INTRODUCTION

Scientific basis of the investigation

This doctoral thesis focuses on the in-depth study of bismuth–tin (Bi-Sn) alloy systems, with additions of Sb and Ag, from the perspective of their use and applicability in contemporary electronics, both at national and international levels. The research topic is justified by the strategic importance of these metallic systems in the current transition toward advanced, eco-friendly functional materials, in line with international regulations on the reduction of hazardous substances in electrical and electronic equipment.

The studied alloy systems represent viable technical solutions in the context of phasing out traditional lead-based solders, due to their favorable thermal, mechanical, chemical, and environmental characteristics. Bi-Sn alloys, particularly ternary compositions modified with antimony (Sb) or silver (Ag), exhibit high potential to replace Sn-Pb solders, thereby meeting the requirements of the RoHS Directive (Restriction of Hazardous Substances) and other international regulations promoting the use of lead-free materials in electronic assembly processes.

Bi-Sn compositions are well known for their excellent performance in low-temperature soldering applications, having eutectic or near-eutectic melting points, which makes them especially suitable for integrating heat-sensitive components on printed circuit boards. Moreover, the addition of alloying elements such as Sb and Ag significantly improves mechanical properties, microstructural stability, and creep resistance of joints, thereby ensuring superior functional performance under thermomechanical stresses.

Another key aspect of the research concerns the physicochemical characterization and compatibility of these alloys with various substrates used in *electronic packaging* processes.

RESEARCH HYPOTHESES

a. Bi–Sn-based alloys, with additions of Sb and Ag, can be produced under controlled conditions by induction melting, resulting in stable, homogeneous, and functional compositions for soldering or thermoelectric applications.

b. The addition of alloying elements (Sb, Ag) to the Bi–Sn system induces significant changes in microstructure and mechanical properties (hardness), positively influencing industrial performance.

c. The EMF method, applied in a galvanic cell with solid electrolyte, allows for precise determination of thermodynamic activities and highlights deviations from ideality in Bi–Sn, Bi–Sn–Sb, and Bi–Sn–Ag systems.

d. The binary Bi–Sn system exhibits non-ideal thermodynamic behavior, determined by specific atomic interactions, reflected in significant variations of activities and activity coefficients, particularly in the equimolar composition range.

e. The thermodynamic behavior of ternary systems Bi–Sn–Sb and Bi–Sn–Ag is significantly influenced by the presence of the minority element (Sb or Ag), which induces thermodynamic instability at low concentrations by increasing activity coefficients.

f. The experimental values obtained (activity, ΔG, λ, γ) can be consistently correlated with theoretical models and simulated using computational methods (CALPHAD, Python), thus validating the integrated theoretical–experimental approach used in this research.

NOVELTY OF THE THESIS

1. Development and characterization of new binary alloys $Bi_{70}Sn_{30}$, $Bi_{60}Sn_{40}$, $Sn_{70}Bi_{30}$ and ternary alloys $Bi_{60}Sn_{35}Sb_5$ and $Bi_{60}Sn_{35}Ag_5$, designed for applications in lead-free soldering, functional materials, or controlled-melting-point systems. These compositions were obtained by controlled induction melting, through a rigorous refining process and protection against oxidation, using solid fluxes (NH_4Cl + KCl).

2. Integrated application of modern and complementary characterization methods (direct current plasma optical emission spectrometry – DCP, X-ray fluorescence spectrometry – XRF, metallographic microscopy, Leeb hardness testing) for a comprehensive evaluation of the chemical, structural, and mechanical properties of the new alloys.
3. Determination of thermal and electrical conductivity for Bi–Sn, Bi–Sn–Sb, and Bi–Sn–Ag systems using the Laser Flash Analysis (LFA) method to measure thermal diffusivity and correlate it with Cp and ρ. This approach provides essential data for understanding the functional behavior of alloys under real operating conditions. For the first time, thermal and electrical conductivity were determined for the binary $Bi_{60}Sn_{40}$ and ternary $Bi_{60}Sn_{35}Sb_5$ and $Bi_{60}Sn_{35}Ag_5$ alloys using LFA, correlated with specific heat (Cp) and density (ρ). This characterization has not been reported in the literature, granting originality to the work and opening new directions for applied research regarding the use of these alloys in functional applications (soldering, thermal interfaces, thermoelectric materials).
4. Evaluation of the thermodynamic behavior of Bi–Sn, Bi–Sn–Sb, and Bi–Sn–Ag systems at high temperatures (1023, 1073, and 1033 K) for the first time, with emphasis on the dilution behavior of the minority elements (Sb and Ag). Zones of thermodynamic instability and local segregation tendencies were identified. Using solid-electrolyte galvanic cells, activities, activity coefficients, and Gibbs free energies were analyzed, revealing significant deviations from ideal behavior, particularly under dilution conditions of the minority elements. Notable differences were highlighted between binary and ternary systems. These data, unreported in the literature for the studied temperature ranges, represent an original contribution applicable to the design of functional alloys with controlled thermal stability.
5. Integration of experimental methods with numerical modeling using Python, enabling data processing, graphical visualization of activities and activity coefficients, as well as automated calculation of thermodynamic mixing functions, in a reproducible and scalable manner.
6. Experimental validation of theoretical data obtained through CALPHAD methods, particularly for thermal conductivity and thermal diffusivity, confirming the applicability of computational models in the design and simulation of functional alloys.

CHAPTER I
1. DOCUMENTARY STUDY ON THE CURRENT STATE OF SOLDER ALLOYS
1.1. CONTEXT OF THE USE OF SOLDER ALLOYS IN INDUSTRY – CURRENT STATE OF KNOWLEDGE

In the field of solder alloys, scientific research plays a crucial role in adapting materials to the increasingly demanding requirements of modern industry. Against the background of the global transition to eco-friendly technologies and the gradual banning of lead-based solders, the focus has shifted to the development of alternative lead-free solutions capable of providing comparable or superior mechanical, electrical, and thermal performance.
Thus, current research does not limit itself to the optimization of classical compositions such as Bi-Sn, but also explores the influence of additions of elements such as Ag, Sb, Cu, or In, which can significantly modify the behavior of alloys in soldering processes.
A central objective of these studies is to increase the reliability of solder joints, especially in the context of the miniaturization of electronic components and their exposure to repeated thermal cycles. Detailed investigations are conducted on phenomena such as creep, interfacial diffusion, intermetallic phase formation, and microstructural changes occurring over time. By understanding these processes, alloys can be designed with extended service life, enhanced dimensional stability, and superior resistance to thermal and mechanical shocks.
Another priority direction is the optimization of the soldering process itself, in order to reduce energy consumption, minimize defects, and increase reproducibility at the industrial scale. In this regard, advanced characterization methods (3D microscopy, thermal simulations, tomography) and digital tools are employed for precise control of dosing and thermal profiles.

1.1.1 Current state of knowledge

Bismuth–tin (Bi–Sn) alloys have become the focus of intense research over the past two decades, particularly in the context of international regulations banning the use of lead in electronic systems (RoHS, Directive 2003/11/EC). Due to their low toxicity and favorable physicochemical properties, the Bi–Sn system is considered a promising alternative to lead-free solder alloys.
The eutectic composition $Bi_{58}Sn_{42}$, with a melting point of approximately 138 °C, exhibits good wettability, moderate thermal conductivity, and chemical stability, being one of the most extensively studied variants (Zeng et al., 2005; Nishimura et al., 2004). However, the mechanical performance of binary Bi–Sn alloys is limited, which is why additions of tertiary elements such as Sb, Ag, In, or Zn have been proposed in order to improve their functional properties.
Studies on the influence of antimony (Sb) in the Bi–Sn system are relatively scarce. Results published by Wang et al. (2007) show that small additions of Sb (below 5%) can improve creep resistance and dimensional stability. Similarly, Lu et al. (2010) demonstrated that Sb contributes to microstructural refinement and solid-solution strengthening in the Sn phase. However, data on the effect of Sb on thermal conductivity or thermal diffusivity are virtually nonexistent.

1.1.2 Justification of the research topic

In this context, the research proposed in this thesis aims to fill these gaps by:

- developing binary and ternary alloys from the Bi–Sn system with additions of Sb and Ag,
- performing a comprehensive characterization of thermal and electrical properties, in both solid and partially liquid states,
- conducting direct measurements using modern methods, with emphasis on Laser Flash Analysis (LFA),
- investigating high-temperature behavior (above 1000 K), not previously addressed in the literature.

Therefore, this thesis has a profoundly original and applied character, proposing new materials and advanced characterization methods that are relevant both scientifically and technologically.

1.2. THE NEED FOR LEAD-FREE ALLOY DEVELOPMENT

In this context, lead-free alloys based on Bi–Sn, doped with minor elements such as Sb or Ag, have become promising alternatives due to their low melting points, good wettability, thermal stability, and favorable conductivity characteristics. However, for their efficient integration into industrial applications, an in-depth understanding of their thermodynamic and functional behavior is essential, especially at high temperatures, typical of soldering processes and long-term operation.

1.2.1. Pressure from international regulations

Beyond the RoHS Directive adopted by the European Union, other countries and regions have introduced similar or even stricter regulations:

- **WEEE (Waste Electrical and Electronic Equipment Directive)** – encourages proper collection and recycling of electronic waste, penalizing the use of toxic materials.
- Regulations in the **USA, Japan, China, and South Korea**, which impose comparable restrictions on lead in electronic equipment.
- Requirements from major global manufacturers (e.g., Apple, Samsung, Intel), which mandate "green" materials compliant with RoHS throughout their supply chains.

1.2.2. The need for environmental and public health protection

Throughout the life cycle of electronic products—from manufacturing to disposal—lead-based solders contribute to:

- contamination of soil and groundwater due to improper disposal of waste equipment,
- worker exposure in factories to toxic vapors and dust during soldering processes,
- major recycling risks: incineration or shredding of obsolete equipment releases lead into the air and dust, affecting surrounding communities.

1.2.3. Current technological requirements

The rapid developments in microelectronics impose increasingly strict technical requirements for soldering materials:

- **Extreme miniaturization** → smaller joints, more sensitive to defects;
- **Lower processing temperatures** → essential for fragile components;
- **Resistance to repeated thermal cycles and vibrations**;
- **Compatibility with new materials** (substrates, pastes, fluxes).

1.2.4. Current research directions

An important research direction is the exploration of multicomponent systems such as Sn-Bi, Sn-Ag, Sn-Sb, or Bi-Sn-Ag. These systems have the potential to generate compositions with eutectic or near-eutectic behavior, meaning a sharp solid-to-liquid transition within a narrow temperature range, favorable for automated assembly processes. At the same time, they allow fine tuning of physicochemical properties such as thermal conductivity, coefficient of thermal expansion, or creep resistance.

1.3. PROPERTIES OF SOLDER ALLOYS

The distinctive properties of various types of non-ferrous alloys are essential to meet the complex requirements of modern technology. These alloys remain indispensable and difficult to replace, which highlights the continuing importance of their development. An alloy represents a homogeneous mixture containing at least two chemical elements, either ferrous or non-ferrous,

with one element present in predominant quantity. The physical and chemical properties of alloys are usually different from those of their individual components, sometimes significantly so .

1.3.1. Processing solder alloys – composition of the main alloys used in technology

Depending on the requirements of the application (operating temperature, mechanical strength, environmental compatibility), different types of solder alloys are used, each with a specific composition.

1.4. PROCESSING AND CASTING OF TIN-BASED ALLOYS

The ternary alloy Sn–Pb–Cd develops a eutectic with a composition of 32% Pb, 50% Sn, and 18% Cd at a low temperature of 145 °C. This alloy, in its specific chemical composition, exhibits superior soldering properties and mechanical behavior compared to binary alloys.

1.4.1. Physical properties of the non-ferrous metals used

Tin is a chemical element with the symbol Sn and atomic number 50. It belongs to the group of p-block metals in the periodic table. It is a soft, bluish-silver metal with a face-centered cubic crystalline structure. Tin is one of the oldest metals known to mankind, having been used since antiquity for various applications.

1.5. ESSENTIAL REQUIREMENTS IN THE CHARACTERIZATION OF ECO-FRIENDLY SOLDER ALLOYS

In the development and selection of lead-free solder alloys, there are a number of fundamental technical issues that determine the functional performance of these materials in electronic applications. Among the most important are eutecticity, melting temperature, wettability, mechanical strength, and long-term reliability. These constitute critical evaluation criteria in the optimization process of alloy compositions for commercial and industrial applications.

1.5.1. Thermal and structural properties

Compositions from the Bi-Sn-Sb system generally have melting temperatures between 135 °C and 160 °C, depending on the proportions of the elements. The addition of antimony slightly increases the melting point but brings notable benefits to the microstructure. Studies have shown that the presence of Sb leads to the formation of finely dispersed intermetallic phases, which hinder crack propagation and stabilize the structure during thermal cycling. The ternary Bi-Sn-Sb phase diagram indicates the existence of regions with eutectic or near-eutectic behavior, favorable for industrial processing. Homogeneous solidification and sharp thermal transitions facilitate the use of these alloys in automated soldering processes.

1.5.2. Thermal and electrical conductivity of materials

Thermal conductivity and electrical conductivity are essential physical properties of materials, describing their ability to transfer heat and electric current, respectively. Good conductors, such as metals (e.g., copper and silver), usually exhibit high values for both types of conductivity, due to the presence of free electrons that facilitate both thermal energy transfer and charge transport.

1.6. THERMODYNAMICS OF METALLIC MELTS

Metallurgical processes involve complex physicochemical reactions that can take place both in homogeneous media (such as the metal bath, molten salts, or slag) and in heterogeneous systems (e.g., at the interface between the metal bath and slag or between molten salts and metal). The efficiency of these processes depends on the ability to control the direction and progress of the reactions involved, according to the thermodynamic conditions of the system.

1.6.1. Partial molar and mixing thermodynamic functions

By definition, the derivative of extensive quantities with respect to the number of moles is called a **partial molar property**. The derivative of thermodynamic potentials with respect to the number of moles is called the **chemical potential (μ)**. The chemical potential corresponding to the reference state is denoted as μ_i^0.

1.6.2. Temperature dependence of mixing thermodynamic functions

$$G=H-TS$$

for integral molar quantities of mixing.

1.6.3. Excess thermodynamic functions

Scatchard defined the partial molar excess quantity corresponding to component *i* as the deviation of the partial molar mixing property .

1.6.4. Methods for determining the activity of melt components

Depending on the nature of the system and the experimental conditions, various methods can be used to determine the activity of melt components. These methods are generally divided into two main categories: **experimental methods** and **empirical methods**.

1.6.4.1. Determination of activity based on electromotive force (EMF) measurements

The method is based on measuring the electromotive force in a reversible concentration cell, which uses either a liquid or solid electrolyte. By definition, electrochemical systems in which the electrodes differ only in the activity (or concentration) of one component are called concentration cells. In these cells, the source of electrical energy is provided by the transfer of matter from the component with higher activity to the one with lower activity.

1.6.5. Determination of the dependence of thermodynamic properties on state parameters using empirical methods

The exact determination of the dependence of thermodynamic properties on state parameters is difficult to achieve using purely theoretical methods, due to the complexity of real systems. For this reason, empirical models are frequently employed, which describe these properties based on relationships derived from experimental observations and data.

1.6.5.1. Guggenheim (Redlich–Kister) model

In the Guggenheim (Redlich–Kister) model, the correlation between coefficients is lower than in the Margules model .

CHAPTER II
2. PROCESSING OF THE Bi–Sn ALLOY
2.1. WORKING METHODOLOGY

For the preparation of the Sn–Bi alloy, Bi of 99.96% purity and Sn of 99.98% purity were used. Three sets of samples were obtained by varying the composition of tin and bismuth. The first alloy sample produced had a composition of **60% Bi and 40% Sn**. The second sample consisted of **30% Bi and 70% Sn**, while the third sample contained **70% Bi and 30% Sn**. The samples were melted and cast into graphite crucibles and molds.

2.2. PHYSICO-CHEMICAL AND STRUCTURAL CHARACTERIZATION OF THE ALLOY

The cast binary Bi–Sn alloy samples were analyzed by optical microscopy using an **Optika B383 MET optical microscope**, equipped with a digital camera and image processing software. Prior to microscopic examination, the samples were metallographically prepared to reveal the structure of the obtained material. The images presented below illustrate the microstructures of the cast alloys. Due to the slow cooling of the samples, microcracks were formed and the grain size is relatively large. To improve this aspect, rapid or forced cooling can be applied, resulting in a finer structure.

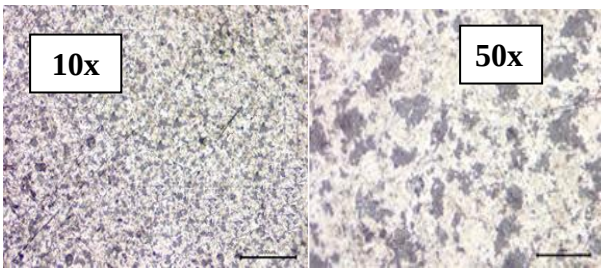


Figure 2.1. Microstructure image of the Sn70Bi30 sample

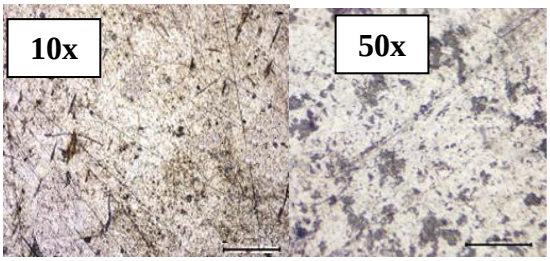


Figure 2.2. Microstructure images of the Bi60Sn40 sample

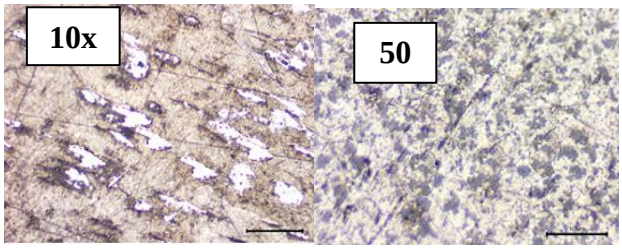


Figure 2.3. Microstructure images of the Bi70Sn30 sample

2.3. STRUCTURAL ANALYSIS USING XRD–ED(P)–XRFS

The most effective method for the elemental and structural characterization of Bi–Sn alloys is performed through **X-ray Fluorescence Spectrometry (XRFS)** and **X-ray Diffractometry**

(XRD). These instrumental techniques require minimal sample preparation and provide a wide range of information regarding the elemental and phase compositions of the investigated samples.

2.4. EXPERIMENTAL RESULTS

Three representative samples of Bi–Sn alloys were analyzed, with the compositions **Sn70Bi30, Bi60Sn40, and Bi70Sn30**. To extract precise information about elemental concentrations, all three spectra were processed using the **TurboQuant-Alloys analytical software**, associated with the **XEPOS spectrometer** produced by *SPECTRO Analytical GmbH*. This software enables accurate and rapid analysis of spectrometric data, providing the elemental concentrations for each analyzed sample.

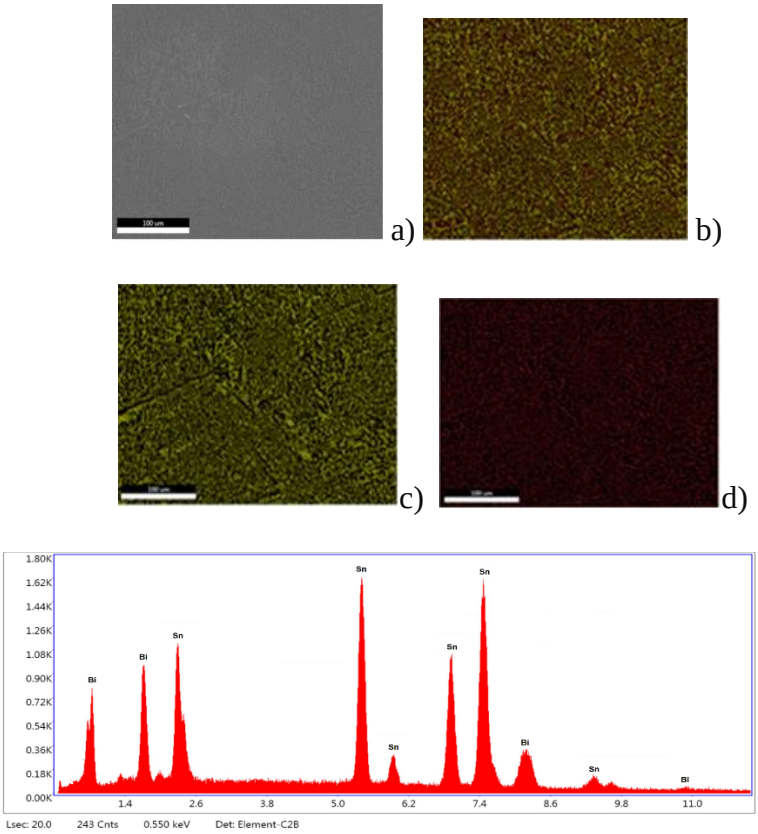
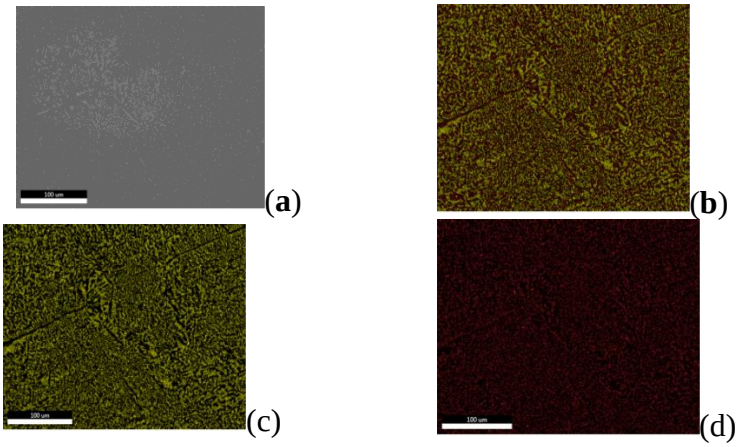


Figure 2.4. BSED images (mapping): (a) backscattered electron micrograph, (b) combined elemental map (Sn – yellow, Bi – red), (c) Sn distribution, (d) Bi distribution, and the EDS spectrum for sample code 1 – Sn70Bi30



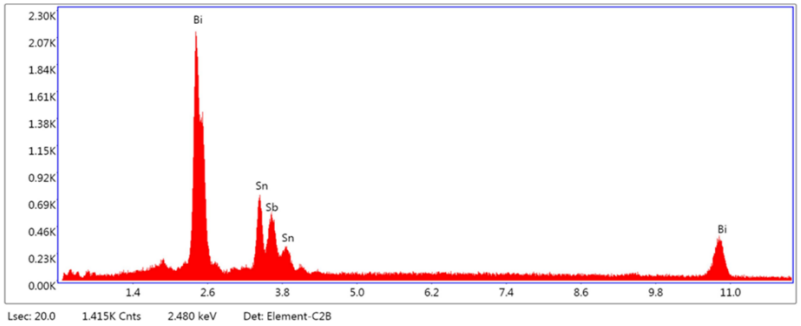
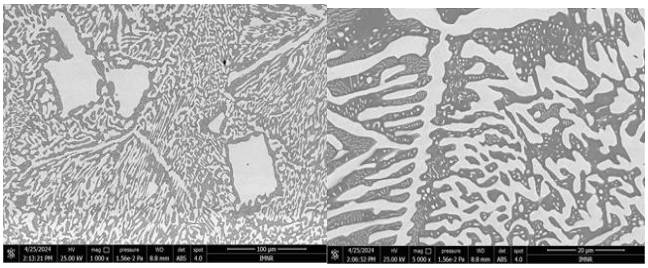


Figure 2.5. BSED images: (a) backscattered electron micrograph, (b) combined elemental map (Sn – yellow, Bi – red), (c) Sn distribution, (d) Bi distribution, and the EDS spectrum for sample code 2 – Bi60Sn40



(a) **(b)**

Figure 2.6. SEM micrographs of the Bi60Sn40 alloy at different magnifications: (a) Fine eutectoid lamellar structure, consisting of alternating Bi-rich (bright) and Sn-rich (dark) phases, with primary Bi particles occasionally visible as larger polygonal regions (magnification: 1000x); (b) Coarser eutectoid morphology, exhibiting directional growth and partial dendritic structures, indicating local variations in the solidification rate (magnification: 5000x).

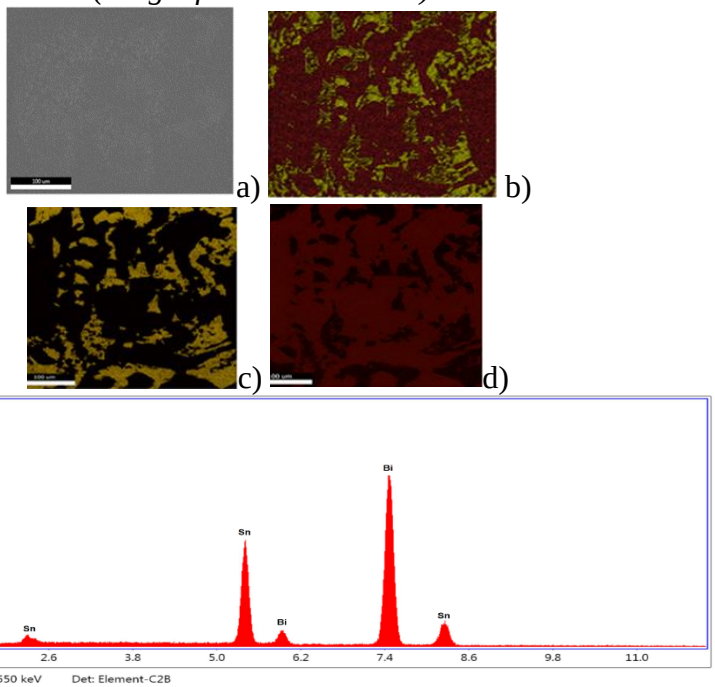


Figure 2.7. BSED images (mapping): (a) backscattered electron micrograph, (b) combined elemental map (Sn – yellow, Bi – red), (c) Sn distribution, (d) Bi distribution, and the EDS spectrum for sample code 3 – Bi70Sn30

CHAPTER III
3. PROCESSING OF Bi60Sn35Sb5 AND Bi60Sn35Ag5 ALLOYS

3.1. WORKING METHODOLOGY

The experimental research carried out within the **Laboratory of Hydro-Electro-Metallurgical Processes and Operations** of the **Department of Engineering and Management of Metallic Materials Processing, Faculty of Materials Science and Engineering**, focused on the development of low-melting metallic alloys, in particular the Bi60Sn35Sb5 and Bi60Sn35Ag5 alloy systems. These alloys were designed with new chemical compositions, aiming to explore improved properties capable of meeting the requirements of modern industrial applications.

3.2. ANALYTICAL CHARACTERIZATION METHODS

In this study, various analytical techniques were employed for the characterization of samples obtained by induction furnace melting and gravitational casting. Among these methods were optical microscopy and chemical analyses using **direct current plasma optical emission spectrometry (DCP, Spectraspan V–Beckman)**, **X-ray spectrometry (Niton XL2 Gold)**, and **laser spectrometry (Sci Apos Z-200 Argon)**. In addition, hardness tests were performed using the **Leeb method**.

3.2.1. Chemical characterization

The **SpectraSpan System V** operates on the principle of atomic emission in a plasma arc generated by electrical discharge in a controlled atmosphere of argon, an inert gas. In this process, atoms from the metallic sample are energetically excited within the plasma arc and emit characteristic electromagnetic radiation. Each chemical element has its own spectrum, and the emitted wavelengths are spectroscopically detected and analyzed to determine the exact concentrations of each alloying element.

3.2.2. Optical characterization

For morphological analysis and preliminary microstructural characterization of the $Bi_{60}Sn_{35}Sb_5$ and $Bi_{60}Sn_{35}Ag_5$ alloys, the **Optika B-383 MET inverted metallographic optical microscope** was used. This is a high-precision instrument designed specifically for observations on opaque metallic surfaces prepared by mechanical polishing and chemical etching.

3.2.3. Hardness determination

To evaluate the mechanical properties of the alloys obtained in this research, hardness measurements were performed using a **SAUTER HMM portable digital hardness tester**, manufactured in Germany.

3.3. EXPERIMENTAL RESULTS AND DISCUSSIONS ON OBTAINING THE Bi60Sn35Sb5 AND Bi60Sn35Ag5 ALLOYS

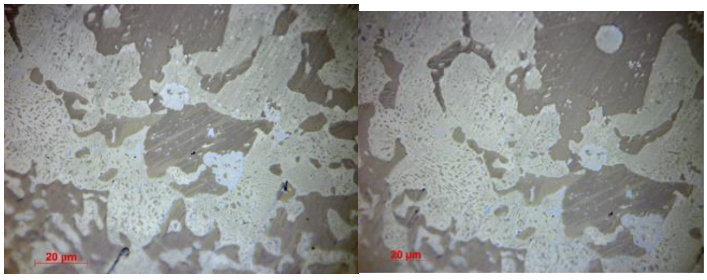


Figure 3.1. Optical microstructures taken from different areas of the Bi60Sn35Sb5 alloy sample

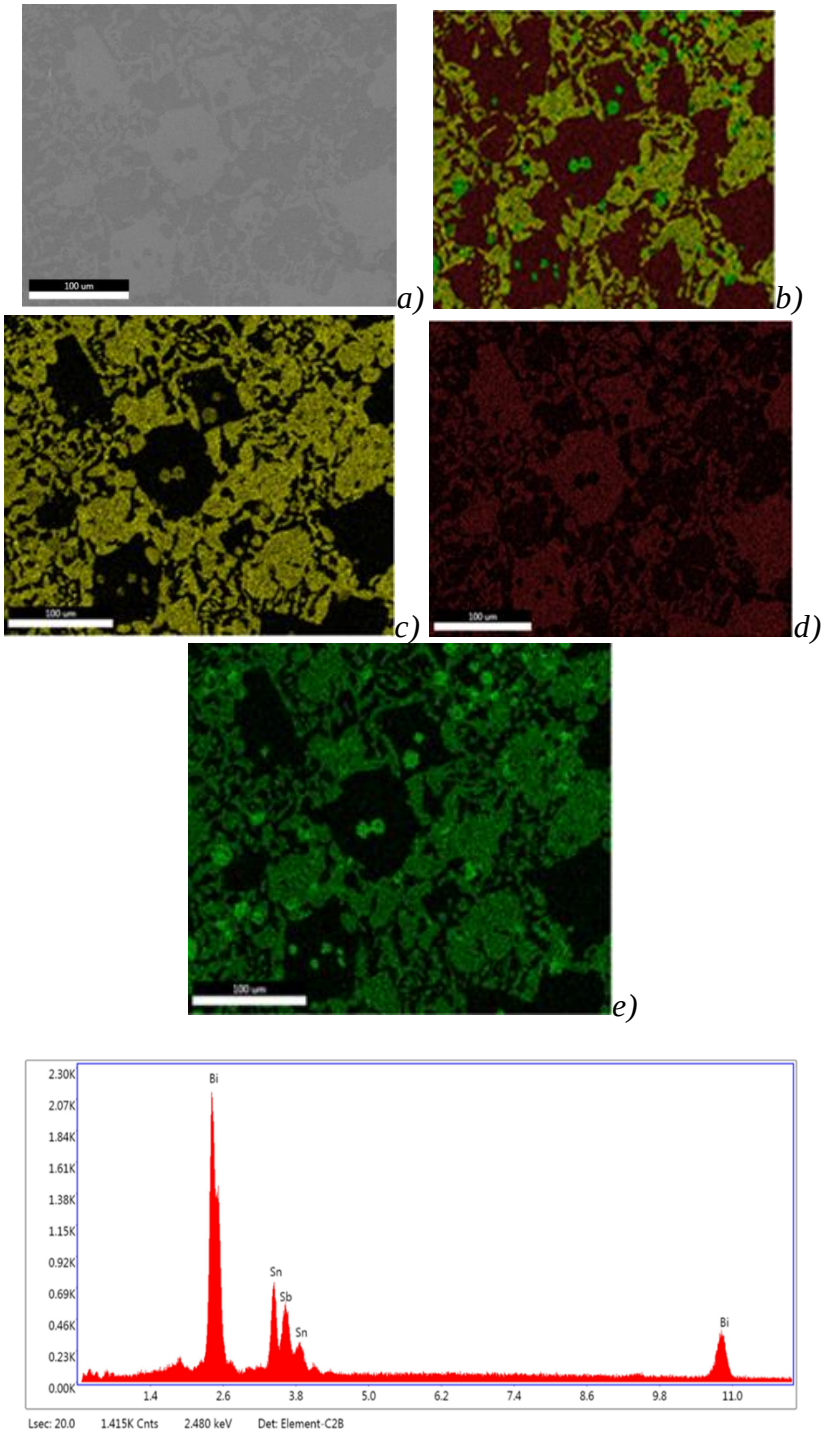


Figure 3.2. BSE and elemental mapping images of the Bi60Sn35Sb5 solder alloy: (a) BSE micrograph; (b) combined elemental map (Sn – yellow, Bi – red, Sb – green); (c) Sn distribution (41%); (d) Bi distribution (34%); (e) Sb distribution (22%); and the EDS spectrum

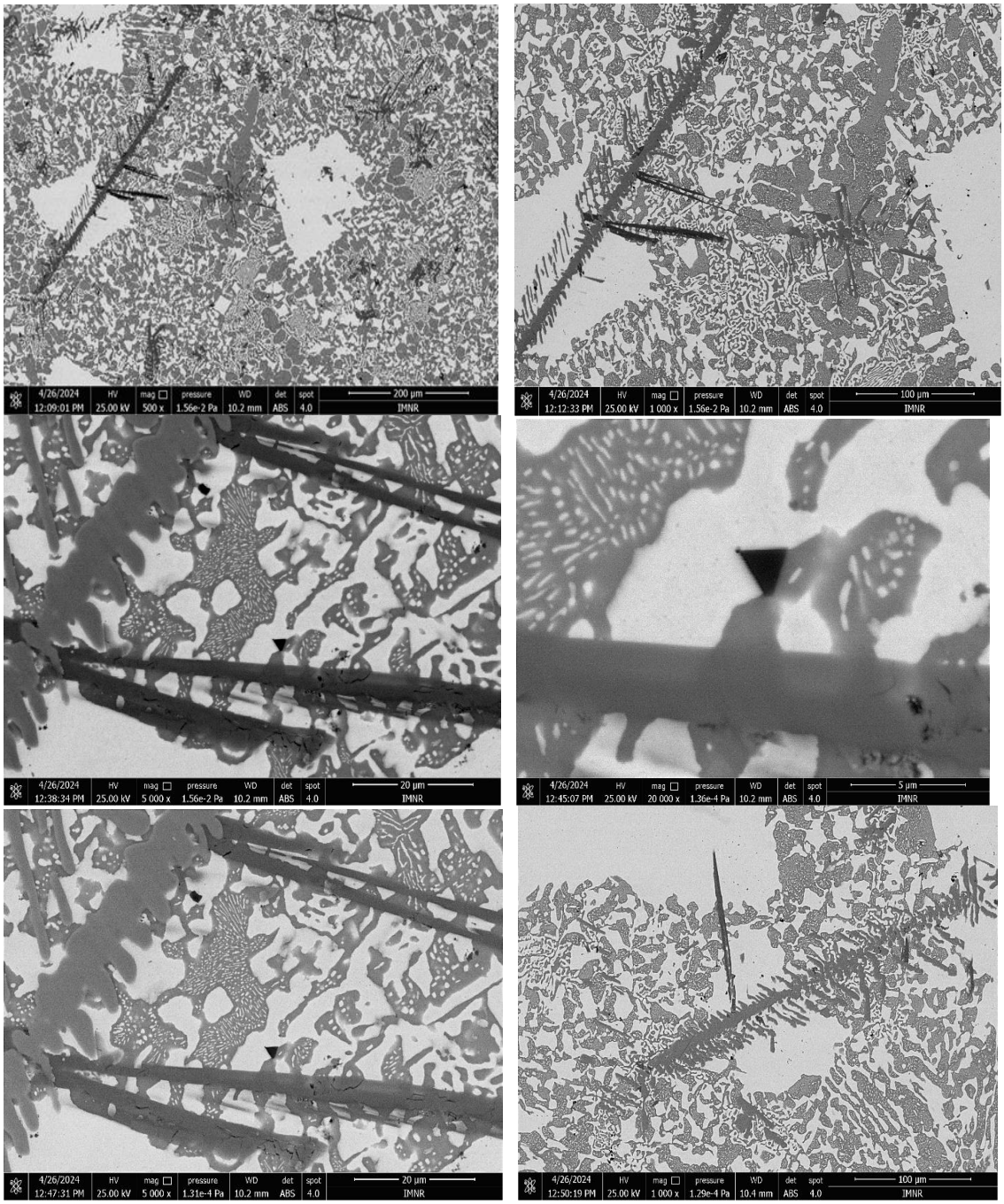
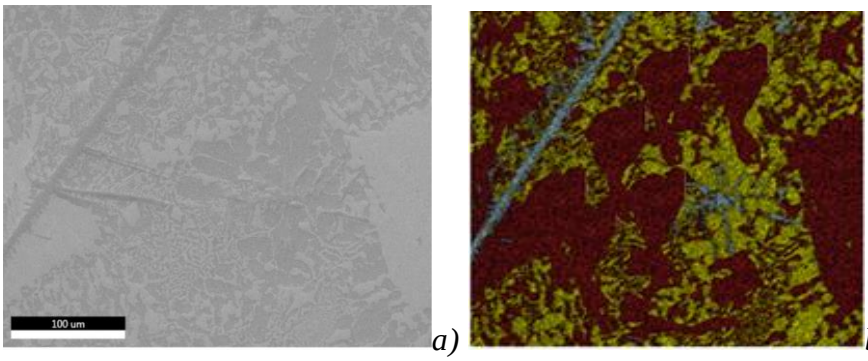
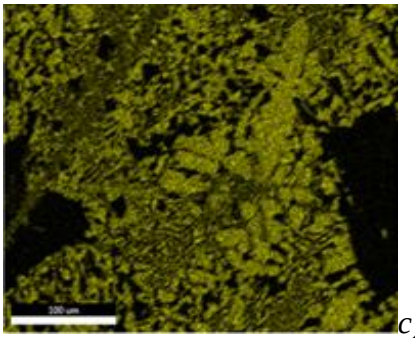
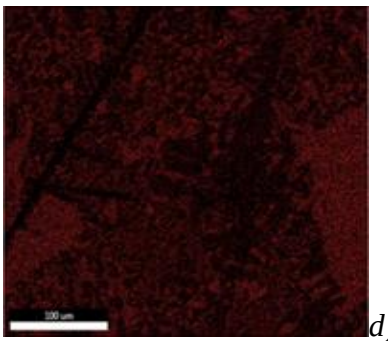


Figure 3.3. Optical microstructures taken from different areas of the Bi60Sn35Ag5 alloy sample



a) *b)*


c)

d)

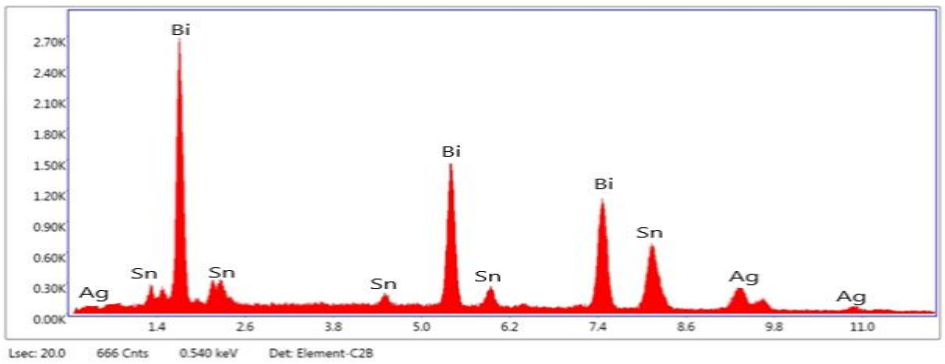
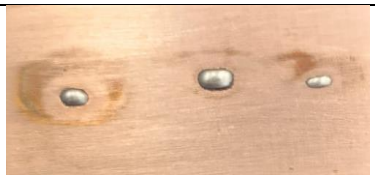
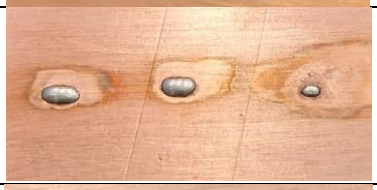
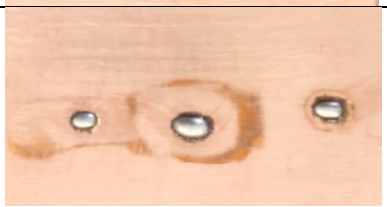
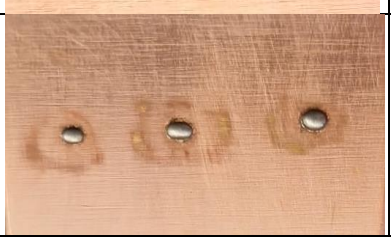
e)


Figure 3.4. BSE and elemental mapping images of the Bi60Sn35Ag5 solder alloy: (a) BSE micrograph; (b) combined elemental map (Sn – yellow, Bi – red, Ag – blue); (c) Sn distribution (65%); (d) Bi distribution (35%); (e) Ag distribution (22%); and the EDS spectru

CHAPTER IV
4. MORPHOLOGICAL AND GEOMETRICAL CHARACTERIZATION OF ALLOY DROPLETS SOLDERED ON COPPER SUBSTRATE

Nr	Composition	Alloy soldered on Cu substrate	Alloy soldered in cross-section on Cu substrate
1	***Bi60Sn35Sb5***		
2	**Bi60Sn35Ag5**		
3	**Sn50Bi45Sb5**		
4	**Sn75Sb5Bi20**		
5	**Bi70Sn30**		
6	**Bi60Sn40**		
7	**Sn70Bi30**		
8	**Sn45Sb10Bi45**		

CHAPTER V

5. DETERMINATION OF THERMAL AND ELECTRICAL CONDUCTIVITY

5.1. DETERMINATION OF THE THERMAL AND ELECTRICAL CONDUCTIVITY OF THE Bi70Sn30 ALLOY

For the determination of the thermal diffusivity (α) of the alloys, the **Netzsch LFA 457 MicroFlash** instrument was used — a high-precision thermal analyzer, recognized for its applicability in the characterization of solid materials. This equipment operates on the principle of the **Laser Flash method**, in which a short energy pulse is applied to one face of the sample, while the temperature variation on the opposite face is recorded in real time by an infrared detector. The Netzsch LFA 457 offers a wide temperature range, from –125 °C to +1100 °C, making it suitable for both low-melting materials and those used at high temperatures. The instrument directly measures thermal diffusivity.

5.2 DETERMINATION OF THERMAL AND ELECTRICAL CONDUCTIVITY OF THE Bi60Sn40 ALLOY

Tabel 5.6
Conductivitatea termică calculată Bi60Sn40

Temperatura (°C)	**α (m²/s)**	**Cp (J/kg·K)**	**ρ (kg/m³)**	**ConductivitateA termică λ (W/m·K)**
25	$10.75x10^{-6}$	184	8560	16.9316
50	$11.85\ x10^{-6}$	188	8500	18.9363
75	$12.90\ x10^{-6}$	192	8450	20.9289
100	$13.93\ x10^{-6}$	196	8400	22.9343
125	$14.93\ x10^{-6}$	200	8350	24.9331
140	$16.06\ x10^{-6}$	202	8300	26.9261

5.3. DETERMINATION OF THE THERMAL AND ELECTRICAL CONDUCTIVITY OF THE Sn70Bi30 ALLOY

Table 5.1. Estimated thermal conductivity values of Sn70Bi30

Temperature (°C)	**α (m²/s) Calphad**	**Cp (J/kg·K) Calphad**	**ρ (kg/m³) Calphad**	**λ (W/m·K) Calphad**
25	$36.19x10^{-3}$	0.145	8050	42.243
50	$35.76x10^{-3}$	0.145	8050	41.741
75	$34.30x10^{-3}$	0.150	8050	41.417
100	$33.09x10^{-3}$	0.155	8050	41.288
125	$31.90x10^{-3}$	0.16	8050	41.087
140	$28.26x10^{-3}$	0.18	8050	40.094

5.4. DETERMINATION OF THE THERMAL AND ELECTRICAL CONDUCTIVITY OF THE Bi60Sn35Ag5 ALLOY

Table 5.2 presents the calculated thermal conductivity values of the Bi60Sn35Ag5 alloy.

Table 5.2. Calculated thermal conductivity values for the Bi60Sn35Ag5 alloy

Temperature (°C)	**α (m²/s)**	**Cp (J/kg·K)**	**ρ (kg/m³)**	**Conductivitatea termică λ (W/m·K)**

25	$11.91x10^{-6}$	175	8770	18.278872
50	$11.56x10^{-6}$	180	8770	18.248616
75	$10.80x10^{-6}$	185	8770	17.522460
100	$10.46x10^{-6}$	190	8770	17.429498
125	$9.89x10^{-6}$	195	8770	16.913383
140	$9.56x10^{-6}$	200	8770	16.768240

5.5. DETERMINATION OF THE THERMAL AND ELECTRICAL CONDUCTIVITY OF THE Bi60Sn35Sb5 ALLOY

Table 5.13 presents the calculated thermal conductivity values of the Bi60Sn35Sb5 alloy.

Table 5.3. Calculated thermal conductivity values for the Bi60Sn35Sb5 alloy

Temperature (°C)	**α (m^2/s)**	**Cp (J/kg·K)**	**ρ (kg/m^3)**	**Conductivitatea termică λ (W/m·K)**
25	9.71e-06	167	8570	13.896855
50	9.11e-06	174	8570	13.584650
75	8.66e-06	181	8570	13.433132
100	7.23e-06	188	8570	11.648687
125	6.81e-06	195	8570	11.380532
140	6.22e-06	200	8570	10.661080

CHAPTER VI
6. METHODS AND TECHNIQUES USED IN THE EXPERIMENTAL RESEARCH OF ALLOY THERMODYNAMICS
6.1. THERMODYNAMICS OF THE Bi70Sn30 ALLOY

Most real mixtures show significant deviations from ideal behavior. Since many thermodynamic quantities are relative, they are defined with respect to a reference state. The most commonly used standard states are based on **Raoult's law**, according to which fugacity – and thus activity – is proportional to the molar fraction xix_ixi of the component in the system.
In this thesis, dedicated to the thermodynamic study of the binary Bi–Sn alloy, several characteristic quantities were calculated and graphically represented: **thermodynamic activities, activity coefficients, and partial molar excess free energies**. These values express the differences between the behavior of real solutions and that of ideal solutions, offering a clear picture of the degree of deviation from ideal mixing.
In the experiment, high-purity metals were used, acquired from specialized suppliers, in order to ensure the accuracy and reproducibility of the obtained electrochemical results. Thus, pure **bismuth (Bi), tin (Sn), antimony (Sb), and silver (Ag)**, each with a purity of at least 99.9%, were used. These metals were handled and stored under controlled conditions, in sealed containers, to avoid contamination or oxidation prior to use. In particular, silver, known for its low reactivity and electrochemical stability, was employed in certain stages as a contact material or reference component, due to its predictable behavior in redox systems. The use of these pure metals was essential for ensuring the accuracy of the data regarding activities and activity coefficients determined by the EMF method.
To investigate the thermodynamic behavior of the Bi–Sn binary system, the method of measuring the **electromotive force (EMF)** in a reversible concentration galvanic cell, equipped with a solid electrolyte, was employed. This method is considered safe, reproducible, and highly accurate for the analysis of metallic systems in the liquid state. The operation of the galvanic cell is based on the difference in thermodynamic activity between the two compartments: the energy transfer from the component with higher activity to that with lower activity generates a measurable voltage, proportional to the difference in chemical potential.

6.1.1. Experimental results
Measurements were carried out in the composition range xBi∈(0,1)x_{Bi} \in (0,1)xBi∈(0,1) using a step of 0.1 in the atomic fraction. For each alloy composition, five experimental determinations were performed at a temperature of 1023 K. Based on the average values of the recorded electromotive force, the **thermodynamic activity of bismuth (Bi)** was calculated.

6.2 THERMODYNAMICS OF THE Bi60Sn35Sb5 ALLOY

The test composition used for the determination of the thermodynamic activity by the EMF method was a ternary alloy consisting of bismuth (Bi), tin (Sn) and antimony (Sb), in which the atomic fraction of Bi was kept constant at 60 at.%, and the Sb content was progressively increased in steps of 0.5 at.% to 5 at.%. As the Sb fraction increased (0.5, 1.0, 1.5, ..., 5.0 at.%), the Sn fraction was correspondingly reduced from 40 at.% to 35 at.% to keep the sum of the atomic fractions at 100%. Thus, the resulting compositions ranged from $Bi_{60}Sn_{40}$ (without Sb) to $Bi_{60}Sn_{35}Sb_5$, keeping Bi as the reference element and slightly modifying the thermodynamic equilibrium by controlled addition of Sb. These variations allowed studying the influence of low Sb concentration on the activity of Sn or Bi in the alloy, offering the possibility of analyzing the behavior deviating from ideality in the liquid phase of the Bi–Sn–Sb system.

CHAPTER VII
7. CONCLUSIONS

Bi–Sn alloys, by combining adequate electrical conductivity, thermal stability, and a low melting point, are ideal for protecting sensitive electronic components and ensuring reliable, durable, and high-quality connections. These technical characteristics make them a popular and efficient choice in the soldering of electronic components, contributing both to the reduction of production costs and to the improvement of performance and reliability of final electronic products.

Thus, the selection of low-melting solder alloys, such as Bi–Sn-based compositions, can substantially contribute to optimizing production costs while also providing ecological and technical benefits. This makes them an ideal option for the electronics industry and other fields where manufacturing cost and environmental impact are essential factors for the long-term success of the product.

Conclusions on the experimental results regarding the activity and thermodynamic behavior of the Bi–Sn system at 1023 K

The experimental analysis performed for the binary Bi–Sn system has provided essential data regarding its thermodynamic behavior, through the evaluation of activities, activity coefficients, and Gibbs free energies of mixing at 1023 K. Electromotive measurements carried out on a representative set of compositions, in steps of 0.1 of the atomic fraction of bismuth, allowed the identification of significant deviations from ideal behavior, confirming the non-ideal character of this binary system.

The experimental data obtained by the EMF method at 1023 K confirm that the Bi–Sn alloy behaves as a binary system with moderate non-ideality, characterized by entropic and enthalpic interactions between components, reflected in clear deviations of activities and activity coefficients from ideal values. These results are essential for:

- supporting CALPHAD models used in thermodynamic simulations;
- understanding solidification and segregation processes in Bi–Sn alloys;
- optimized alloy design for applications such as electronic soldering, cooling systems, or functional interfaces.

By integrating experimental data with theoretical modeling, this research provides a solid framework for the advanced thermodynamic characterization of binary metallic systems.

The experiment on the Bi–Sn–Sb ternary system at 1073 K highlights an overall near-ideal thermodynamic behavior, with significant deviations only under dilution conditions for the minor component, Sb. The thermodynamic activities of Sn and Bi remain almost constant or vary slightly with Sb content, suggesting weak interactions between the major components and good atomic-level homogenization.

In contrast, the activity and activity coefficient of Sb show a strong positive deviation from ideality at very low concentrations, reflecting initial thermodynamic instability caused by the introduction of a poorly compatible chemical species into the lattice. The extrapolated value of the activity coefficient γSb\gamma_{Sb}γSb at infinite dilution (≈88.21) underlines this non-ideal character of the minor component, although it tends to gradually integrate as its fraction increases.

Thus, the experiment demonstrates that in high-temperature ternary metallic systems, the major components may maintain a nearly ideal behavior, while diluted components play a crucial role in altering thermodynamic properties through selective and localized interactions. These observations are essential for optimizing alloy composition in applications where thermodynamic stability, homogeneity, and phase control are critical.

The thermodynamic study of the Bi–Sn–Ag ternary system at 1033 K reveals a clearly non-ideal behavior, mainly determined by the progressive introduction of silver (Ag) into the composition.

CHAPTER VIII
8. ORIGINAL CONTRIBUTIONS OF THE RESEARCH

The research carried out in this doctoral thesis brings a series of original contributions in the field of **materials science and engineering**, with applicability in interconnection technologies and the development of **lead-free alloys**. The major contributions can be summarized as follows:

1. **Development and characterization of new Bi–Sn-based compositions modified with alloying elements (Sb, Ag):**
   - The compositions **$Bi_{60}Sn_{35}Sb_5$** and **$Bi_{60}Sn_{35}Ag_5$** were proposed, produced, and experimentally characterized for the first time in the specialized literature.
   - The influence of antimony and silver additions on the thermal and electrical properties of the bismuth–tin system was investigated.
2. **Direct experimental determination of thermal and electrical conductivity for the studied alloys:**
   - The values obtained through direct measurements complement the existing database, especially for compositions that are not documented in international scientific sources.
3. **Application of the Laser Flash Analysis (LFA) method for measuring thermal diffusivity in Bi–Sn–X metallic compositions:**
   - The LFA method was used to determine thermal diffusivity, followed by the calculation of thermal conductivity by correlating with **specific heat capacity (Cp)** and **density (ρ)**, all determined experimentally.
   - Such measurements are rare in the specialized literature for these compositions, particularly in the high-temperature domain.
4. **Investigation of thermodynamic behavior at elevated temperatures (above 1000 K) for Bi–Sn and Bi–Sn–X alloys:**
   - For the first time, the behavior of the **$Bi_{60}Sn_{40}$ (at 1023 K)**, **$Bi_{60}Sn_{35}Sb_5$ (at 1073 K)**, and **$Bi_{60}Sn_{35}Ag_5$ (at 1033 K)** compositions was studied.
   - These temperatures exceed the usual values analyzed in previous studies and provide relevant data for industrial applications under severe thermal conditions.
5. **Correlation of chemical composition with thermophysical properties and phase behavior:**
   - The influence of composition on thermal stability, thermal and electrical conductivity, as well as on potential high-temperature phase transition behavior, was observed and analyzed.
   - The results provide a foundation for the design of new materials with optimized thermal properties.
6. **Contribution to the understanding and development of improved-performance lead-free alloys:**
   - Through the obtained results, this research supports international objectives regarding the replacement of traditional lead-based alloys with environmentally friendly materials, without compromising functional performance.