

(Bi_{0.25}Sb_{0.75})₂Te₃ THERMOELECTRIC PELLET CRYSTALLIZED BY HOT ZONE MELTING METHOD TO FIX IN A SEMICONDUCTOR ELECTRIC GENERATOR

G. Kavei¹ A. Kavei²

1. Material and Energy Research Center (MERC), Tehran, Iran, g-kavei@merc.ac.ir, prof.kavei@hotmail.com

2. Solar Energy Research Division, Parseh Company, Tehran, Iran, ashkan3623@yahoo.com

Abstract- Bi₂Te₃-Sb₂Te₃ thermoelectric compound with rich side of Sb₂Te₃ were prepared by the zone melting method and processed under hot pressing method in order to study their thermoelectric properties at different status. (Bi_{0.25}Sb_{0.75})₂Te₃ compound is a well known p type material with optimal properties in a module of the thermoelectric semiconductor electric generator. The compound was crystallized then, pulverized as powder. The powder was sintered in a heat up to 350-500 °C under pressure of 500 MPa (hot pressing). Thermoelectric properties of hot pressed specimens were changed as a function of particle size, pressing, time compressive force and hot pressing temperature. Intrinsic structures were characterized by X-ray diffraction and scanning electron microscopy. The acquired images show homogeneous structures for hot pressed samples. The transport properties of thermoelectric pellets were defined to consider the efficiency. Seebeck coefficient, electrical and thermal conductivities of the pellets are the ruling parameters regarding figure of merit (*Z*), for the power generator.

Keywords: Hot Zone Melting, Thermal Conductivity, Thermoelectric, Electric Generator, Crystal, Hot Press.

I. INTRODUCTION

The acts of renewable energy replacements in global communities and increasing concerns on reduction of greenhouse gases the utilization of renewable energy resources as an alternative to fossil fuels has been proposed by the scientist in recent years. Economical aspects of renewable energies appliances as alternative of fossil energy have been considered by many authors. Renewable energies may obtain directly from the natural reservoirs such as solar, wind and geothermal energies or conversion of waste energy e.g. waste heat by thermoelectric system [1-2].

Thermoelectric devices are used in a variety of applications; thermoelectric electric generator from waste heat is a well known application. They are also used in electronic cooling and portable refrigerators systems. A thermoelectric device operates on a circuit that incorporates both thermal and electrical effects to convert

heat energy into electrical energy or electrical energy to a temperature gradient. Thermoelectric elements are in a totally solid state, which contains semiconductor and semimetal elements such as Te, Bi, Sb, Se, Pb and Ge depend on the temperature where the appliance is used, [3].

Bismuth telluride based solid solutions have been widely used as materials for thermoelectric energy conversion near room temperature. In general, these materials are grown by a directional solidification method the method exhibits excellent thermoelectric properties in the growth direction. Materials grown by a directional solidification method have a disadvantage of poor mechanical properties because the basal plane its rhombohedral structure is cleavage plane. Currently, elements with robust mechanical property are required in the response to an increased demand for micro modules. One of methods to enhance the mechanical properties is to use the powder metallurgy [4-6].

Thermoelectric power generator is a solid-state heat engine in which the electron gas serves as the working fluid and converts a flow of heat into electricity. The phenomenon is also used to convert electric energy directly into cooling or heating energy. Design of thermoelectric system is an endeavor for the scientist [7-8]. Thermoelectric modules as a thermocouple (p and n types) are typically designed from bulk thermoelectric elements with flat ceramic plates for heat extraction and dissipation from surfaces of solid bodies. Each couple with different materials and properties requires extensive research for optimizations [9-11]. Single and polycrystalline (Bi₂Te₃)_x(Bi₂Se₃)_{1-x} alloys have been extensively investigated as p-type materials for Peltier coolers and thermoelectric generators if and when they are used at nearly room temperature. The thermoelectric figure of merit was found to be optimum as crystal has (Bi_{0.25}Sb_{0.75})₂Te₃ stoichiometry [12].

At present, there are several fabrication methods to improve cooling and mechanical properties of Bismuth Telluride-based compounds. One of these methods is the unidirectional crystal growth which usually improves thermoelectric properties. However, this process usually lasts long and their products are mechanically weak.

To improve mechanical properties of elements, several methods have been proposed, one example of which is pulverization of crystal rods [13], or $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ was fabricated by mechanically alloying then the product was hot pressed [14-15]. The present study discusses the efficiency of fabricated $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ compound which was crystallized by hot zone melting method then powdered eventually hot pressed and sintered at 350, 425 and 500 °C to improve its mechanical strength.

II. MATERIALS AND METHODS

A cylindrical rod of p-type thermoelectric crystals of $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ was prepared the same way as described in [16]. The rod was crushed in an agate mortar and pestle. The alloy powder to a particle size ratio of [64% with mesh 80 (200 μm^2)/36% with mesh 60 (250 μm^2)] was obtained. Several volumes of powder 2.1 g of weight were filled in steel mold of 5x5x20 mm³ pressed under 500 MPa compressive force to acquire samples of 5x5x20 mm³ size. These samples were sintered at the sintering temperatures of 350, 425 and 500 °C under 500 MPa compressive forces for a period of 10 min. Sintering condition including an axial pressure of 500 MPa and a sintering time of 10 min was tentatively obtained as optimally as possible. The density of the samples at each stage of hot pressing was measured as listed in Table 1. A number of characterizations were carried out under longitudinal and transverse directions. Longitudinal and transverse directions are those directions parallel and perpendicular to a direction that the sample is pressed, respectively.

Phase identification of the sintered compacts was examined by X-ray diffraction (XRD) in a Philips X'pert-system. In order to obtain a reference sample for the XRD profiles, some crushed powder was milled with ball-milling technique. Fractured surfaces of sintered material in longitudinal and transverse sections were examined using a Cambridge-30S scanning electron microscope (SEM). Thermal conductivity (κ) of the samples at different sintering temperatures was measured along the longitudinal direction by a device designed in our laboratory, details of the device can be sited in [17]. Density of the samples was measured on the base of Archimedes experiment by means of a balance system (Mettler-Toledo Model AG285) to understand the thermal conductivity behavior and mechanical strength variation.

III. RESULTS AND DISCUSSION

The results have been analyzed on the following two physical bases:

A. Material Structure Characterization

Structure formation was sensitive to chemical stoichiometry, so the fractions of the elements in the compounds had to be well defined. Structure characterization of the samples was carried out by XRD and SEM. Alongside the hot pressing process preferred orientations of grains in the crystals were studied; Figure

1(a) shows powdered $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ compound XRD pattern and indices as a reference data. The XRD patterns were recorded for different sintering temperatures and sample surfaces. Figure 1(b) and 1(c) illustrate XRD patterns from both transverse and longitudinal sections of samples that were hot pressed at various sintering temperatures of 350, 425 and 500 °C, the later found to be optimal in a view of mechanical strength.

Comparison of the sintered samples peaks intensity and indices have been made with the reference X-ray diffraction data. It will make clear that the microstructures of all samples in longitudinal direction (Figure 1(c)) are preferably orientated to (110) plane. However, in a transverse direction (Figure 1(b)) at 500 °C, not only strong diffraction peaks of the basal plane, (110), but also (006) and (205) planes, were observed. This indicates that the microstructures of materials were preferably orientated to the basal plane at 500 °C and the relative diffraction intensities are similar to those as referred to in the pulverizing result.

Micro-structural texture can be clearly verified by viewing fracture surfaces of the materials. Figure 2 summarizes the SEM images expose microstructures in the samples that were sintered at three typical temperatures (350, 425 and 500 °C) in both longitudinal and transverse directions. Images in longitudinal direction from the samples as sintered at different temperatures, especially those that have been sintered at lower temperatures demonstrate a layered structure and decomposed when it is handled for test. On the contrary to transverse direction, particularly those samples sintered at lower temperatures. Large cleaved flat grain facets were observed showing that basal planes (110) are well-matched with the XRD results. Once sintered at 500 °C, grains were rather randomly oriented, and the grain size was lowered. These observations suggest that the dynamic recrystallization has occurred during the sintering process at high temperatures.

B. Transport Properties

It is necessary to study the electronic transport properties of thermoelements to define its efficiency and figure of merit. Thermal conductivity is a reasonably straightforward concept when you are discussing heat transfer and allow you to make reasonable calculations

$$\dot{Q} = \kappa \frac{A\Delta T}{\Delta x} \quad (1)$$

where \dot{Q} heat flux (W) and A cross section (m²), ΔT thermal gradient (K) at length of Δx (m).

Thermal conductivity dominated by electronic, κ_{el} , lattice or phonon thermal conductivity, κ_L , and the bipolar thermal conductivity, κ_b [18].

$$\kappa = \kappa_{el} + \kappa_L + \kappa_b \quad (2)$$

As long as the band gap $E_g \geq 10kT$ and according to approximate relationship $E_g \approx 2e\alpha T$, we can neglect κ_b , thus:

$$\kappa = \kappa_{el} + \kappa_L \quad (3)$$

where κ_{el} expressed by Wiedemann-Franz law. This law in macroscopic conductors relates the electrical and thermal conductivities σ, κ via the condition $\kappa / \sigma T = L_o$, where the Lorenz number

$$L_o \equiv (\pi^2 / 3)(k_B / e)^2 \quad (4)$$

where k_B and e are Boltzmann's constant and the electron charge and L_o is normally close to the classical value of $L_o = (1.5 - 2.45) \times 10^{-8} \text{ V}^2 \text{K}^{-2}$, for metals and for semiconductors varies with the level of doping, σ is electrical conductivity. The law is satisfied with an accuracy of 5-10% in most metals and semiconductors at room temperature but fails in the temperature range $T \approx 10 - 100 \text{ K}$ [19]. Qualitatively, this relationship is based upon the fact that the heat and electrical transport both involve the free electrons in the metal. The thermal conductivity increases with the average particle velocity since that increases the forward transport of energy. However, the electrical conductivity decreases with particle velocity increases because the collisions divert the electrons from forward transport of charge.

At room temperature the thermal conductivity of metals, semiconductors and insulators is expressed as follow: for metals; $\kappa_{tot} = \kappa_L + \kappa_{el} \approx \kappa_{el}$;

$$\kappa_{tot} \approx 10 - 1000 \text{ W} \cdot (\text{m}^{-1} \text{K}^{-1}), \quad \text{semiconductors};$$

$$\kappa_{tot} = \kappa_L + \kappa_{el}; \quad \kappa_{el} < \kappa_L; \quad \kappa_{tot} \approx 1 - 100 \text{ W} \cdot (\text{m}^{-1} \text{K}^{-1}),$$

and insulators; $\kappa_{tot} = \kappa_L + \kappa_{el} \approx \kappa_L$;

$$\kappa_{tot} \approx 0.1 - 1 \text{ W} \cdot (\text{m}^{-1} \text{K}^{-1}).$$

It is also shown the contribution of the electronic, κ_{el} or lattice, κ_L dominates the thermal conductivity. However, study shows that the lower limit of lattice thermal conductivity for semiconductors is nearly $2 \text{ mW} \cdot (\text{m}^{-1} \text{K}^{-1})$. It is evident that the κ_{el} part of thermal conductivity shows the same variation under either orientation or sintering temperature. On the other hand, another part of the thermal conductivity, i.e. κ_L , is highly influenced by the grain size: fine-grain microstructure gives higher quantity of specific grain boundaries which result in an accelerated phonon-grain boundary scattering, and reduced thermal conductivity. The results obtained in this study are consistent with this theory. That is, with an increase in the sintering temperature, particularly when sintered at a temperature higher than $425 \text{ }^\circ\text{C}$, the grain boundaries were reduced due to recrystallization.

Considering electrical conductivity largely depends on the orientation tendency of the grains by sintering temperature as discussed in former paper [20].

Measuring Seebeck voltage carried out as one end was heated up and net voltage appeared between two ends of the leg. The Seebeck voltage was directly measured on the foam, as expressed by [21]. In metals, the Seebeck coefficient is much too low and often the thermal conductivity is too high, while in insulators the electrical conductivity is very small. Among the four

quantities involved in transport aspect, $\alpha, \sigma, \kappa_{el}$ and κ_L three of them are mainly related to the electronic structure of the material ($\alpha, \sigma, \kappa_{el}$) and one is mainly related to the lattice (κ_L). One possible way to improve the figure of merit is to reduce the lattice thermal conductivity without significantly altering the electronic properties of the material.

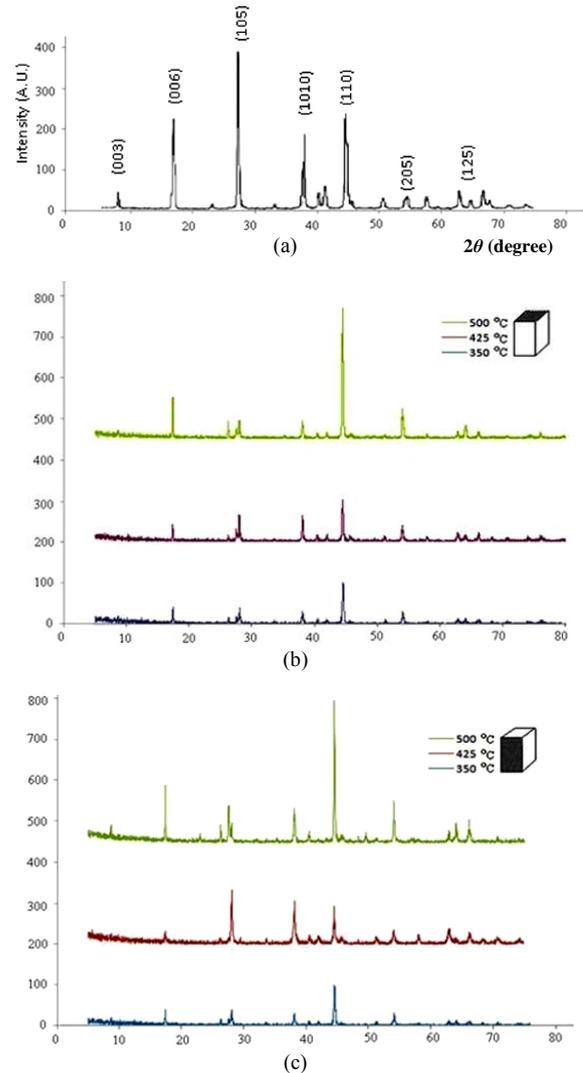


Figure 1. XRD patterns from: (a) powdered $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ compound as a reference, (b) the transverse and, (c) longitudinal sections of the samples sintered at typical temperatures (350, 425 and $500 \text{ }^\circ\text{C}$) sintering temperatures

Typical results of electrical conductivity of selected samples in longitudinal direction are $452, 523$ and $533 \text{ } (\Omega \cdot \text{cm})^{-1}$ at $350, 425$ and $500 \text{ }^\circ\text{C}$, respectively. Alongside, the measured values for thermal conductivity were $1.37, 1.46$ and $1.53 \text{ W} \cdot (\text{mK})^{-1}$ at $350, 425$ and $500 \text{ }^\circ\text{C}$, respectively. Table 1 listed these items accompanied with figure of merit and density. The table reveals that compressive force has severe effect on the thermoelectric parameters compared with, [15]; in particular it increases the inexplicable value for thermal conductivity. The values are very high for thermoelectric elements and results in an inferior figure of merit.

IV. CONCLUSIONS

Cylindrical rod of the p-type thermoelectric material $(Bi_{0.25}Sb_{0.75})_2Te_3$ was pulverized with to particle size below $220 \mu m^2$ [64% with mesh 80 ($200 \mu m^2$)/36% with mesh 60 ($250 \mu m^2$)]. Defined quantity of powder was pressed under 500 MPa simultaneously sintered at 350, 425 and 500 °C (hot pressed) for 10 min. The material structure, transport characteristics and thermoelectric properties were studied. Following conclusions were drawn from the experimental data:

Table 1. Typical results of electrical conductivity, thermal conductivity, figure of merit and density, were measured in longitudinal direction of selected samples pressed at 500 MPa, and three different temperatures for sintering time of ten minutes

Parameters	Present study Press at 500MPa. Sintering Time 10 minutes		
	350	425	500
$T(^{\circ}C)$	350	425	500
$\sigma_H ((\Omega.cm)^{-1})$	452	523	533
$\kappa (W.(mK)^{-1})$	1.37	1.46	1.53
$\alpha (\mu V.K^{-1})$	225	227.6	235
$Z = \alpha^2 \sigma / \kappa \times 10^{-3} (K^{-1})$	1.67	1.83	1.92
$d (gr.cm^{-3})$	6.43	6.54	6.71

1) Microstructures of hot pressed samples were well aligned along the basal planes in a transverse direction, particularly when sintered at lower sintering temperatures (i.e. 350 °C). However, an increased sintering temperature to 500 °C reduced this preferential orientation in the microstructure substantially by recrystallization and reducing the available grain boundaries. Increased temperature results in a position in which a sample becomes stringent against brittleness.

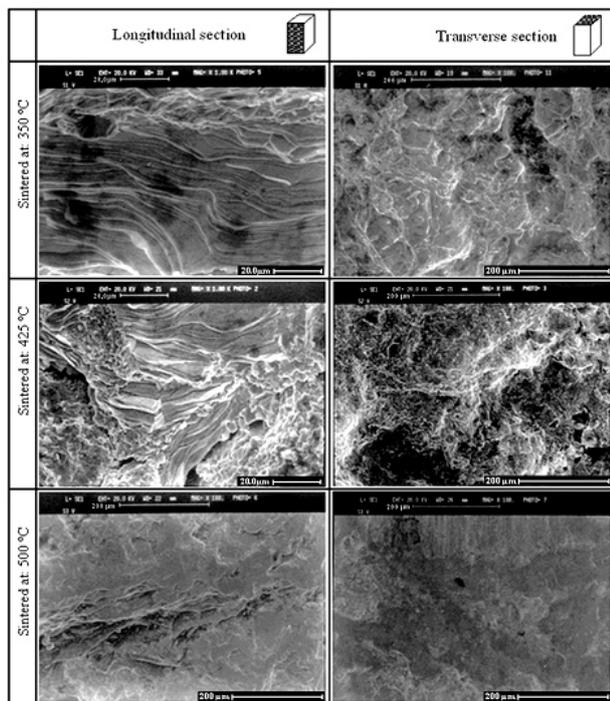


Figure 2. SEM microscopic images of microstructures of the materials sintered at three typical temperatures: 350, 425 and 500 °C, in both longitudinal and transverse directions

2) Hot press oxidized thermoelectric elements and unwanted impurities entered into the powder, that have sever effect on the thermoelectric parameters in particular they increase inexplicable value for thermal conductivity. The value is high enough for thermoelectric elements to results in an inferior figure of merit.

3) In terms of figure-of-merit the optimum sintering temperature was 500 °C leading to a maximum (Z) value.

4) Density of the samples depended on particle size and sintering temperature, small particle size resulted in an increment in density. This is reflected by the moderate variation in thermal conductivity of the materials at the higher part of the sintering temperature.

REFERENCES

[1] G.Sh. Mammadov, U.F. Samadova, F.F. Mammadov, "Economical Estimation of Solar and Wind Energies Application as Alternative of Fire Wood", International Journal on Technical and Physical Problems of Engineering (IJTPE), Issue 3, Vol. 2, No. 2, pp. 8-12, June 2010.

[2] Y. Aslan, "The Impacts of Renewable Energy Law on Turkish Wind Energy Sector", International Journal on Technical and Physical Problems of Engineering (IJTPE), Issue 5, Vol. 2, No. 4, pp. 92-96, December 2010.

[3] E.H. Cooke-Yarborough, F.W. Yeats, "The Harwell Thermomechanical Generator", Aere-R7714, Ukaea Publication, 1974.

[4] Y. Gelbstein, Z. Dashevsky, M.P. Dariel, "Powder Metallurgical Processing of Functionally Graded p-Pb_{1-x}Sn_xTe Materials for Thermoelectric Applications", Physica B: Condensed Matter, Vol. 391, Issue 2-1, pp. 256-265, April 2007.

[5] C.H. Lim, K.T. Kim, Y.H. Kim, Y.S. Lee, C.H. Lee, D.C. Cho, C.H. Lee, "Effect of Powder Mixing on Thermoelectric Properties in Bi₂Te₃ Based Sintered Compounds", Intermetallics, Vol. 14, Issues 10-11, pp. 1370-1374, October-November 2006.

[6] J.L. Cui, X. Qian, X.B. Zhao, "Mechanical And Transport Properties of Pseudo-Binary Alloys (PbTe)_{1-x}(SnTe)_x by Pressureless Sintering", Journal of Alloys and Compounds, Vol. 358, No. 1, pp. 228-234, August 2003.

[7] G. Casano, S. Piva, "Experimental Investigation of the Performance of a Thermoelectric Generator Based on Peltier Cells", Experimental Thermal and Fluid Science, Vol. 35, Issue 4, pp. 660-669, May 2011.

[8] M.G. Molina, L.E. Juanico, G.F. Rinalde, E. Tagliavolare, S. Gortari, "Design of Improved Controller for Thermoelectric Generator Used in Distributed Generation", International Journal of Hydrogen Energy, Vol. 35, Issue 11, pp. 5968-5973, 2010.

[9] M.A. Karri, E.F. Thacher, B.T. Helenbrook, "Exhaust Energy Conversion by Thermoelectric Generator: Two Case Studies", Energy Conversion and Management, Vol. 52, Issue 3, pp. 1596-1611, 2011.

[10] J.G. Noudem, S. Lemonnier, M. Prevel, E.S. Reddy, E. Guilmeau, C. Goupil, "Thermoelectric Ceramics for Generators", Journal of the European Ceramic Society, Vol. 28, Issue 1, pp. 41-48, 2008.

- [11] C.T. Hsu, G.Y. Huang, H.S. Chu, B. Yu, D.J. Yao, "Experiments and Simulations on Low-Temperature Waste Heat Harvesting System by Thermoelectric Power Generators", *Applied Energy*, Vol. 88, Issue 4, pp. 1291-1297, 2011.
- [12] H. Scherrer, S. Scherrer, "Handbook of Thermoelectrics", Edited by D.M. Rowe, CRC Press, Boca Raton, pp. 211, 1995.
- [13] K. Park, J.H. Seo, D.C. Cho, B.H. Choi, C.H. Lee, "Thermoelectric Properties of p-Type Te Doped $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ Fabricated by Powder Extrusion", *Materials Science and Engineering: B*, Vol. 88, Issue 1, pp. 103-106, January 2002.
- [14] T.S. Oh, D.B. Hyun, N.V. Kolomoets, "Thermoelectric Properties of the Hot-Pressed $(\text{Bi,Sb})_2(\text{Te,Se})_3$ Alloys", *Scripta Materialia*, Vol. 42, Issue 9, pp. 849-854, 2000.
- [15] N. Keawprak, Z.M. Sun, H. Hashimoto, M.W. Barsoum, "Effect of Sintering Temperature on the Thermoelectric Properties of Pulse Discharge Sintered $(\text{Bi}_{0.24}\text{Sb}_{0.76})_2\text{Te}_3$ Alloy", *Journal of Alloys and Compounds*, Vol. 397, pp. 236-244, 2005.
- [16] G. Kavei, M.A. Karami, "Fabrication and Characterization of The p-Type $(\text{Bi}_2\text{Te}_3)_x(\text{Sb}_2\text{Te}_3)_{1-x}$ Thermoelectric Crystals Prepared via Zone Melting", *Bulletin of Materials Science*, Vol. 29, No. 7, pp. 659-664, December 2006.
- [17] G. Kavei, Y. Zare, A. Seyyedi, "Tentative Design for Measurements of Absolute Value of Thermal Conductivity of Semi-Conducting Thermoelectric Elements: Material and Energy", *Journal of Thermoelectricity*, No. 2, pp. 57-61, 2008.
- [18] G.A. Slack, M.A. Hussain, "The Maximum Possible Conversion Efficiency of Silicon-Germanium Thermoelectric Generators", *Journal of Applied Physics*, Vol. 70, No. 5, pp. 2694-2698, September 1991.
- [19] M.G. Vavilov, A.D. Stone, "Failure of the Wiedemann-Franz Law in Mesoscopic Conductors", *Physical Review B*, Vol. 72, pp. 205107, 2005.

- [20] G. Kavei, B. Alinejad, K.Sh. Kahramanov, A. Kazemzadeh, M.A. Karami, "Effect of Sintering Temperature on the Properties of Powdered $(\text{Bi}_{0.25}\text{Sb}_{0.75})_2\text{Te}_3$ Thermoelectric", *Journal of Thermoelectricity*, No. 3, pp. 31-45, 2008.
- [21] A.V. Petrov, ed. V.A. Kutasov, "Thermoelectric Properties of Semiconductors", New York: Consultants Bureau, pp. 17-22, 1964.

BIOGRAPHIES



Ghassem Kavei received his B.S. in Applied Physics from Tabriz University, Tabriz, Iran, and the M.S. degree in Atomic Physics from the Southampton University, UK and the Ph.D. in Surface Physics from the Keele University, UK. He is a member of Iranian Crystallography Association (ICA) and Iranian Physics Society (IPS). He has co-authored approximately 11 books, and has published over 85 publications on various aspects of atomic physics, thermoelectric, TiO_2 thin film, SPM application, ITO thin film and nano-science and technology. He was also a lecturer at several universities in Iran teaching different subject in electron physics. Currently, he is a Research Professor at the Material and Energy Research Centre (MERC) in Tehran, Iran and applied for a permission to publish a periodical scientific "International Materials Physics Journal".



Ashkan Kavei was born in Iran, 1990. He is a second year mechanical engineering student. Along his studying, he is intended to continue his research in renewable energies. He is a member of Renewable and Solar Energy Society sponsored by Parseh Company, Tehran, Iran.