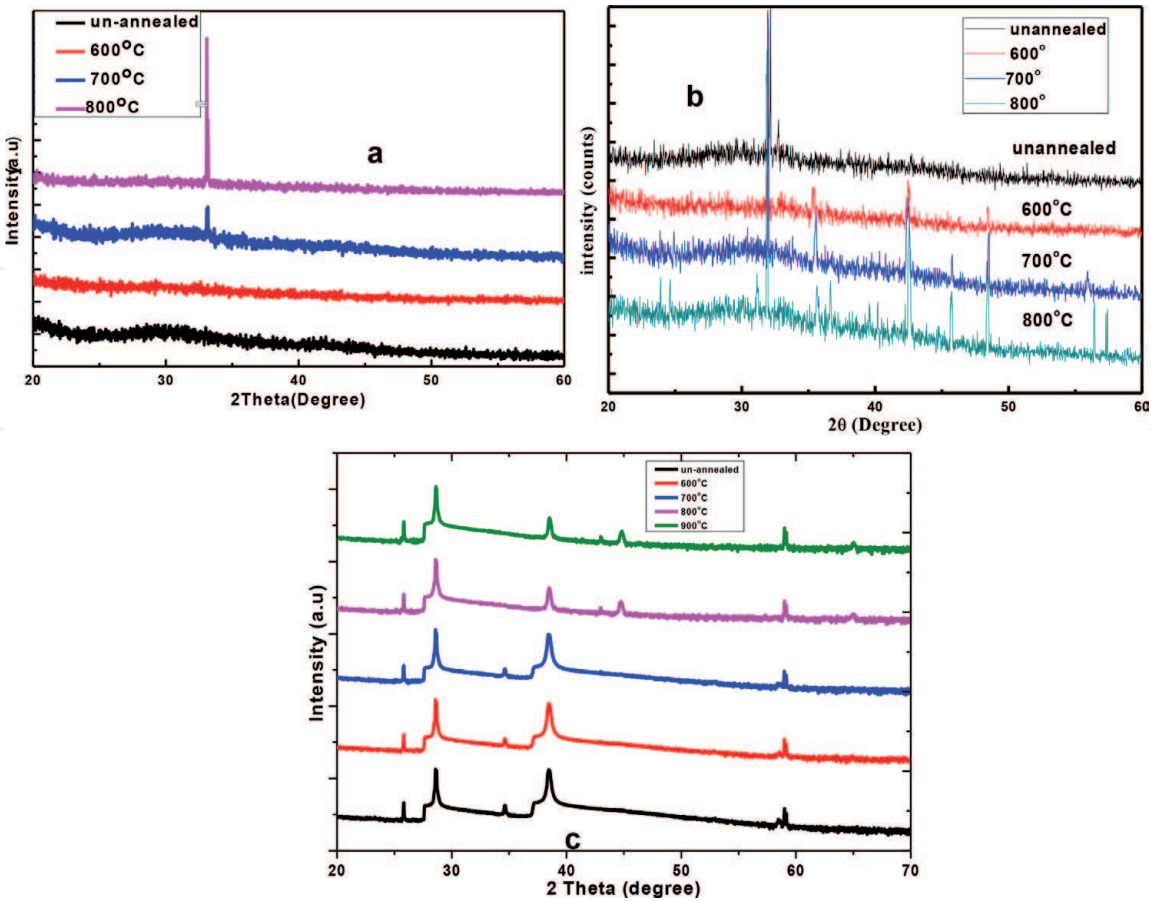

Figure 3.
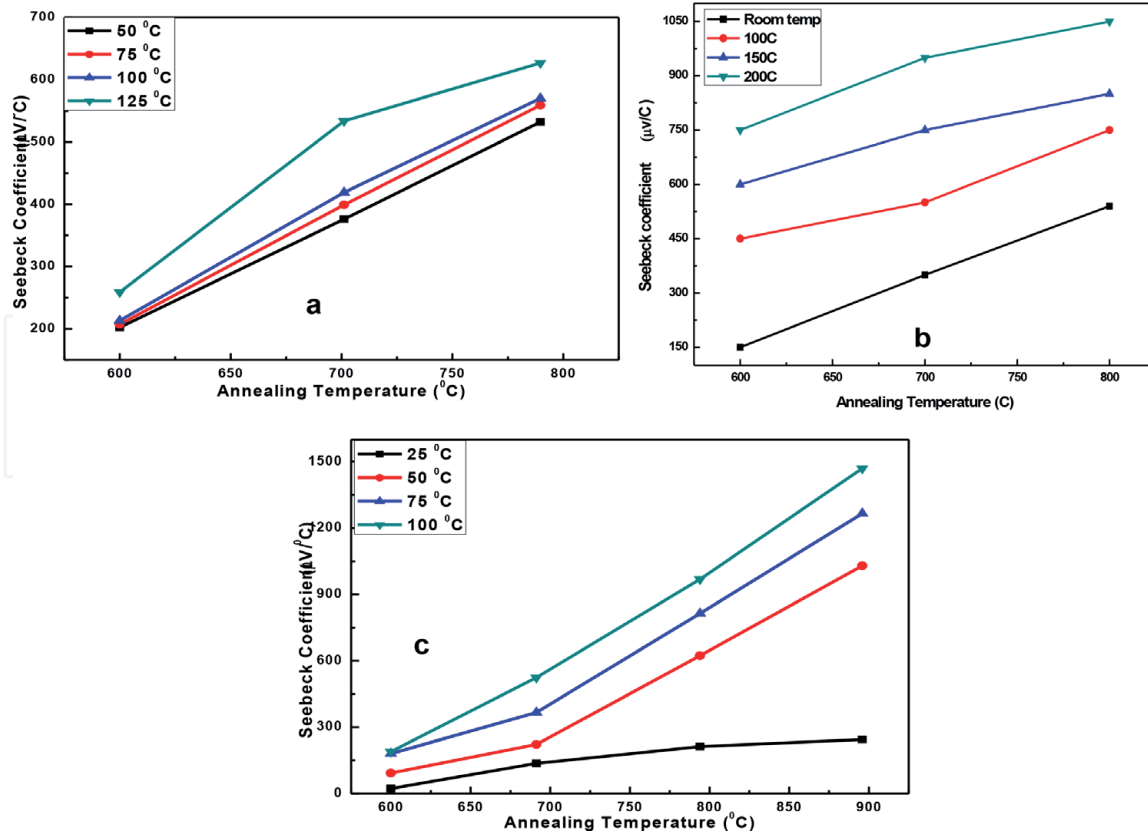*(a–c) XRD patterns of Cu_2InO_4, $CuAlO_2$, and Zn_2GeO_4, respectively.*

Figure 4.
(a–c) Effect of annealing temperature on the Seebeck coefficient of Cu₂InO₄, CuAlO₂, and Zn₂GeO₄, respectively.

which are indexed as (2 2 0), (6 0 0), (0 0 6), (6 3 0), and (7 1 3), respectively [14]. The peak which appears at 28.6° and 38.4° is belonging to (1 1 1) plane of Si and Au [15, 16], respectively, along with peak of ZnO at 34.6° having (0 0 2) plane [17]. It is observed that substrate and pre-deposited gold shows maximum intensity in all the samples which is attributed to the thin porous layer deposited over the substrate. The XRD data also demonstrated that the sample annealed at 900°C has three additional peaks at 45.7° and 65° which are related to the secondary phases of Zn₂GeO₄.

Figure 4(a–c) demonstrated the effect of annealing temperature on the Seebeck coefficient of Cu₂InO₄, CuAlO₂, and Zn₂GeO₄ thin films grown by thermal evaporation technique, respectively. All graphs showed that the value of Seebeck coefficient increases as the annealing temperature increased. It is also observed that the value of Seebeck coefficient also increases as the measurement temperature increases from 25 to 100°C. Zn₂GeO₄ has the highest value of the Seebeck coefficient (1470 µV/K) as compared to Cu₂InO₄ and CuAlO₂. The observed result can be explained as post-growth annealing enhances the density of oxygen atoms and also provides more thermal energy to Ge atoms which resulted in the creation of GeO-based secondary phases. These newly developed secondary phases act as barrier for charge carriers at the interface of secondary phases. Due to this barrier, the low-energy carriers are filtered out at the interface and caused the enhancement in the Seebeck coefficient. As other two samples have no secondary, therefore have lower value of the Seebeck coefficient as evident by XRD data (**Figure 5**).

To further probe the effect of annealing temperature on the thermoelectric properties of grown oxide semiconductors, we have calculated the power factor using the following formula:

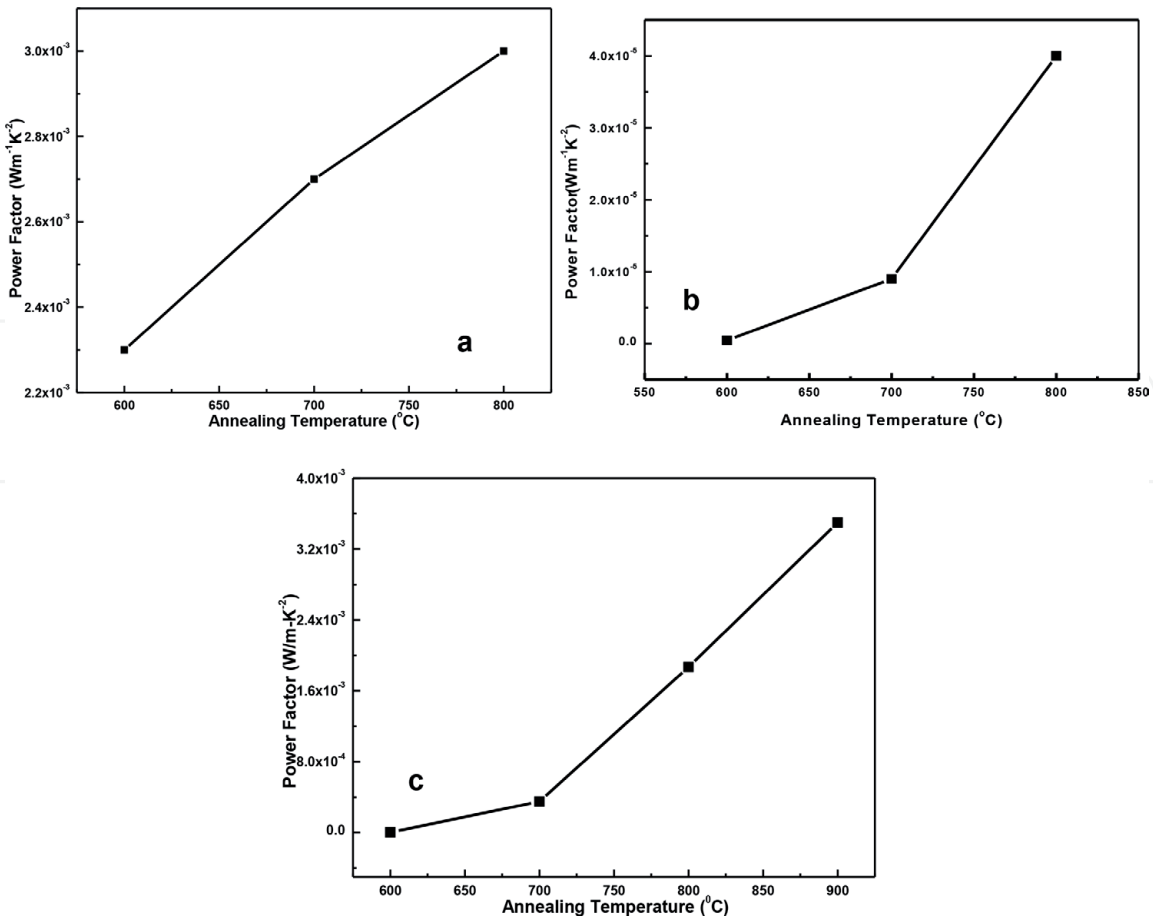$$P = S^2 . \alpha \qquad (5)$$

Figure 5.
(a–c) Effect of annealing temperature on the power factor of CuInO, CuAlO, and ZnGeO thin films grown by thermal evaporation, respectively.

where S is Seebeck coefficient and α is electrical conductivity. The power factor is enhanced significantly with increasing annealing and measurement temperature because both Seebeck coefficient and electrical conductivity increases.

4. Conclusion

This chapter described the effect of annealing temperature on the thermoelectric properties of oxide semiconductors. All samples were grown by thermal evaporation technique using tube furnace under vacuum using similar growth conditions. After growth, oxide semiconductors were annealed in oxygen environment at various temperatures. The reported results have suggested that Zn_2GeO_4 has good potential to be used as thermoelectric material because it has the highest value of Seebeck coefficient and power factor.

Author details

M. Ajaz Un Nabi[1], Adnan Ali[1], M. Imran Arshad[1], Sofia Akber[1], A. Manzoor[1], M. Sharif[1], Kashif Javaid[1], Nasir Amin[1], Nadeem Sabir[1], Khaalid Mahmood[1*], S. Ikram[1], Sajad Hussain[2] and H. Naeem Ur Rehman[3]

1 Department of Physics, Government College University Faisalabad, Pakistan

2 Department of Physics, Division of Science and Technology, University of Education, Pakistan

3 Department of Physics, Khawaja Fareed University of Engineering and Information Technology, Rahim Yar Khan, Pakistan

*Address all correspondence to: khalid_mahmood856@yahoo.com

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