INTERNATIONAL BULLETIN OF APPLIED SCIENCE AND TECHNOLOGY
IF = 9.2
IBAST
ISSN: 2750-3402

THERMOELECTRIC ENERGY CONVERSION: PHYSICAL PRINCIPLES AND METHODS FOR HIGH-PERFORMANCE MATERIAL GROWTH

Abdujabborov Murodjon Abdugafur ugli
Yusupov Abdurashid Khamidillaevich
Andijan state technical institute

https://doi.org/10.5281/zenodo.18015793

Abstract: Thermoelectric instrumentation is today one of the most rapidly developing high-tech fields, both in our country and abroad. Fundamental research by scientists has established the theory for the energetic application of thermoelectric phenomena, opening up broad scientific and practical opportunities to use semiconductor thermoelectric converters effectively in various technical fields.

Key words: Thermoelectric materials; Seebeck effect; Peltier effect; Thermoelectric energy conversion; Semiconductor thermoelectrics; Crystal growth methods; Zone melting; Czochralski method; Extrusion process; Narrow-gap crystallization; Material purification; Figure of merit (ZT); Bismuth telluride–based compounds

Introduction

Over the last decade, the worldwide production of thermoelectric cooling modules has grown at an average annual rate of 15–25%. Such high and stable growth rates are typically characteristic of advanced technological products like computer hardware and software. The rapid development of this field in recent decades is primarily explained by the emergence of compact thermal management systems for various devices, the creation of localized cooling zones, the intensification of heat exchange processes in complex structures, and the possibility of generating electric power based on alternative methods.

The main factor behind the sharp rise in interest in thermoelectric energy conversion is the absolute environmental cleanliness of this method. Unlike conventional vapor-compression power conversion technologies, the thermoelectric conversion process produces no harmful emissions and has no negative impact on the environment. As the global community increasingly recognizes the urgency of environmental protection, this factor is being promoted as a key advantage of thermoelectric technology.

For the stable and rapid development of this technical field, it is important to continuously supply highly qualified specialists who have a strong command of thermoelectric energy conversion theory and practice, thermoelectric materials science, and the application characteristics of these technologies in various sectors. This article is aimed at systematizing the existing knowledge in the field of thermoelectric energy conversion.

Theoretical part

Theoretical and experimental studies have identified three fundamental thermoelectric phenomena that occur at junctions of dissimilar metals, semiconductors, or conductors. These are the Seebeck, Peltier, and Thomson effects.

Seebeck Effect: This effect was first discovered in 1821 by the German scientist T. Seebeck and described scientifically. The Seebeck effect is characterized by the generation of an electromotive force (EMF) in a closed electric circuit made of different materials when a temperature difference exists between the junctions. In other words, the presence of a temperature gradient in the system serves as the driving factor that produces an electric current.

Qualitatively, the Seebeck effect can be explained by the fact that increasing temperature leads to an increase in the number of free charge carriers (especially in semiconductors) and an increase in their energy. If a temperature difference is maintained along a conductor, the electrons at the hot end have higher energy and velocity than those at the cold end. As a result, charge carriers migrate from the hot region toward the cold region, and an electric charge accumulates at the cold end corresponding to the charge of those carriers.

This charge accumulation continues until the electric (Coulomb) field produced in the thermoelement network by the separated charges balances the diffusion forces caused by the temperature gradient. That is, the flow of charge carriers from the hot end to the cold end ceases. The sum of the potential differences generated in the circuit constitutes one component of the thermoelectric EMF.

A second component of the thermoelectric EMF is associated with contact potential differences. If both junctions of the thermoelectric element are at the same temperature, the contact potential differences at the two junctions are equal in magnitude but opposite in direction, and thus they cancel each other out. Conversely, if the junction temperatures are different, the contact potential difference contributes significantly to the total thermoelectric EMF.

The Seebeck phenomenon is observed in virtually all types of materials, including electrolytic environments, liquid solutions, and crystalline solids. The temperature dependence of the thermoelectric EMF has been studied over a wide temperature range, even down to absolute zero.

It has been found that if the direction of an electric current flowing through a junction coincides with the direction of the contact potential difference, Peltier heat is absorbed. On the other hand, if the current flows opposite to the contact potential difference, heat is evolved at the junction.

Peltier Effect: The Peltier effect occurs due to the movement of charge carriers (electrons or holes) from one material to another when an electric current passes through a junction of two different materials. The key point is that the equilibrium energy of electrons and holes is not the same in different materials. As a result, charge carriers that move from material I to material II across a junction carry excess energy relative to the carriers in material II (Figure-2). This excess energy is transferred to the lattice of material II during the carriers' initial collisions with lattice atoms, which leads to heat being released at the junction and a rise in temperature in the contact region.

If the current direction is reversed such that charge carriers move from material II (where their energy is lower) toward material I (where their energy is higher), then as the carriers cross the junction they compensate for their energy deficit by drawing energy from the crystal lattice of material II. This process also occurs during the carriers' first collisions with lattice atoms, and as a result heat is absorbed at the junction — a cooling effect is observed [1].

The Peltier phenomenon is a surface (contact) effect, meaning that the energy exchange between charge carriers and the crystal lattice occurs over very short distances on the order of only a few times the carriers' mean free path. Essentially, the charge carriers exchange energy with lattice atoms in the very first collisions after crossing the junction.

In terms of its physical nature, the Peltier effect is the inverse of the Seebeck effect. Just like the Seebeck phenomenon, the Peltier effect is observed in many different materials, and the Peltier coefficient has a complex dependence on temperature.

The cost of semiconductor thermoelectric materials constitutes a significant portion of the overall production expenses for thermoelectric modules. For this reason, most leading manufacturers of thermoelectric modules engage in the independent synthesis and growth of these materials. To remain competitive in the market, thermoelectric materials are required to have sufficiently high physicochemical and technological performance. However, as the quality of a material improves, its production cost also rises markedly. Consequently, all current technologies for producing thermoelectric materials represent a certain compromise between material quality and economic efficiency [2].

This situation is explained by several fundamental factors: First, Non-stoichiometric Composition: Most thermoelectric materials do not have a strict stoichiometric composition; they belong to the class of berthollide compounds. In such compounds, the ratio of cations to anions can vary within certain limits, leading to changes in the concentration of charge carriers. As a result, the carrier concentration deviates from the optimal value and the material's thermoelectric efficiency decreases. Moreover, the crystallization (melting) temperature often corresponds to neither the stoichiometric composition nor the optimal composition. Therefore, special technological measures and controlled growth methods must be employed to obtain crystals with the required composition and properties.

Second, Anisotropy and Thermal Stresses: Thermoelectric materials are characterized by significantly anisotropic electrical and mechanical properties. When growing large-diameter single crystals, uneven heat distribution can occur throughout the crystal volume, causing increased internal thermal stresses. These stresses lead to the formation of cracks and other mechanical defects in the crystal structure.

Third, Multi-component Segregation: Thermoelectric materials are multi-component solid solutions. In these systems, each component has a different distribution (segregation) coefficient during crystallization. As the crystal grows, this can result in a non-uniform composition along the length of the crystal. Consequently, without special technological interventions, the electrical parameters of the material can vary significantly from one end of the crystal to the other.

Therefore, in the process of obtaining high-quality thermoelectric materials, it is crucial to employ specialized technological approaches that take into account all the above factors in combination — ensuring compositional stability, controlling the charge carrier concentration, and carefully managing the crystal growth conditions [3].

Methods

To grow high-quality single crystals or achieve an oriented polycrystalline structure in thermoelectric materials, it is important to start with sufficiently pure raw elements such as bismuth (Bi), antimony (Sb), selenium (Se), and tellurium (Te). In practice, selenium is available at relatively high purity on an industrial scale, but the purification of tellurium, antimony, and bismuth presents certain challenges, with tellurium in particular often posing the greatest difficulties.

Some manufacturers prefer to use relatively cheap but unrefined tellurium, while others work with highly purified but much more expensive tellurium. As a result, certain companies carry out additional in-house purification of tellurium. The method of vacuum distillation (sublimation) is considered effective for removing many impurities from tellurium. The same physicochemical principle can be applied to the purification of antimony.

However, it is known that sublimation of antimony is not sufficiently effective for removing impurities such as lead (Pb) and arsenic (As). Arsenic impurities typically do not significantly affect the material's properties, whereas lead acts as a donor and alters the charge carrier concentration. Therefore, the antimony purification process via sublimation must be organized in a way that maximizes the use of the small differences in the physical properties of Sb, As, and Pb to achieve effective separation of these impurities.

The process for purifying bismuth, on the other hand, usually follows a standard technological procedure well documented in the scientific and technical literature. It involves filtering the molten bismuth to remove oxides (which are invariably present in metallic bismuth) in order to eliminate these impurities.

Virtually all known crystal growth methods can be utilized for obtaining thermoelectric materials. The primary requirement is to sufficiently adapt the chosen method to the specific physicochemical properties of the material in question. Since each crystal growth technique has its own unique advantages and limitations, no single method can be considered absolutely superior to the others. Therefore, in practice, the choice of growth method is made by taking into account a combination of factors such as the material's composition, the intended application, and economic efficiency.

Currently, the vertical zone melting method is one of the most widely used technologies for producing thermoelectric materials. In this method, the aim is usually not to grow a perfect single crystal, but rather to form a polycrystalline ingot comprised of aligned (directionally oriented) crystals. The main advantage of this method is that it is relatively simple and stable from a technological standpoint [4].

In the zone melting process, the thermoelectric material is placed inside an ampoule made of quartz or a special high-temperature resistant glass. By moving the ampoule in the vertical direction, the material sequentially passes from bottom to top through different temperature zones (growth stages). Crystallization occurs primarily in the lower part of the ampoule, and it is in this region that the oriented crystal structures form (Figure-4).

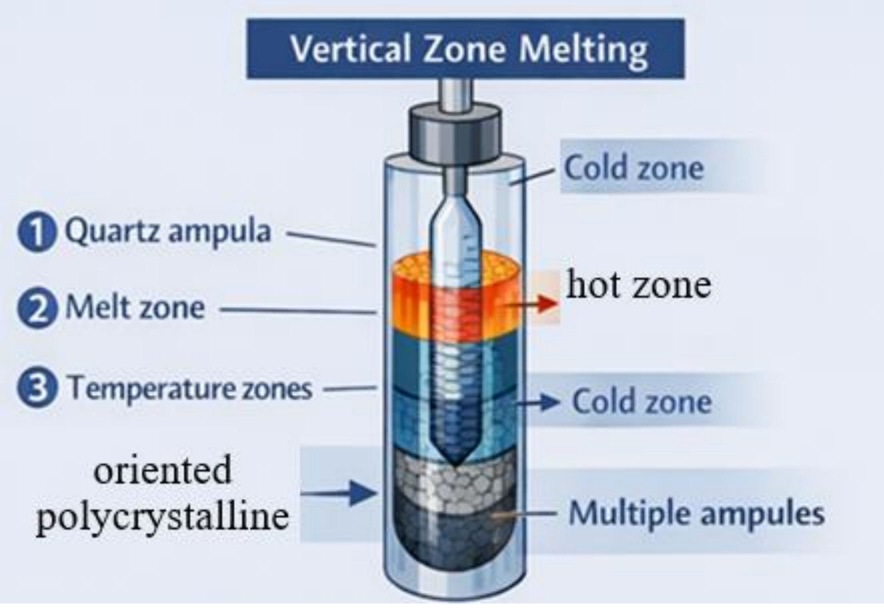

Figure-1. vertical zone melting method of obtaining thermoelectric material

Preparation of the ampoules involves coating their inner surfaces with a layer of pyrolytic graphite. This graphite layer serves to prevent the molten thermoelectric material from chemically interacting with the quartz ampoule. The crystal growth rate is typically on the order of ~0.1 mm/min for n-type materials, whereas slightly higher growth rates can be used for p-type materials. The temperature gradient at the solidification front is generally on the order of 100–150 C/cm.

In the classical zone melting technique, the width of the molten zone is usually kept small. However, in some cases it is advantageous to widen the molten zone, since a wider molten zone can lead to a more uniform distribution of material properties along the length of the ingot.

The principal advantage of the vertical zone melting method — and a key reason for its widespread adoption — is that it allows simultaneous processing of multiple ampoules (Figure 5). This yields a high production throughput for the method. The heaters (or groups of heaters) are typically connected in series. Temperature control is achieved using a thermocouple installed in a special empty (dummy) ampoule that models the heating conditions of the working ampoules. Moreover, the equipment designed for this technology is relatively inexpensive and compact, and the crystal growth process does not require continuous active intervention by an operator.

One serious drawback of this technology is the necessity of using expensive quartz ampoules. To reduce production costs, these ampoules are usually reused after undergoing chemical etching and thorough washing processes. Such treatments are aimed at completely removing any residual thermoelectric material from the previous growth cycle.

However, if an ampoule is accidentally damaged during operation, the thermoelectric material inside becomes entirely unusable. In addition, if the molten material leaks onto the furnace's heating elements, it can cause the entire equipment to fail. Therefore, the equipment's design must include an emergency safety system that can quickly shut off each heater or group of heaters in the event of an emergency. After crystal growth, the ingot is cut from both the top and bottom ends. In modern industrial practice, these cut-off pieces are reused as secondary raw material. The ingots, with their ends removed, are then sent for evaluation of their thermoelectric properties. This quality control typically involves measuring the Seebeck coefficient (α) and the electrical conductivity (σ) of the material [5].

Sorting of the products by quality (grading) is often carried out based on the values of these parameters and the degree of their uniformity along the ingot, since these parameters are the primary factors determining the practical performance of thermoelectric materials.

In practice, a certain amount of scatter in the electrical properties of the ingots is observed. Therefore, in subsequent processing steps, batches of ingots are formed such that each batch consists of ingots providing the required average values of the electrical parameters. Using the zone melting method, thermoelectric materials can achieve a figure of merit up to about $Z \approx (3.0–3.2)\times10^{-3}\ K^{-1}$.

The Czochralski method is widely used in modern electronics to grow large-diameter single crystals, including Si, GaAs, and other semiconductor materials. A schematic diagram of this method is shown in Figure 6. In this process, the thermoelectric material is melted in a crucible (marked 2 in the figure). To prevent the melt from evaporating, a flux layer of boron oxide (B_2O_3) (marked 3) is maintained on top of the melt [6].

The crucible is placed inside a special holder (6) that rotates the crucible during the process. The required thermal conditions are provided by a graphite heater (5). A pre-prepared seed crystal is introduced into the melt, and a single crystal is pulled (drawn) from the melt using this seed. The holder to which the seed crystal is attached is pulled upward at a controlled speed, and at the same time the crucible is rotated in the opposite direction to the holder's rotation.

All components of the process are contained within a hermetically sealed chamber. The chamber is initially evacuated, and then filled with an inert gas. Additional technological devices and control systems are used to make the composition and physical properties of the growing crystal more uniform.

In some cases, the crucible used in the Czochralski method can be a floating crucible, which is connected to the main body of molten material through a narrow opening. The crystal is pulled from a small volume of melt in this floating crucible. This approach helps to maintain a stable composition of the melt in the crucible. In addition, independent feeding systems can be employed to supply extra amounts of specific components (dopants or constituents) to the melt to compensate for their depletion during the growth process [7].

Figure-2. Czochralski method of obtaining thermoelectric material

Using the Czochralski method, single crystals up to 50 mm in diameter can be obtained. The crystals produced by this technique exhibit the highest thermoelectric performance. However, high-quality crystals can easily fracture along certain cleavage planes. In practice, this often occurs during the process of cutting the grown material into segments (for example, when slicing ingots into elements for modules), which leads to a high reject rate.

Another disadvantage of the Czochralski method is the high cost of the crystal growth equipment and its lower production throughput compared to the vertical zone melting method. For this reason, the Czochralski method is primarily recommended in special cases when unique, high-quality crystals with particular properties are required for thermoelectric modules [8-9].

Extrusion Method

In recent years, the extrusion method has become increasingly widespread for the production of thermoelectric materials. The essence of this method is illustrated in Figure 7. The thermoelectric material (4) is placed into a special press-die (matrix) (2) which has been preheated to approximately $T_e \approx 0{,}8T_{pl}$ (about 80% of its melting temperature). A punch (1) is then placed on top of the material, and the required pressure is applied. Under this pressure, the material is forced out through the die orifice (5). In this way, a polycrystalline rod with a well-defined texture is obtained.

In practice, the process is carried out as follows: first, a “tablet” (pellet) of the thermoelectric material is formed in a cold or slightly warmed press die. This pellet is then coated with a colloidal graphite solution in water (known as Aquadag) to prevent the material from sticking to the hot walls of the press die. The pellet is then placed into the heated die, and the extrusion process begins.

The extrusion process yields rods of material with a diameter of about 20–25 mm. For a thermoelectric material with composition $Bi_{0.5}Sb_{1.5}Te_3$, the die’s operating temperature is maintained in the range of 370–410 °C. The punch moves at a speed of approximately 1–2 mm/min, and the applied pressure ranges from about 20–30 t/cm^2. These parameters serve to form the polycrystalline structure of the material and improve its texture characteristics [10-12].

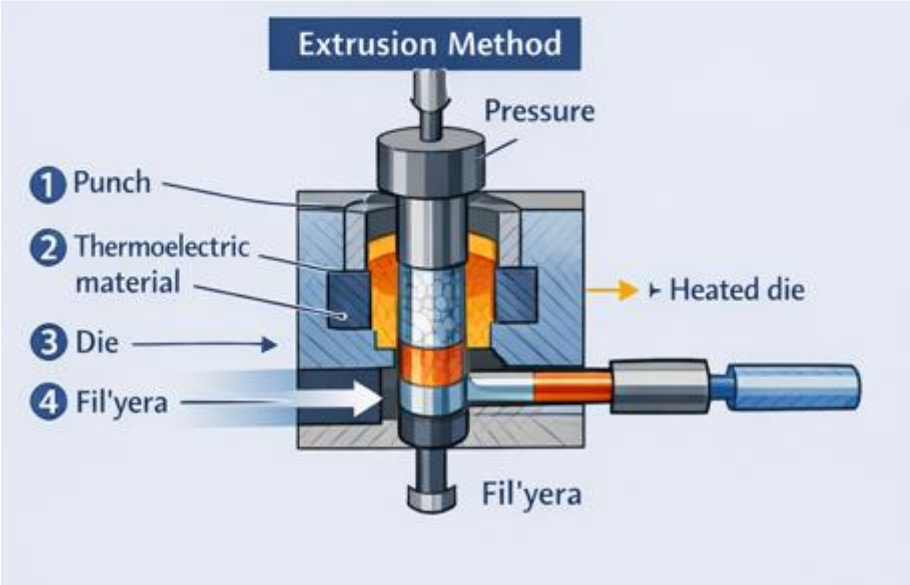

Figure-3. Extrusion method of obtaining thermoelectric material

The primary advantage of this method is its technological simplicity and straightforwardness. Another important positive aspect is the near-complete utilization of the material – there is very little waste. The p-type materials obtained by this method exhibit high thermoelectric efficiency, with a figure of merit Z reaching approximately $3\cdot10^{-3}\ K^{-1}$. The rods produced by extrusion also possess high mechanical strength.

However, a limitation of the extrusion method is that it produces highly efficient materials only of p-type. The thermoelectric efficiency of n-type materials obtained by extrusion is considerably lower, usually not exceeding about $2{,}7\cdot10^{-3}\ K^{-1}$. Nevertheless, in many practical applications, a combination of a high-performance p-type material with a medium-performance n-type material is sufficient to provide the required overall performance [13-14].

Crystallization in Narrow Gaps. In this method, the thermoelectric material melt is poured between two narrow graphite plates, and a temperature gradient is established along the plates. The main advantage of the narrow-gap crystallization method is that by using multiple narrow-gap layers simultaneously, it is possible to manufacture a large number of thermoelectric plates at once (Figure 8). Pouring the melt into the graphite assembly can be performed in open air because the graphite creates a reducing environment that protects the material from oxidation.

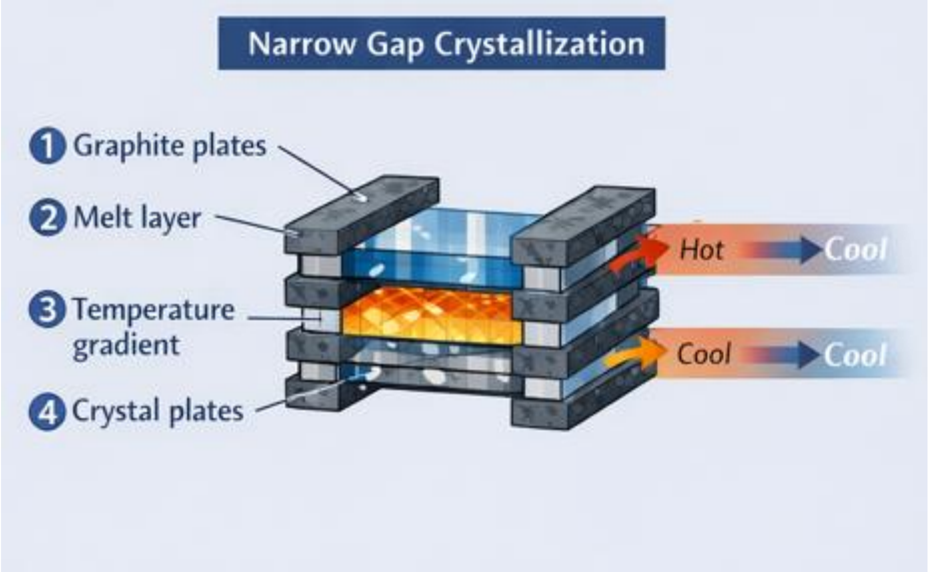

Figure-4. Narrow gap crystallization method of obtaining thermoelectric material

This crystal growth method offers high productivity and technological simplicity, and it does not require large labor expenditures.

However, the method does have drawbacks. Because crystallization in this approach is not tightly controlled, the proportion of defective products (rejects) is significant. On the other hand, the ease with which the material can be recycled and remelted provides a partial compensation for this drawback. Another issue is the necessity of applying anti-diffusion coatings to the thermoelectric material ingots instead of to individual plates, which makes the process more labor-intensive [15-16].

The methods described above do not encompass all possible techniques for obtaining thermoelectric materials. Nevertheless, in today's production of thermoelectric modules, the aforementioned methods are among the most widely used and practically effective technologies.

Conclusion

This study analyzed the fundamental thermoelectric effects and the main technological approaches used for the production of thermoelectric materials. The results confirm that the performance of thermoelectric devices is strongly governed by material properties such as charge carrier concentration, crystal structure, anisotropy, and compositional uniformity. These factors directly determine the efficiency and reliability of thermoelectric energy conversion systems.

A comparative assessment of vertical zone melting, Czochralski growth, extrusion, and narrow-gap crystallization demonstrates that no single technology is universally optimal. Each method represents a trade-off between material quality, production cost, mechanical yield, and scalability. Vertical zone melting is well suited for large-scale production, Czochralski growth provides the highest-quality single crystals, extrusion enables efficient fabrication of mechanically robust p-type materials, and narrow-gap crystallization offers high productivity with reduced process control.

The study further emphasizes the critical role of raw material purity and purification techniques, particularly for tellurium, antimony, and bismuth, in achieving stable and reproducible thermoelectric properties. Overall, the findings indicate that the successful development of advanced thermoelectric materials requires an integrated approach combining fundamental understanding, controlled material synthesis, and rational selection of growth technologies. Future progress in thermoelectric cooling and power generation will depend on continued optimization of synthesis processes and the development of cost-effective, scalable manufacturing methods.

References:

1.Priyadarshini Balasubramanian, Manjusha Battabyal*, Raghavan Gopalan. Improving the oxidation resistance of thermoelectric Mg2Si leg with silica coating. Materials Letters 312 (2022) 131599. https://doi.org/10.1016/j.matlet.2021.131599

2.Roberta Farris, Maria Barbara Maccioni, Alessio Filippetti, and Vincenzo Fiorentini. Theory of thermoelectricity in Mg3Sb2 with an energy- and temperature-dependent relaxation time. Article in Journal of Physics Condensed Matter·November 2018. DOI: 10.1088/1361-648X/aaf364; https://www.researchgate.net/publication/329157932

3.Md. Mahmudur Rahman, A.K.M. Ashiquzzaman Shawon, Soon-Chul Ur. Effect of Excessive Antimony on the Thermoelectric and Transport Properties of Mg3Sb2 Synthesized by Controlled Melting, Pulverizing Followed by Vacuum Hot Pressing. Electronic Materials Letters (2021) 17:102– https://doi.org/10.1007/s13391-020-00251-y

4.Jiawei Zhang, Lirong Song and Bo Brummerstedt Iversen. Insights into the design of thermoelectric Mg3Sb2 and its analogs by combining theory and experiment. npj Computational Materials (2019) 5:76; https://doi.org/10.1038/s41524-019-0215-y.

5.Lihong Huang, Tong Liu, Xiaobo Mo, Guocai Yuan, Runyu Wang, Hang Liu, Xiaobo Lei, Qinyong Zhang, Zhifeng Ren. Thermoelectric performance improvement of p-type Mg3Sb2-based materials by Zn and Ag co-doping. Materials Today Physics 21 (2021) 100564; https://doi.org/10.1016/j.mtphys.2021.100564

6.Thermoelectricity: Electronic Skutterudites". J. Applied Solar Energy 2017 No.2, pp. 37-40.

7.B.M. Abdurakhmanov, M.M. Adilov, M.Kh. Ashurov, Kh.B. Ashurov, Sh.K. Kuchkanov, S.E. Maksimov, B.L. Oxengendler. "Thermoelectric characteristics of granular semiconductors with resonant tunneling of charge carriers for the conversion of the thermal component of solar radiation" J. Applied Solar Energy, 2015. No. 4. S.22-27.

8.10. F.L. Omonboev, L.O. Olimov, B.M. Abdurakhmanov. Conductivity and Seebeck coefficient in granular silicon. The American Journal of Engineering and Technology. March 25, 2021. Pages: 28-35. Doi: https://doi.org/10.37547/tajet/Volume03Issue03-05

9.Patent UZ № FAP 01593 "Method of preparation of thermoelectric material". L.O. Olimov, I.I.

10.Anarboev, A.Mamirov, F.L. Omonboev, M.L. Omonboeva (eds) (2021)

11.Patent Uz IAP 0561 Thermoelectric material and its preparation method. 29.06.2018. Bull., No. 6.

12.B.M. Abdurakhmanov, M.M. Adilov, M.Kh. Ashurov, and others.

13.L.O. Olimov, Anarboyev I.I. Some Electrophysical Properties of Polycrystalline Silicon Obtained in a

14.Solar Oven. Silicon 14(8), PP3817 – 3822. 2022. https://doi.org/10.1007/s12633-021-01596-1

15. L.O. Olimov, I.I. Anarboyev. Some electrophysical properties of polycrystalline silicon obtained in a solar oven. International Journal of Physics & Mathematics, 4(1), 39-45. (2021). https://media.neliti.com/media/publications/410793-some-electrophysical-properties-of-polyc-4e03e9d.pdf

16.L.O. Olimov, I.I. Anarboyev. Microcructure of Polycrystal Silicon Heated by Sunlight. RA Journal Of Applied research. V:07 11 November-2021. Page no.-2669-2671. (2021) Available online at www.rajournals.in