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SYNTHESIS OF NH_4I-DOPED Bi_2Te_3-BASED THERMOELECTRIC MATERIALS IN AN INERT GAS ATMOSPHERE USING AN AUTOMATED SYSTEM

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This article presents a comprehensive approach aimed at the full automation of the technology for producing semiconductor thermoelectric materials. The main stages of the technological chain are automatic dosing of high-purity raw materials in precise stoichiometric ratios. The combined use of vacuum at 10^{-3} Torr and an inert gas atmosphere (argon at 1.5 atm), holding at a temperature of 720°C for 5–6 hours, crystal growth by the zone melting method, and the cooling (annealing) regime—are analyzed as a single optimized process. The temperature–time profile, diffusion processes, and cooling dynamics are substantiated on the basis of physical models, including Fick's law and Newton's law of cooling. It is shown that real-time control of technological parameters using PLC controllers, SCADA systems, and artificial intelligence algorithms ensures phase homogeneity of the material, reduces defect density, and stabilizes electrophysical parameters. In ammonium iodide–doped Bi_2Te_3 thermoelement samples, the stability of electrical conductivity, the Seebeck coefficient, and the power factor along the entire sample length confirms the homogeneous distribution of dopant additives and the formation of a high-quality crystal structure. The obtained results demonstrate the high potential of the proposed automated technology for the effective application of Bi2Te3-based materials in low- and medium-temperature thermoelectric devices.
Keywords: *Thermoelectric materials; Bi_2Te_3; Automation; Vacuum environment; Inert gas; Zone melting; Annealing; SCADA; PLC; Seebeck coefficient; ZT*

1. INTRODUCTION

Thermoelectric materials can directly convert thermal energy into electrical energy and therefore play an important role in modern energy technologies, space engineering, and microelectronics [1,2]. Achieving high efficiency requires precise control over the material composition, crystal structure, and defect concentration [3]. For this reason, the full automation of thermoelectric material synthesis technologies represents a pressing scientific and practical challenge [4,5,6].

In the fabrication of semiconductor thermoelectric materials, it is crucial to prepare high-purity chemical elements in exact stoichiometric ratios using automated weighing and vacuum dosing systems [7,8,9]. High-purity raw materials, namely Bi-000 and Te-T-B3, were utilized in this process. Such high material purity effectively prevents the formation of secondary phases during synthesis, thereby stabilizing the electrophysical parameters of the resulting material [1,5]. In the production of semiconductor thermoelectric materials, the preparation of high-purity chemical elements in exact stoichiometric ratios using automated weighing systems and vacuum dosing units is of critical importance [4,10]. Accurate control of the raw material composition prevents the formation of secondary phases during subsequent synthesis stages and stabilizes the material's electrophysical parameters [5,11]. In technological processes, the granularity and degree of grinding of the raw materials are also of particular significance [4,6], since the amount of heat required to melt and initiate chemical reactions is directly related to particle size. If the granularity of the raw material is too large, complete melting requires more energy, reducing the efficiency of the technological process. Moreover, high temperatures increase the probability of evaporation of volatile components (such as tellurium or selenium), leading to stoichiometric imbalance in the material composition and degradation of thermoelectric properties [5,11]. Therefore, selecting an optimal grinding degree and controlling it via automated systems are key prerequisites for obtaining high-quality thermoelectric materials [7,8,9].

The synthesis stage is one of the most critical steps in the technology of producing semiconductor thermoelectric materials. This process is typically carried out under vacuum conditions at pressures on the order of 10^{-3} Torr. Such a vacuum level significantly reduces the influence of oxygen and other reactive gases, thereby preventing oxidation of the material [2]. Although partial evaporation of volatile components (e.g., tellurium) may occur under reduced pressure, optimizing the vacuum level minimizes these losses. The vacuum environment enhances diffusion processes during synthesis and ensures melt homogeneity [1,4,6]. As a result, a precursor with optimal chemical and structural properties suitable for subsequent crystal growth is obtained. Therefore, continuous automated control of the temperature–time profile and the vacuum level is a fundamental condition for producing high-quality thermoelectric materials [12,13,14].

Melting is carried out in automated furnaces operating in an inert gas atmosphere. The use of inert gases such as argon prevents oxidation of the material during the reaction process and reduces the loss of volatile components [6].

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During melting, the temperature regime, heating rate, and holding time are precisely controlled using digital controllers [12,13,14], ensuring complete reaction of components and the formation of a homogeneous melt. Automated control systems minimize deviations from preset temperature values, thereby guaranteeing chemical composition stability and phase homogeneity of the synthesized material. Precise control of synthesis parameters reduces stoichiometric deviations and creates optimal conditions for subsequent crystal growth, which directly affects the electrophysical and thermoelectric properties of semiconductor thermoelectric materials.

Accurate control of the temperature–time profile during synthesis is crucial for ensuring melting efficiency and compositional uniformity. The melting process is generally implemented using a stepwise heating regime, where the temperature variation over time can be described by the following relation:

$$T(t) = T_0 + \beta t$$

where (T_0) is the initial temperature, ($\beta = dT/dt$) is the heating rate, and (t) is time.

The optimal heating rate is selected based on the melting temperatures and thermal conductivity properties of the components [4,6]. Excessively high heating rates may lead to thermal instability and localized overheating. Whereas excessively low rates unnecessarily prolong the synthesis process.

Maintaining the material at the maximum melting temperature for a specified duration (isothermal stage) ensures complete melting of components and completion of chemical reactions. Stable temperature conditions during this stage positively influence the stoichiometric accuracy of the material composition [1,4,6].

The performance of thermoelectric materials is closely governed by their structural homogeneity and defect levels. Conventional synthesis techniques often suffer from stoichiometric disruptions due to deviations in the temperature profile, oxidation, and evaporation of volatile elements such as tellurium. Additionally, doping with standard pure iodine introduces significant drawbacks, including high hygroscopicity and a heterogeneous distribution of electrophysical properties across the bulk sample.

In the fabrication of semiconductor thermoelectric materials, the crystal growth stage is a decisive process that determines the microstructure, defect density, and electrophysical properties of the material [1,6]. The zone melting method is widely recognized as one of the most effective techniques for producing high-quality, phase-homogeneous, and low-defect crystals [1,6].

The fundamental principle of this method is to create a localized molten zone within a limited region of the sample and move it along the length of the material at a controlled velocity. As the molten zone travels, recrystallization occurs, resulting in the formation of a solid phase with improved structural quality [1]. The temperature gradient during zone melting plays a critical role: excessively large gradients increase thermal stress and may cause cracking, whereas excessively small gradients can lead to unstable crystal growth. Therefore, the gradient value is optimally selected according to the specific material [1,6].

The velocity of the molten zone is one of the most important parameters of the zone melting process [1,6]. If the zone velocity is too high, there is insufficient time for diffusion, leading to compositional inhomogeneity and increased defect density. Conversely, excessively low velocities prolong the process and reduce technological efficiency. In practice, the zone movement speed is typically selected in the millimeter-per-hour range [1].

An additional advantage of the zone melting method is its ability to achieve compositional purification (zone refining) [1]. Certain impurity elements and contaminant atoms accumulate in the molten zone and are displaced toward the end of the sample during crystal growth. This enables high purity in the main portion of the crystal, which is critically important for thermoelectric materials.

2. METHODS

Conducting the zone melting process under vacuum or an inert gas prevents oxidation and limits the formation of vacancies and defects. Automated control of all parameters—temperature, zone length, movement speed, and ambient pressure—ensures high reproducibility of crystal quality [12,13,14]. As a result, semiconductor thermoelectric crystals obtained by the zone melting technique exhibit high structural homogeneity, low defect density, and stable thermoelectric parameters, making them suitable for use in high-efficiency thermoelectric devices.

The synthesis of semiconductor thermoelectric materials is carried out using a combination of vacuum and inert gas environments (Fig. 1). Initially, the prepared raw materials are placed in a specially designed hermetic container, and the system is evacuated stepwise using vacuum pumps. When the vacuum level reaches approximately 10^{-3} Torr, the container is hermetically sealed. This stage significantly reduces the concentrations of oxygen and other reactive gases in the reaction environment. After evacuation, the container is filled with an inert gas—argon—under a pressure of 1.5 atm [6]. The use of an inert gas atmosphere prevents oxidation of materials during synthesis and limits the loss of volatile components. At the same time, increased inert gas pressure stabilizes evaporation processes during melting.

The container is then placed into an automated high-temperature furnace. The temperature regime is increased gradually until the sample reaches the melting stage. A melting temperature of 720 °C is selected, which is considered optimal for semiconductor thermoelectric materials, particularly bismuth telluride–based compounds [1,6]. The holding time at the melting temperature is set to 5–6 hours to ensure complete melting of the components and completion of chemical reactions [1,4,6]. All temperature–time parameters are controlled with high precision using digital

controllers [12,13,14]. These controllers automatically correct deviations from the set temperature, maintaining thermal stability. Such precise control enhances the homogeneity of the melt composition and creates optimal structural conditions for the subsequent crystal growth stage. Thus, a synthesis process conducted under coordinated vacuum conditions, inert gas pressure, and temperature-time regimes provides a solid foundation for obtaining high-quality materials with stable composition and superior thermoelectric properties.

In the synthesis of semiconductor thermoelectric materials, particularly bismuth telluride–based compounds, the choice of melting temperature directly influences the chemical composition, phase stability, and subsequent crystal structure of the material. The melting point of bismuth telluride is approximately 585°C; therefore, selecting a temperature above this value during synthesis ensures complete melting of the components and the formation of a homogeneous melt [6,7].

This work aims to optimize the synthesis of Bi_2Te_3-based thermoelectric materials into a single, fully automated process governed by PLC controllers, SCADA systems, and artificial intelligence algorithms, ensuring highly stable electrophysical parameters across the entire sample length.

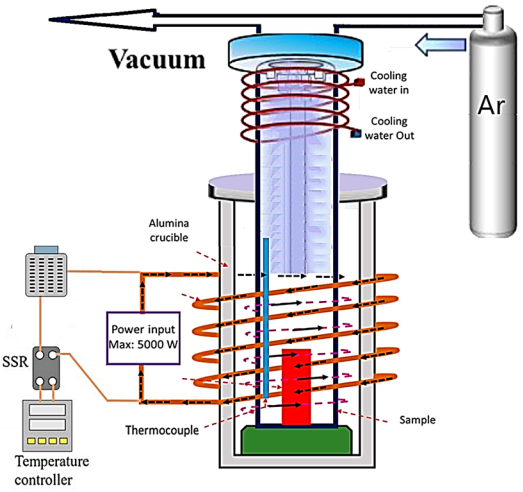

Figure 1. Automated scheme for the technology of obtaining semiconductor thermoelectric materials in a vacuum and inert gas environment during the zone melting process

The choice of 720°C is primarily driven by the need to achieve a high degree of melt homogenization [1,4,6]. At temperatures significantly above the melting point, atomic mobility within the material increases, diffusion processes intensify, and chemical reactions proceed more effectively. This prevents phase imbalance and microscopic segregation during synthesis. Moreover, a temperature of 720°C ensures thermodynamic stability among the material's components. From an energetic perspective, within this temperature range the free energy of the system is minimized, favoring a single-phase state. This creates favorable conditions for the formation of a stable structure during subsequent cooling and crystal growth stages.

Additionally, a temperature of 720°C is considered optimal for limiting the loss of tellurium atoms. An excessive temperature increase may intensify evaporation, leading to compositional imbalance. The selected temperature provides an optimal balance between complete homogenization of the melt and preservation of volatile components [1,6]. Therefore, appropriate temperature selection during the melting process ensures full phase uniformity, optimal diffusion conditions, and compositional stability. These factors play a decisive role in forming high structural quality and stable thermoelectric parameters in semiconductor thermoelectric materials.

3. DISCUSSION

During the synthesis of semiconductor thermoelectric materials, the holding time at the melting temperature is crucial for ensuring the chemical and structural homogeneity of the melt. At 720°C, the melt is maintained for 5–6 hours. At the melting temperature, atomic mobility increases sharply and diffusion between the constituent components becomes significantly enhanced. Fick's law [4,15,16] describes the efficiency of diffusion.

$$J = -D\frac{dc}{dx}$$

where, J - is the diffusion flux, D - is the diffusion coefficient, c - is the concentration, and x - is the spatial coordinate.

The diffusion coefficient is exponentially dependent on temperature, and at higher temperatures, the value of D increases significantly, leading to the elimination of concentration differences between atoms over time. Holding the sample for a specific time, typically 5–6 hours, is sufficient to ensure structural homogenization throughout the material volume [1,4,6,15,16]. During this period, the components fully melt, chemical reactions are completed, and phase inhomogeneities are eliminated. In cases where the holding time is too short, there is an increased likelihood that reactions

will not be fully completed, and microsegregation may persist. Furthermore, excessive extension of the holding time can have negative effects. Prolonged exposure to high temperatures can lead to the evaporation of volatile components, excessive grain growth, and structural instability [1,6]. A 5-6 hour duration ensures an optimal balance between the full completion of diffusion processes and the preservation of the material's composition. Thus, holding the sample at 720 °C for 5–6 hours, considering both thermodynamic and kinetic factors, ensures an ideal initial state for high chemical homogeneity, phase stability, and subsequent crystal growth in semiconductor thermoelectric materials. This plays a crucial role in shaping the high and stable thermoelectric properties of the obtained materials.

4. COOLING AND ANNEALING STAGE

The cooling (annealing) stage that follows the synthesis of semiconductor thermoelectric materials plays a crucial role in forming the material's structural stability, defect density, and electrophysical properties [1,4,6]. After the melting and high-temperature holding process, internal thermal stresses, structural irregularities, and defects (e.g., vacancies and dislocations) develop within the material. The annealing stage is specifically aimed at reducing these negative factors. To slow and control the cooling process, a ceramic container is placed inside the chamber, and a quartz glass tube, approximately 10 mm in diameter and 180–200 mm in length, is positioned within it. This arrangement limits heat exchange and increases the system's overall thermal inertia. Such a construction limits heat exchange, preventing a sharp drop in temperature, and ensures a stable cooling environment for the sample. Both ceramic and quartz are materials with relatively low thermal conductivity, which reduce heat exchange with the external environment and prevent a rapid decrease in temperature. Thermal inertia is physically expressed through the system's "thermal capacitance." The equivalent thermal capacitance for the composite system (ceramic + quartz + sample) is written as follows:

$$C_{eq} = \sum_i m_i c_i$$

Here, m_i denotes the mass of each component (ceramics, quartz, sample), and c_i denotes its specific heat capacity. The larger the value of C_{eq}, the greater the system's resistance to temperature change, meaning the rate of cooling/heating decreases.

The dynamics of the cooling process can be described in a simplified form by Newton's law of cooling [4].

$$\frac{dT}{dt} = -\frac{hs}{C_{eq}}(T - T_{amb})$$

In this context, h - is the convective heat transfer coefficient, s - is the external surface area, T – is the system temperature, and Tamb is the ambient temperature. From this equation, it can be seen that an increase in C_{eq} leads to a decrease in $\frac{dT}{dt}$, meaning that the cooling process slows down. The decrease in heat exchange in the ceramic-quartz combination also influences this trend.

From a practical perspective, the cooling rate should not be too rapid in semiconductor thermoelectric materials to reduce thermal stresses and defect concentrations. In laboratory practices relying on conventional technological guidelines, the optimal cooling rate is selected within the following range [6]:

10–30°C/hour: Suitable for achieving high-quality crystal structure (thermal stresses are minimal, and there is sufficient time for rearrangement).

30–60°C/hour: Accepted when there is a need to shorten technological time, but defect and internal stress risks may increase.

60°C/hour: Generally not recommended (as it approaches the quenching regime, the likelihood of an unbalanced structure and high defect density increases).

Thus, for the ceramic-quartz system, the cooling process can be maintained in the "safest and most efficient" range of 10–30°C/hour by increasing the thermal inertia and limiting heat exchange. This, in turn, improves structural stability, stabilizes the electrophysical parameters, and enhances the overall thermoelectric efficiency (ZT) [5,6].

From a physical standpoint, slow, controlled cooling provides sufficient time for atoms to rearrange themselves into thermodynamically stable states within the crystal lattice. During this process, the system's internal free energy is minimized, and the most energetically favorable configuration of the structure is formed. As a result, deformations in the crystal lattice decrease, and phase stability improves. Diffusion mechanisms play a significant role during the annealing process [16,17]. As the temperature is gradually lowered, atomic mobility does not suddenly disappear but decreases slowly. This allows for the elimination of compositional imbalances, microsegregation, and the homogenization of the structure. In contrast, under very rapid cooling (quenching), atoms "freeze" in an unbalanced state, resulting in a structure with high defect density. The cooling rate also significantly affects the grain size. Controlled annealing leads to moderate grain growth, preventing excessive coarsening or the formation of a very fine-grained structure [16,17]. The optimal distribution of grain sizes balances electrical and thermal conductivities, thereby improving thermoelectric efficiency. The annealing stage is especially crucial for thermoelectric materials, as it stabilizes the concentration and mobility of charge carriers. As a result, parameters such as the Seebeck coefficient, electrical conductivity, and thermal conductivity reach stable values, thereby increasing the overall thermoelectric efficiency coefficient (ZT) [4,6].

5. PROCESS OPTIMIZATION

All synthesis parameters used in the technology for obtaining semiconducting thermoelectric materials—raw material preparation, vacuum and inert gas environments, temperature-time regime, crystal growth, and cooling stages—are interrelated. Therefore, they should be considered not individually, but as a single optimized technological regime. The first stage of the optimized regime involves preparing high-purity elements in precise stoichiometric ratios using automated balances and vacuum dosing systems. The degree of particle size reduction and granularity is set to optimal values that ensure effective heat transfer, thereby reducing energy consumption and the loss of volatile components during the melting process. During synthesis, the container is initially evacuated to a pressure of 10^{-3} Torr, minimizing the influence of oxygen and reactive gases. It is then filled with inert gas (argon) at 1.5 atm pressure to create a chemically stable environment. This combination plays a crucial role in preserving the material's composition and preventing oxidation. The temperature regime for the melting process is set to 720°C, which is maintained for 5-6 hours. This regime ensures complete melting of the components, completion of diffusion processes, and high homogeneity of the melt. Temperature and time parameters are precisely controlled through digital controllers, eliminating thermal irregularities. After melting, crystal growth is carried out in a zone-based method, with temperature gradients and zone movement rates maintained at optimal values. This method allows for compositional purification, reduction of defect density, and improvement of structural uniformity. All parameters are continuously monitored via automated control systems. In the final stage, a controlled annealing process is employed. Slow cooling reduces internal thermal stresses in the material, facilitates the redistribution of defects, and promotes the transition of the structure to a thermodynamically stable state. This contributes to the stabilization of the electrophysical parameters and the achievement of high thermoelectric efficiency.

6. RESULTS

Although the manuscript provides detailed descriptions of raw material preparation, the technological level of vacuum, inert gas pressure, the temperature–time profile of synthesis, and the annealing process, information regarding the technological parameters of crystal growth via the zone melting method—such as temperature gradient, zone length, and zone travel velocity, and their direct influence on crystal dimensions—remains limited. However, investigations aimed at identifying a novel, more effective doping additive that ensures high reproducibility of the material's thermoelectric parameters in both quartz and graphite crucibles have successfully resolved these technological uncertainties. Regardless of the crystal growth parameters, the ammonium iodide NH_4I salt was proposed as a doping agent to ensure superior electrophysical properties and high efficiency of the material.

As a dopant, ammonium iodide possesses several significant technological advantages over conventional pure iodine. It exhibits low hygroscopicity and does not decompose when heated up to 551°C. The material undergoes direct sublimation at 551°C without passing through a liquid phase. Above 551°C, ammonium iodide decomposes according to the following reversible pathways:

$$NH_4 \rightleftarrows NH_3 + HI$$

$$2HI \rightleftarrows H_2 + I_2$$

The released hydrogen iodide, HI, acts as a substantially more active chemical reagent compared to standard iodine. Concurrently, the ammonia (NH3) generated within the system acts as a potent reducing agent, completely eliminating any remaining traces of oxides in the alloy composition. These chemical advantages of ammonium iodide play a decisive role in stabilizing the thermoelectric parameters of the alloys. The optimal thermoelectric performance for thermogenerators was observed when 0.04 mol % of ammonium iodide was introduced into the mixture. Under these conditions, the electrophysical characteristics of the fabricated thermoelements were found to be $\sigma = 1000\ \Omega^{-1}$ and $\alpha = 150\ \mu V/K$, respectively. Since thermoelectric materials operate at elevated temperatures, the temperature dependence of the material's thermoelectric parameters was comprehensively investigated. Figure 3 illustrates the temperature-dependent variations in electrical conductivity, Seebeck coefficient, thermal conductivity, and figure of merit Z for Bi_2Te_3 samples doped with 0.04 mol % ammonium iodide. The average integral value of the material's figure of merit over the temperature range of 20 ÷ 300°C was determined to be $Z = 1.59 \cdot 10^{-3}\ K^{-1}$. This performance indicator demonstrates that high-efficiency, thermally stable materials can be successfully obtained through the proposed modification technology, regardless of the zone-melting method's technological parameters.

The stability of the main thermoelectric parameters along the sample length in Bi_2Te_3-based thermoelements alloyed with ammonium iodide is an important criterion that indicates the high quality of the material synthesis [5,6]. The almost unchanged electrical conductivity, Seebeck coefficient, and power factor in the phase direction suggest a homogeneous distribution of the alloying additions and the absence of significant defects or gradients in the crystal structure [6,7]. This condition confirms that the electron and phonon transport processes have a uniform mechanism throughout the entire sample volume. In particular, the stability of the Seebeck coefficient indicates that the Fermi level remains phase-stable, significantly reducing the possibility of the emergence of internal parasitic electrical driving forces in thermoelectric modules. From this perspective, the results demonstrate that Bi_2Te_3 materials alloyed with ammonium iodide are highly suitable for practical thermoelectric device applications.

Figure 2 clearly shows the stability of the $\alpha^2\sigma$ power factor along the entire length of the thermoelement alloyed with ammonium iodide, and presents the distribution of the main thermoelectric parameters along the sample length.

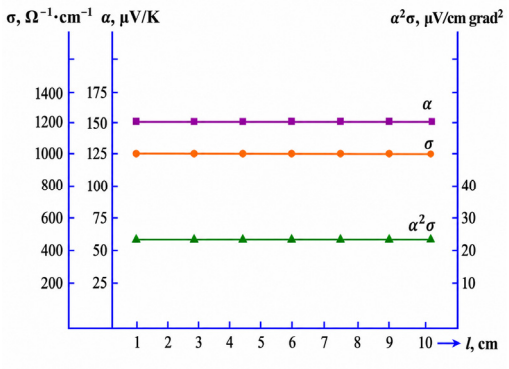

Figure 2. Variation of thermoelectric parameters along the length of a Bi_2Te_3 thermocouple doped with ammonium iodide

The main thermoelectric parameters of the Bi_2Te_3 thermocouple doped with ammonium iodide maintain almost constant values along the length of the sample. This indicates a high degree of structural, compositional and electronic homogeneity of the material. The electrical conductivity is uniform along the entire length [5].

$$\sigma = ne\mu$$

where n is the concentration of charge carriers, μ is the mobility.

The invariance of the electrical conductivity (σ) indicates that the concentration of dopants is uniform along the length, and there is no gradient in the grain boundaries and dislocation density, and the electron-phonon scattering is spatially uniform. This indicates that the Bi_2Te_3 alloy was synthesized technologically correctly.

The value of the Seebeck coefficient α also remains constant along the entire length of the sample. A simplified Mott expression is used for the Seebeck coefficient:

$$\alpha = \frac{\pi^2 k_B^2 T}{3e} \frac{d \ln \sigma(E)}{dE} | E = E_F$$

Here, α depends on the location of the Fermi level, the shape of the band structure, and the asymmetry of the energy conductivity.

The fact that α = const indicates that the Fermi level does not change along the length, the band structure of the material is spatially uniform, and there is no local doping or defect effect [6]. In thermoelectric modules, the spatial instability of α leads to internal EDCs.

Power factor: $PF = \alpha^2\sigma$

The high and stable performance of the Bi_2Te_3 alloy in a real device is of scientific importance. The peculiarities of Bi_2Te_3 thermoelements are that these compounds are characterized by a narrow and complex (divalent) energy band structure. Strong spin-orbit interaction usually causes a nonlinear change in parameters with temperature. However, the absence of such nonlinearity in the spatial coordinate indicates that the band structure is not deformed along the space, there are no internal mechanical stress gradients, and there is no compositional gradient or phase separation.

In Bi_2Te_3-based thermoelectric materials doped with ammonium iodide, the temperature-dependent changes in electrical conductivity, Seebeck coefficient, thermal conductivity, and thermoelectric coefficient of quality are closely related to the electronic band structure of the material. With increasing temperature, changes in the location of the Fermi level and the emergence of bipolar conductivity led to a maximum in the Seebeck coefficient. In this regard, these graphs reveal the importance of Bi_2Te_3 as a highly efficient thermoelectric material in the low- to medium-temperature range.

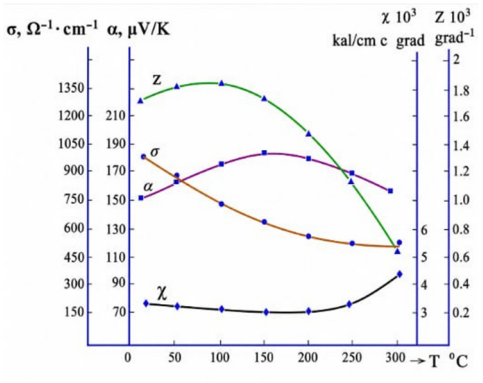

Figure 3. Temperature dependence of thermoelectric parameters of Bi_2Te_3 doped with ammonium iodide

It can be seen from the graph that all the main thermoelectric parameters characteristic of Bi_2Te_3 — electrical conductivity σ(T), Seebeck coefficient α(T), thermal conductivity χ(T) and thermoelectric coefficient of quality Z(T) —

exhibit a complex, interconnected evolution with temperature. This is directly related to the complex band structure and multi-extremum energy spectrum of Bi_2Te_3. Bi_2Te_3 is a semiconductor with a narrow energy gap ($E_g \approx 0.15–0.17$ eV) and has the following features [6,7]. The band structure, with several equivalent extrema in the valence and conduction bands, is characterized by strong anisotropy and a very strong spin–orbit interaction, leading to bipolar conductivity at high temperatures. These factors cause a curvilinear (maximum) character in the temperature dependence of the Seebeck coefficient.

$$\alpha = \frac{1}{eT}\frac{\int (E - E_F)\sigma(E)\left(-\frac{\partial f}{\partial E}\right)dE}{\int \sigma(E)(-\frac{\partial f}{\partial E})dE}$$

where: EF - is the Fermi level, f(E) - is the Fermi–Dirac distribution, and σ(E) - is the energy-dependent permittivity. α is very sensitive to the asymmetry of the energy spectrum and the location of the Fermi level.

For degraded semiconductors (a typical case of Bi_2Te_3), the Seebeck coefficient is written as [5,14]:

$$\alpha = \pm\frac{k_B}{e}\left[\frac{(r+2)F_{r+1}(\eta)}{(r+1)F_r(\eta)} - \eta\right]$$

where r - is the scattering mechanism index, $\eta = \frac{E_F}{k_BT}$ is the reduced Fermi level, Fr(η) - is the Fermi integrals.

In Bi_2Te_3, as temperature increases, η decreases (the Fermi level shifts toward the middle of the bands); the ratio of the Fermi integrals changes; as a result, α(T) first increases and then decreases. At high temperatures, bipolar conductivity begins in Bi_2Te_3. In this case, the Seebeck coefficient is [5]:

$$\alpha = \frac{\alpha_n\sigma_n + \alpha_p\sigma_p}{\sigma_n + \sigma_p},$$

Because the contributions of electrons and holes are of opposite sign, they compensate each other; as a result, the total α decreases. This fully explains the decrease observed in the 200–300°C range in the graph. The curved formation of the Seebeck coefficient is not accidental, but is determined by the zone structure of Bi_2Te_3 narrow gap, multiple zone extrema, strong spin–orbit interaction. The maximum of α(T) is the result of the optimal Fermi level of zone asymmetry. At high temperatures, the bipolar effect sharply limits α and Z. Therefore, materials based on Bi_2Te_3 are considered the most suitable for low and medium-temperature thermoelectric devices [16,17].

CONCLUSIONS

This study developed and scientifically substantiated a comprehensive approach that fully automates the technology for obtaining semiconductor thermoelectric materials. The interrelation of all technological stages, from raw material preparation to synthesis, crystal growth, annealing, and quality control, and the need to implement them within a single optimized regime, was shown. The results of the study show that accurate dosing of high-purity raw materials, the combined use of vacuum and inert gas environments, holding at 720 °C for 5–6 hours, and a controlled cooling regime ensure the homogeneity and phase stability of the material composition. Crystal growth by the zone melting method reduces defect density and increases structural uniformity.

For the first time, the individual stages of thermoelectric material fabrication have been integrated, based on physical models, into a single, optimized, and comprehensive digital technology, controlled in real time via a PLC-SCADA-AI framework. Ammonium iodide NH_4I salt, at a concentration of 0.04 mol %, has been proposed as an alternative doping agent to conventional pure iodine. It was discovered that the ammonia (NH_3) generated during its decomposition acts as a potent reducing agent, completely eliminating residual oxide traces within the alloy. An ideally stable spatial distribution of the Seebeck coefficient and electrical conductivity along the sample length was achieved owing to the spatial invariance of the Fermi level and the absence of deformation of the energy band structure.

It was proven that full automation of the technological process in the production of semiconductor thermoelectric materials is a decisive factor in ensuring the material's structural uniformity. The combined use of vacuum (10^{-3} Torr) and argon atmosphere (1.5 atm) significantly reduced the effect of oxygen, limited oxidation, and minimized the risk of loss of volatile components. Precise control of crystal growth parameters in the zone melting method enhanced structural purification, reduced defect density, and increased the repeatability of crystal quality. The annealing mode reduced internal thermal stresses, created conditions for the structure to transition to a thermodynamically stable state, and ensured stabilization of electrophysical parameters. The near-constant main thermoelectric parameters along the length of Bi_2Te_3 thermocouple samples doped with ammonium iodide confirmed the high degree of homogeneity in the material's synthesis and its suitability for practical application.

Automated control based on PLC–SCADA–AI minimized the human factor and enabled real-time optimization of technological modes; this led to the formation of a stable set of parameters that increased ZT. The optimized technology will play an important role in the development and implementation of high-efficiency thermoelectric devices in the future.

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СИНТЕЗ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ НА ОСНОВІ Bi_2Te_3, ЛЕГОВАНИХ NH_4I, В АТМОСФЕРІ ІНЕРТНОГО ГАЗУ З ВИКОРИСТАННЯМ АВТОМАТИЗОВАНОЇ СИСТЕМИ

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У цій статті представлено комплексний підхід, спрямований на повну автоматизацію технології виробництва напівпровідникових термоелектричних матеріалів. Основні етапи технологічного ланцюга — автоматичне дозування високочистої сировини в точних стехіометричних співвідношеннях. Спільне використання вакууму при 10^{-3} Торр та атмосфери інертного газу аргону при 1,5 атм, витримка при температурі 720°C протягом 5–6 годин, вирощування кристалів методом зонного плавлення та режим охолодження (відпалу) — аналізуються як єдиний оптимізований процес. Температурно-часовий профіль, процеси дифузії та динаміка охолодження обґрунтовуються на основі фізичних моделей, зокрема законів Фіка та Ньютона. Показано, що керування технологічними параметрами в режимі реального часу за допомогою *PLC*-контролерів, SCADA-систем та алгоритмів штучного інтелекту забезпечує фазову однорідність матеріалу, зменшує щільність дефектів і стабілізує електрофізичні параметри. У зразках термоелементів Bi2Te3, легованих йодидом амонію, стабільність електропровідності, коефіцієнта Зеєбека та коефіцієнта потужності по всій довжині зразка підтверджує однорідний розподіл легуючих добавок і формування високоякісної кристалічної структури. Отримані результати демонструють високий потенціал запропонованої автоматизованої технології для ефективного застосування матеріалів на основі Bi2Te3 у низькотемпературних і середньотемпературних термоелектричних пристроях.

Ключові слова: *термоелектричні матеріали; Bi_2Te_3;автоматизація; вакуумне середовище; інертний газ; зонне плавлення; відпал; SCADA; PLC; коефіцієнт Зеєбека; ZT*