**ELECTRICAL AND THERMAL CONDUCTIVITY AND PHONON CONTRIBUTION TO THE THERMAL CONDUCTIVITY IN THE BI-IN SYSTEM**

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**Abstract:** In this study, the contribution of phonon to the thermal conductivity in the In-Bi (Indium-Bismuth) system due to its composition variation was determined from their electrical and thermal conductivity measurements. Because of the common usage of In-Bi system in many technological applications, thermal and electrical conductivity variations with temperature for different compositions of Bi component were measured. Four-Point Probe (FPP) and Linear Heat-Flow (LHF) methods were used for electrical and thermal conductivity measurements respectively. Intermetallic systems’ electrical conductivity values were determined between 0.8524 (1/Ω m) ×10^6 and 2.8381 (1/Ω m) ×10^6 thermal conductivity values were found between 14.50 (W/Km) and 35.93 (W/Km) at the melting temperature. Electron and phonon contributions to the thermal conductivity were calculated by using Wiedemann-Franz Law (WFL) from the measured values. The temperature coefficients values (α) of electrical and thermal conductivity were calculated between 0.46-2.54 (K^-1) x10^-3 and 1.29-4.34 (K^-1) x10^-3 respectively. In order to observe microstructure of the Bi-In intermetallic alloy Scanning Electron Microscopy (SEM) and to determine the composition of the phases in the structures, Energy Dispersive X-Ray Analysis (EDX) were used. Also melting temperatures (349.03 K-387.24 K), enthalpy of fusion (17.97 J/g- 42.37 J/g) and specific heat change (0.159 J/gK-0.372 J/gK) of Bi-In alloy systems were measured by using Differential Scanning Calorimeter (DSC).

**Keywords:** Microstructure, Electrical properties, Thermal properties.

**BI-IN SİSTEMİNDE ELEKTRİKSEL VE ISİL İLETKENLİK VE ISİL İLETKENLİĞE FONON KATKISI**

**Özet:** Bu çalışmada, elektriksel ve isıl iletkenlik ölçümlerini isıl iletkenliğe fonon katkıları kompozisyon değişimine bağlı olarak belirlenmiştir. In-Bi sistemlerinin birçok teknolojik uygulamaları yaygın olarak kullanılmak sebebiyle farklı kompozisyonlardaki Bi bileşimlerinin sıcaklık bağılı elektriksel ve isıl iletkenlik değerlerini ölçülmüştür. Elektriksel ve isıl iletkenlik ölçümlerinde srasıyla Dört Nokta Prob (FPP) ve Lineer Isı Akışı (LHF) yöntemleri kullanılmıştır. Erime sıcaklığında, intermetalik sistemlerin elektriksel iletkenlik değerleri 0.8524 (1/Ω m) ×10^6 ve 2.8381 (1/Ω m) ×10^6 arasındayken ve isıl iletkenlik değerleri 14.50 (W/Km) ve 35.93 (W/Km) arasında bulunmuştur. Ölçülen değerlerde, Wiedemann-Franz Kanunu (WFL) kullanılarak, isıl iletkenliğe elektron ve fonon katkıları hesaplanmıştır. In-Bi intermetalik sistemlerinin mikroşaraplarını gözlemleme için Taramalı Elektron Mikroskobu (SEM) ve yapılardaki fazların kompozisyonlarını belirlemek için, Enerji Dağışıçi X-İşlemi (EDX) analizi kullanılmıştır. Bi-In iletkenlik sistemlerindeki erime sıcaklıkları (349.03 K-387.24 K), füzyon entalpisi (17.97 J/g- 42.37 J/g) ve spesifik ısı değişimi (0.159 J/gK-0.372 J/gK) Diferansiyel Taramalı Kalorimetre (DSC) ile ölçülmüştür.

**Anahtar Kelimeler:** Mikroşarap, Elektriksel özellikler, Isıl özellikleri.
NOMENCLATURE

In    Indium  
Bi    Bismuth  
Zn    Zinc  
Ag    Silver  
Sb    Antimony  
Sn    Tin  
w.t.  Weight  
mm    Millimeter  
mL    Milliliter  
g    Gram  
FPP    Four-point probe  
LHF    Linear heat flow  
WFL    Wiedeman Franz law  
SEM    Scanning electron microscopy  
EDX    Energy dispersive X-ray  
DSC    Differential scanning calorimeter  
K\text{thermal}    Total thermal conductivity  
K_e    Electron contribution to the thermal conductivity  
K_{ph}    Phonon contribution to the thermal conductivity  
\sigma    Electrical conductivity  
\alpha_{ETC}    Electrical conductivity's temperature coefficient  
T_0    Set reference temperature  
\alpha_{T}    Electrical conductivity at Temperature T_0  
RCF    Resistivity correction factor  
V    Voltage  
I    Current  
A    Amper  
K    Kelvin  
G    Coefficient that includes the surface geometric boundaries and thickness of the sample.  
s    The difference between probes,  
t    The thickness of the sample  
d    The diameter of the sample.  
Q    Input power  
A    Cross-sectional area of the specimen  
\Delta T    Temperature difference  
\Delta X    Distance between two measurement points  
H    Enthalpy  
\Delta C_p    The change of specific heat  
T_M    The melting temperature  
T_{max}    Peak temperature  
T_{end}    End temperature  
T_{onset}    Onset temperature  

INTRODUCTION

Electrical and thermal conductivity values are very crucial parameters for intermetallic and metallic alloy systems owing to their wide variety of the use in practical application in industry and electronics. In reported works, there is no detailed investigation and explanation about thermal and electrical conductivities of intermetallic alloy systems. Therefore, providing thermal and electrical conductivity values for intermetallic alloy systems will be beneficial for researchers. In this work, seven different intermetallic compositions of Bi-In system were chosen to measure the electrical and thermal conductivities.

The thermal conductivity of a material can be defined as the rate of heat transfer through an unit thickness of the material per unit area per unit temperature difference. In solids, heat conduction depends on two effects: the lattice vibrational waves induced by the vibrational motions of the molecules positioned at relatively fixed positions in a periodic manner called lattice, and the energy transported via free flow of electrons in solid. The thermal conductivity of a solid is obtained by adding the lattice and electronic components. Thus, the total value of thermal conductivity (K) can be identified with the equation below.

\[ K_{\text{thermal}} = \frac{1}{3} \sum_{j} C_j v_j l_j \]  

(1)

Here j shows sort of the carrier, C_j means specific heat per unit volume, v_j is the velocity of the carrier and l_j is mean free path.

In a metal, major heat carriers are electrons and phonons. The total thermal conductivity can be written as the sum of both electron and phonon contributions as shown below:

\[ K_{\text{thermal}} = K_e + K_{ph} \]  

(2)

here K_e is the electron contribution and K_{ph} is the phonon contribution (Touloukian et al., 1970). In pure metals, the electrons' contribution is bigger than the phonons'. However, in impure metals they are nearly same (Kittel, 1965).

The value K_e can be calculated by using the Wiedeman Franz Law (WFL) (Kittel, 1965) as shown in Eq. (3). Here \sigma is the electrical conductivity value, L is Lorentz number that equals to \text{2.44x10^{-8}W}ΩK^{-2} (Kittel, 1965) and T is the given temperature value.

\[ \frac{K_e}{\sigma} = LT \]  

(3)

The main idea behind of this research was to calculate the phonon contribution in binary alloys. In order to determine this contribution, we measured the variation of the electrical and thermal conductivity with respect to different temperatures by using Four-Point Probe (FPP) and Linear Heat Flow (LHF) methods. The electron contribution to thermal conductivity (K_e) was calculated from WFL at given temperature by the help of calculated electrical conductivity (\sigma) values. Then the phonon contribution (K_{ph}) was calculated by Eq. (2) providing K_e and K_{thermal} values which were obtained before.
In the present work, Bi-12 wt.% In, Bi-15 wt.% In, Bi-35.4 wt.% In, Bi-45 wt.% In, Bi-47.6 wt.% In, Bi-53 wt.% In, Bi-62 wt.% In binary alloys’ thermal and electrical conductivity values were measured.

It is difficult to produce wires or sheets by using Bi-based alloys because of bismuth’s brittle nature and its tendency to segregation. Therefore, Bi-based alloys are inappropriate for many technological applications. Although some particular compositions of Bi-In binary alloys are used for lead-free solders owing to their low-melting point (Sun et al., 2014; Takahashi et al., 1977; Sammes et al., 1999; Jiang et al., 2002). Bi-In based ternary alloys including Zn, Ag, Sb and Sn are mostly used as lead-free solders in electronic industry. Bi-In-Sn is the most promising one within these ternary alloy systems. The mechanical properties improve significantly by adding Sn into the Bi-In binary alloy. At the previous studies (Pandher and Healey, 2018; Pandher et al., 2007; Huang and Wang et al., 2005; Liu and Shang, 2001; Zhao et al., 2004; Cheng at al., 2017), it has been found that adding Bi to lead-free solders has healing properties in alloys such as wettability, solder spreading, and reducing melting temperature and Bi can reduce the surface tension of the alloy compared to Sn. However, there are several binary and eutectic compounds that have low melting points as a result of melting in the Bi-In system. At a relatively high operating temperature of some soldering interconnects, serious problems arise regarding the effect of reaction products at the solder/substrate interface on the performance and reliability of the connections. Even small changes in the chemical composition of the interface between solder alloy and substrate, can lead to large changes in macroscopic behavior of soldered zone. Hence this effects the reaction behavior and morphological evolution of the solder-substrate system and therefore further progress in these areas become difficult (Biglari et al., 2018). In addition to use of Bi-In intermetallic compounds containing Zn in the production of alkaline batteries, Bi-In amalgams have been used to improve the properties of the fluorescent lamps. Thus, the knowledge of thermophysical properties of the Bi-In based ternary alloys, which have many technological applications, are very crucial (Sun et al., 2014; Takahashi et al., 1977; Sammes et al., 1999; Jiang et al., 2002; Rudnev et al., 2003; Yang et al., 2011; Liu et al., 2010; Benceze, 2006; Vizdal et al., 2007; Yang and Messler, 1994). In this study, in order to contribute to the thermophysical properties of Bi-In based ternary alloys, electrical and thermal conductivities of seven different intermetallic phases of Bi-In binary alloy have been investigated. These intermetallic phases of the Bi-In binary alloy system are Bi4In, Bi5In, Bi6In, Bi7In, Bi8In, Bi9In and Bi10In (ASM, 1992). In order to obtain these metallic phases, the compositions of Bi-In binary alloys were chosen as Bi-12 wt.% In, Bi-15 wt.% In, Bi-35.4 wt.% In, Bi-45 wt.% In, Bi-47.6 wt.% In, Bi-53 wt.% In, Bi-62 wt.% In by the help of phase diagram in previously published work (ASM, 1992).

In this study, the first step was to measure electrical and thermal conductivity variations with temperature. The second step was to obtain the phonon contribution to thermal conductivity. Finally, the microstructure and structural characteristics of Bi-In intermetallic alloys were investigated by using Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX) and Differential Scanning Calorimeter (DSC).

**EXPERIMENTAL PROCESS**

**Production of the samples**

Bi-12 wt.% In, Bi-15 wt.% In, Bi-35.4 wt.% In, Bi-45 wt.% In, Bi-47.6 wt.% In, Bi-53 wt.% and Bi-62 wt.% In alloys were prepared in a vacuum furnace system. Graphite crucibles that used in production, are drilled with 50 mm depth and 8 mm diameter for thermal conductivity measurements. During the experimental process, an alumina tube was used to facilitate the insertion of the thermocouples that used to determine the temperature difference into the sample. For this reason, 1.2 mm diameter hole was drilled at the rear end of the sample crucible. The sample crucibles that used for electrical conductivity measurements were also processed on a lathe to be 50 mm depth and 4 mm in diameter. Two different castings were made for both electrical and thermal conductivity measurements. Metals with 99.9% purity were melted in a vacuum melting furnace. The melted metals were stirred at regular intervals to form an alloy. The molten alloy was placed in a heated casting furnace for unidirectional solidification and left to solidify for one day. Also the same process was repeated for the production of the other alloy systems. The produced alloys have been prepared for the measurements and analyzes by cutting them in appropriate sizes according to their usage areas like thermal and electrical conductivity, microstructure and thermal properties. The samples used for conductivity measurements were prepared under directionally solidification. The details of the experimental system can be found in Refs Gündüz and Hunt (1985), Maraşlı and Hunt (1996), Aksöz (2013).

**Microstructure of the Systems**

In order to observe microstructure and determination of the phases in the sample, SEM was used for different compositions of the In-Bi alloy system. Well-known metallographic process as polishing and etching were used to pick out the different phases in the microstructure. Bi-12 wt.% In, Bi-15 wt.% In, Bi-35.4 wt.% In were etched for 5-10 seconds in the mixture of 20 mL hydrogen chloride, 4 g picric acid and 400 mL of ethanol. Bi-45 wt.% In, Bi-47.6 wt.% In, Bi-53 wt.% In, Bi-62 wt.% In were etched for 5-10 seconds in proper solution prepared with 1.3 g of potassium dichromate,
4.3 mL of sulfuric acid, 2.7 mL of sodium chloride, 17.7 mL of hydrogen fluoride, 8.8 mL of nitric acid and 66.3 mL of water. SEM images of the microstructures and EDX analysis of the In-Bi alloy samples with different composition were carried out to obtain the phases of Bi-In intermetallic alloys. As an example, in Figure 1, SEM image and EDX analysis results are given together for Bi-12wt. %In system.

Figure 1. The chemical composition analysis of Bi-12 wt.% In alloy by using EDX.

Electrical Conductivity

Electrical conductivity is an essential characteristic for metallic alloy systems and affected by many parameters such as impurities, heating process, grain size and plastic deformation. However, the temperature and the chemical composition affect the electrical conductivity more than other parameters (Rudnev et al., 2003).

The vibration of the atoms increases with the increasing of the temperature and these vibrations result in some dislocations (Meydaneri et al., 2012). Probability of the electron waves deviation increases owing to the dislocations that are formed in the corners of the blank lattice, grain boundaries, and via substituted atoms (Onaran, 2009). These dislocations result in increasing inelastic collisions between electrons-phonons and mean free path decreases with increasing collisions. So, electrical resistivity of the metal increases and electrical conductivity decreases by the rise in temperature. The dependency of electrical conductivity to the temperature is shown in Eq. (4)

$$\sigma(T) = \sigma_0 \left[ 1 + \alpha_{ETC} (T - T_0) \right]$$  \hspace{1cm} (4)

where, $\alpha_{ETC}$ is electrical conductivity's temperature coefficient, $T_0$ is the set reference temperature (generally room temperature), $\sigma_0$ is the conductivity at temperature $T_0$. $\alpha$ value can be expressed as;

$$\alpha_{ETC} = \frac{\sigma - \sigma_0}{\sigma_0 (T - T_0)} = \frac{I}{\sigma_0} \frac{\Delta \sigma}{\Delta T}$$  \hspace{1cm} (5)

The resistivity of a sample in FPP system as shown in Figure 2 can be written as

$$\rho = \frac{RCF V_{\text{measured}}}{I_{\text{measured}}}$$  \hspace{1cm} (6)

here RCF called resistivity correction factor which is obtained from thickness, the size of structure, electrode and the position of electrodes (Valder, 1954). Electrical resistivity is calculated by measuring the current and voltage values of four probes that positioned with a distance of 1 mm. Two inner probes measure voltage (V) and outer two probes measure current (I) values.

Figure 2. The schematic diagram of four-point probe method used for measuring electrical resistivity/conductivity.

The geometric properties of the materials are also important for determining the electrical resistivity values of the materials. The electrical resistivity expression is given as;

$$\rho = \frac{V_{23}}{I_{14}} G$$  \hspace{1cm} (7)

where $G$ is a coefficient that includes the surface geometric boundaries and thickness of the sample. The geometry of the samples are discs with a thickness $t$ and a circle geometry of diameter $d$. The dimensions of these discs and the distance $s$ between the terminals are measured. Also the ratios of geometry are calculated. Looking at these rates, it is seen that $se$1 and $d / s <40$. In this case, the required geometric correction factor is calculated by the following equation.

$$G = 2\pi F_1(t/s) F_2(d/s)$$  \hspace{1cm} (8)

where $s$ is the difference between probes, $t$ is the thickness and $d$ is the diameter of the sample. $F_1$ and $F_2$ are correction functions (Yilmaz, 2008). In order to determine the electrical resistivity value, the cast alloys are cut in 35 mm length in the precision cutting device and made ready to be placed in the FFP system. FFP
system consists of Keithley 2400 programmable power supply, Keithley 2700 multimeter, Proterm ash furnace and a computer. For each sample the electrical resistivity values were calculated by writing the current and voltage values that measured from the FPP system into Eq. (7). Electrical resistivity values were determined with approximately 5 % error.

**Thermal Conductivity**

In this study, a LHF apparatus which can reach up to 673 K and can be set to the desired temperature has been used to measure the thermal conductivity of solids. The system has three parts called hot-stage, cold-stage and sample holder as shown in Figure 3. The specimen is heated from one side by using the hot stage in steps of 20 K up to approximate 10 K below the melting temperatures of the materials and the other side of the specimen was kept cool by using a cold stage to get linear temperature gradient. The hot-stage is composed of two brass plates, which are heated by NiCr wires. A transformer was placed in the supply circuit to maximize the thermal stability of the hot-stage, stepping the maximum current down to 4 A. The temperature of the hot-stage was controlled with an accuracy of ±0.01 K with a Eurotherm 2604 type controller. The cold-stage’s design is similar with the hot-stage. However, cooling is accomplished by using a Poly Science digital 9102 model heating/refrigerating circulating bath that contains an aqueous ethylene glycol solution.

![Block diagram of linear heat flow apparatus used for measuring thermal conductivity.](image)

The thermal conductivity (K) at steady-state condition could be determined by the one-dimensional Fourier-Biot equation, (Kittel, 1965; Touloukian et al., 1970)

$$K = -\frac{Q \Delta X}{A \Delta T}$$  \hspace{1cm} (9)

where Q is the input power and A is the cross-sectional area of the specimen. \(\Delta T = T_2 - T_1\) is the temperature difference and \(\Delta X = X_2 - X_1\) is the distance between two measurement points.

To have a constant linear temperature gradient at the LHF system, while one side of the specimen was heated with a hot stage and the other side of specimen was cooled by the help of cold stage. The specimen has been kept for at least two hours to reach equilibrium at each measurement temperature.

One has to measure Q, A, \(\Delta T\) and \(\Delta X\), to evaluate the thermal conductivity of a binary alloy system from Eq. (9). Q was determined for every measurement temperature by measuring the input power given into the linear heat flow system for without \((Q_{WOS})\) and with specimen \((Q_{WS})\). The cross-sectional area of the specimen \((A = \pi r^2)\) was calculated by measuring the radius of the specimen. The temperature difference \((\Delta T)\) between two thermocouples was determined via a data-logger. The distance between two measurement points \((\Delta X)\) was determined from the photos of the thermocouple’s positions. After the measurement of A, Q, \(Q_{WS} - Q_{WOS}\), \(\Delta T\) and \(\Delta X\) values, the thermal conductivities of Bi-In intermetallic alloy systems were determined from Eq. (9).

For solid phase, the temperature dependency of the thermal conductivity is given as (Touloukian, 1970; Callendar and Nicolson, 1897)

$$K_s = K_{so} \left[1 + \alpha_{TTC} (T - T_0)\right]$$  \hspace{1cm} (10)

here \(K_s\) and \(K_{so}\) are thermal conductivity values of the solid phase at temperature \(T\) and reference temperature \(T_0\), respectively and \(\alpha_{TTC}\) is thermal temperature coefficient. By using Eq. (10),

$$\alpha_{TTC} = \frac{K_s - K_{so}}{K_{so}(T - T_0)} = \frac{1}{K_{so}} \frac{\Delta K}{\Delta T}$$  \hspace{1cm} (11)
can be written. The expression is the slope of the graph of thermal conductivity with temperature. So $\alpha_{TTC}$ can be determined by Eq. (11) with the help of this graph.

Experimental error in measuring thermal conductivity is equal to the sum of the uncertainties in the measurements of the heat flow rate, the temperature difference, the cross sectional area of the sample and the thermocouple locations. The total uncertainty in the measurements of thermal conductivity in this study is approximately 9%, since there is an error of around 5% from the heat flow rate, around 2.5% from the measurement of temperature differences, around 0.5% from the measurement of the cross-sectional area and around 0.3% from the fixed distance measurement.

The Enthalpy of Fusion and the Specific Heat Change of the Materials

The specific heat of a material (at a constant pressure) is given as

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$  \hspace{1cm} (12)

By integration of Eq. (12), the enthalpy of a material, can be obtained as ($H=0$ at 298 K)

$$H = \int_{298}^{T} C_p \,dT$$  \hspace{1cm} (13)

During the phase transformation from solid to liquid phase with given heat, the temperature of the sample doesn’t increase. This heat has been called enthalpy of fusion or latent heat of melting and used to transform from solid to liquid phase. The enthalpy of fusion can be given as

$$\Delta H \approx \Delta C_p T_M$$  \hspace{1cm} (14)

here $\Delta C_p$ is the change of specific heat and $T_M$ is the melting temperature. Since the enthalpy of fusion and the specific heat of Bi-In alloys are necessary for practical application in industry, these parameters have been measured in present work. Bi-In intermetallic alloys have been heated by using a Perkin Elmer Diamond model DSC with a heating rate of 10 K/min up to 823 K. The variations of heat flow with temperature for Bi-In intermetallic alloys.

RESULTS AND DISCUSSION

Microstructure

Different amounts of In were added to the Bi-[x] wt.% In systems in order to improve the properties of them. The amounts of In in the Bi-[x] wt.% In system were chosen from the phase diagram (ASM, 1992) as 12, 15, 35.4, 45, 47.6, 53 and 62 wt.%, respectively. By scanning every region of the used phase diagram (ASM, 1992), changes in the microstructure were observed with the dependence of In amount.
The Enthalpy of Fusion and the Specific Heat Change of Material

The variations of heat flow with temperature for Bi-In alloys have measured by DSC equipment and the graphs have been given in Figure 5.

Figure 5. The heat flow versus temperature curve for Bi-In intermetallic alloys at heating rate of 10 K/min.

As seen from Table 1, the increment in transition temperature range is considered as a disadvantage. Because when phase transition temperature range is increased, the soldering wire may be solidified later than expected. However, at this point it is also an advantage because of decreasing the melting temperature. The specific heat change for Bi-[x] wt.% In (X=12, 15, 35.4, 45, 47.6, 53 and 62) alloys are calculated and presented in Table 1.

In Figure 5, two peaks were observed from the DSC curves of Bi-15 wt.% In ve Bi-47.6 wt.% In alloy systems. When the Bi-In phase diagram is examined for the Bi-15 wt.% In alloy, the melting temperature of Bi$_3$In intermetallic is observed approximately 382.7 K. It was concluded that the sharp peak in the DSC curve is intermetallic Bi$_3$In. The curve where the peak temperature arises to 355.171 K was considered as Bi phase. The peak temperature for the Bi-47.6 wt.% In alloy system was analysed as 368.11 K. From the phase diagram, it was observed that there is an intermetallic Bi$_3$In phase with a melting temperature of 363 K. It was concluded that the curve with the peak temperature of 364.88 K is the γ$_1$ phase which is rich in Bismuth. Although one sharp peak was observed in other alloys, two phases were revealed in the microstructures. Since the phases in the Bi-12wt.% In alloy remain in the same curve and the Bi-[x] wt.% In (X=35.4, 45, 53 and 62) alloys are close to the eutectic point, it is thought that the phases exposed in the microstructure are coincident in the peaks in the DSC curves. Therefore, it is concluded that the coincident phases have the same thermal properties.

| Composition (wt.%) | Onset Temperature, $T_{onset}$ (K) | Peak Temperature, $T_{max}$ (K) | End Temperature, $T_{end}$ (K) | $\Delta T=T_{end}-T_{onset}$ (K) | Enthalpy of Fusion (J/g) | Specific Heat of Fusion (J/gK) |
|-------------------|----------------------------------|---------------------------------|-------------------------------|-------------------------------|------------------------|-------------------------------|
| Bi-12 In          | 383.84                           | 385.78                          | 386.78                        | 2.94                          | 17.97                  | 0.159                         |
| Bi-15 In          | 354.43                           | 355.17                          | 355.98                        | 1.55                          | 0.003                  | 0.364$x10^{-4}$              |
| Bi-35.4 In        | 382.47                           | 384.61                          | 385.54                        | 3.07                          | 25.14                  | 0.225                         |
| Bi-45 In          | 384.27                           | 387.24                          | 388.23                        | 3.96                          | 42.37                  | 0.371                         |
| Bi-47.6 In        | 366.18                           | 368.27                          | 370.84                        | 4.66                          | 35.36                  | 0.372                         |
| Bi-53 In          | 363.38                           | 364.88                          | 365.62                        | 2.24                          | 0.40                   | 0.004                         |
| Bi-62 In          | 365.62                           | 368.11                          | 369.03                        | 3.41                          | 31.79                  | 0.334                         |
|                   | 362.30                           | 367.09                          | 368.08                        | 5.78                          | 29.26                  | 0.311                         |
|                   | 347.01                           | 349.03                          | 353.53                        | 6.52                          | 24.71                  | 0.325                         |
Electrical Conductivity-Temperature Relation

Electrical conductivity-temperature graphs are given in Figure 6. As seen in the graphs, electrical conductivities of the systems decrease linearly with increasing temperature.

In Figure 6, calculated electrical conductivity values were compared to the values of pure Bi and pure In. The electrical conductivity lines for Bi-In intermetallic alloys are between pure Bi and pure In lines. Since Bismuth is semimetal, its electrical conductivity value is about 30 times smaller than Indium’s. Therefore, the electrical conductivities of Bi-In intermetallic alloys change with the Bismuth addition in the alloy. As can be seen from the phase diagram and the images of microstructures given in Figure 5, while the amount of Indium in the alloy increases, phase numbers and volume fraction of intermediate phases between Bi and In increase. Therefore, the electrical conductivity of Bi-In alloy increases with increasing the amount of In content in Bi-In alloys and the electrical conductivity lines for Bi-In intermetallic alloys approach to the line of pure Indium.

From electrical conductivity-temperature graphs, electrical conductivity's temperature coefficients were obtained as 2.41, 1.61, 1.95, 2.28, 2.54, 0.46 and 1.65 ($\times 10^{-3}$) K$^{-1}$ respectively (Table 2).

Thermal Conductivity-Temperature Relation

Pure metals have high thermal conductivities, and generally it has been supposed that metal alloys should also have high conductivities. Thermal conductivity of the binary alloy can be expected to lie between the thermal conductivity of its components. However, this turns out not to be the case. The thermal conductivity of binary alloy is usually much lower than that of either metals. Even small amounts in a pure metal of “foreign” molecules that are good conductors themselves seriously disrupt the flow of heat in that metal.

For Bi-12 wt.% In, Bi-15 wt.% In, Bi-35.4 wt.% In, Bi-45 wt.% In, Bi-47.6 wt.% In, Bi-53 wt.% In and Bi-62 wt.% In alloys, at their melting temperatures, the electrical conductivity values were obtained as 0.8524, 0.9128, 1.6567, 2.1422, 2.0622, 2.1146 and 2.8381 ($\times 10^6$) /Ωm, respectively.

Table 2. Some electrical and thermal properties of solid phase for In-Bi intermetallic alloys.

| Materials  | Melting Temperature $K$, (°C) | Temperature Coefficient of Electrical Conductivity $\alpha$ ($K^{-1}$) $\times 10^{-3}$ | Temperature Coefficient of Thermal Conductivity $\alpha$ ($K^{-1}$) $\times 10^{-3}$ | Electrical Conductivity at the Melting Temperature $\sigma$ (1/Ωm) $\times 10^6$ | Thermal Conductivity at the Melting Temperature $K$ (W/Km) |
|------------|-----------------------------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|--------------------------------------------------------------------------------|-------------------------------------------------------------|
| Bi-12 8wt.%In | 385.78 (112.78)             | 2.41                                                                            | 1.36                                                                            | 0.8524                                                                          | 14.50                                                        |
| Bi-15 8wt.%In | 384.61(111.61)              | 1.61                                                                            | 1.29                                                                            | 0.9128                                                                          | 16.23                                                        |
| Bi-35.4 8wt.%In | 387.24 (114.24)            | 1.95                                                                            | 3.27                                                                            | 1.6567                                                                          | 19.42                                                        |
| Bi-45 8wt.%In | 368.27 (95.27)              | 2.28                                                                            | 2.86                                                                            | 2.1422                                                                          | 25.63                                                        |
| Bi-47.6 8wt.%In | 368.11 (95.11)             | 2.54                                                                            | 2.47                                                                            | 2.0622                                                                          | 25.98                                                        |
| Bi-53 8wt.%In | 367.06 (94.06)              | 0.46                                                                            | 1.79                                                                            | 2.1146                                                                          | 31.83                                                        |
| Bi-62 8wt.%In | 349.03 (76.03)              | 1.65                                                                            | 4.34                                                                            | 2.8381                                                                          | 35.93                                                        |
Thermal conductivity-temperature graphs were shown in Figure 4 and the related data are given in Table 3. In Figure 4, a linear decrease in the values of thermal conductivity is seen with increasing temperature at high temperatures [T >> Debye temperature (Q_D)].

The phonon density is proportional to the temperature. So the higher the temperature, the more the phonon collision frequency, resulting in smaller mean free paths. Since C_v approaches the constant Dulong-Petit value, the change in the thermal conductivity has overwhelmingly controlled by the variance in mean free path. So that with increasing temperature, thermal conductivity decreases (Touloukian et al., 1970).

| Table 3. The experimental data in the measurement of thermal conductivity variations with temperature for Bi-In intermetallic alloys |
|---|---|---|---|---|---|---|---|
| Bi-12 wt.%In | Bi-15 wt.%In | Bi-18 wt.%In | Bi-21 wt.%In | Bi-24 wt.%In | Bi-27 wt.%In | Bi-30 wt.%In |
| T(K) | Q(W) | σTTC | K(W/Km) | T(K) | Q(W) | σTTC | K(W/Km) | T(K) | Q(W) | σTTC | K(W/Km) | T(K) | Q(W) | σTTC | K(W/Km) | T(K) | Q(W) | σTTC | K(W/Km) | T(K) | Q(W) | σTTC | K(W/Km) |
| 313 | 1.41 | 5.01 | 16.84 | 313 | 1.41 | 5.01 | 16.84 | 313 | 1.41 | 5.01 | 16.84 | 313 | 1.41 | 5.01 | 16.84 | 313 | 1.41 | 5.01 | 16.84 | 313 | 1.41 | 5.01 | 16.84 | 313 | 1.41 | 5.01 | 16.84 |
| 333 | 2.02 | 7.64 | 15.76 | 333 | 2.02 | 7.64 | 15.76 | 333 | 2.02 | 7.64 | 15.76 | 333 | 2.02 | 7.64 | 15.76 | 333 | 2.02 | 7.64 | 15.76 | 333 | 2.02 | 7.64 | 15.76 | 333 | 2.02 | 7.64 | 15.76 |
| 353 | 2.49 | 10.34 | 15.70 | 353 | 2.49 | 10.34 | 15.70 | 353 | 2.49 | 10.34 | 15.70 | 353 | 2.49 | 10.34 | 15.70 | 353 | 2.49 | 10.34 | 15.70 | 353 | 2.49 | 10.34 | 15.70 | 353 | 2.49 | 10.34 | 15.70 |
| 373 | 3.37 | 13.56 | 15.41 | 373 | 3.37 | 13.56 | 15.41 | 373 | 3.37 | 13.56 | 15.41 | 373 | 3.37 | 13.56 | 15.41 | 373 | 3.37 | 13.56 | 15.41 | 373 | 3.37 | 13.56 | 15.41 | 373 | 3.37 | 13.56 | 15.41 |

T: Temperature, Q: Heat flow rate into specimen, AT: Temperature difference into specimen, K: Thermal conductivity of specimen.

The melting temperature is the transformation temperature from solid state to liquid state. Thus, thermal properties of materials such as specific heat, thermal conductivity and enthalpy change with the melting temperatures. These kinds of thermal properties play critical role in transformation from liquid to solid or vice versa progress. One of them is the thermal conductivity of materials at its melting temperature. Solidification rate or solid phase growth rate exactly depends on conduction heat transfer rate and their thermal conductivity values and conduction can take place through either solid or liquid depending on the temperature gradients and thermal conductivity of phases at the interface and their thermal conductivities at the melting temperatures, respectively. Consider for example solid growing at a velocity v with a planar interface into a superheated liquid. The heat flow away from the interface through the solid must balance that from the liquid plus the latent heat generated at the interface. The value of thermal conductivity at the melting temperature is a required parameter for all kinds of materials. Therefore, the values of K at their melting temperature for Bi-12 wt.% In, Bi-15 wt.% In, Bi-35.4 wt.% In, Bi-45 wt.% In, Bi-47.6 wt.% In, Bi-53 wt.% In and Bi-62 wt.% In alloys were obtained as 14.50, 16.23, 19.42, 25.63, 25.63, 31.83 and 35.93 W/Km, respectively as seen from Table 2.

Also the temperature coefficients of thermal conductivity for same alloy systems were calculated as 1.36, 1.29, 3.27, 2.86, 2.47, 1.79 and 4.34 (×10^-5) K^-1, respectively. Electrical temperature coefficient (α_TTC) and thermal temperature coefficient (α_TTC) are main physical properties of materials. Variations of electrical and thermal conductivities with temperature for solid materials depend on the values of α_TTC and α_TTC. The values of α_TTC and α_TTC are usually the highest and the smallest values for good conductor and insulator materials, respectively. As can be seen from Table 2 and Figure 4, it is concluded that the values of α_TTC and α_TTC increase with increasing In content in the Bi-In alloys.

A comparison was done to obtained and pure Bi, In thermal conductivity values (Figure 4). The thermal conductivity lines for Bi-In intermetallic alloys were occurred between pure Bi and In that shown in Figure 4. As the amount of Indium in the alloy systems increases, the measured thermal conductivity values are close to the thermal conductivity lines of pure Indium. It’s seen in Figure 4 that the measured thermal conductivity data are in good compatibility with the thermal conductivity values of pure alloying elements.

**Thermal Conductivity’s Electron and Phonon Components**

As explained above, a LHF system was used to measure the thermal conductivity and a FPP system was used to measure the electrical conductivity values of the binary alloy systems. K_e value was calculated by using the measured σ from Eq. (3) at given temperature. Than K_α was calculated by using the measured K_e and calculated K_e from Eq. (2). The data that were used is given in Table 4. Also in Figure 7 the electron and phonon contribution to the thermal conductivity versus temperature is given. In Table 4 and Figure 7, it is clearly seen that the value K_e wasn’t changed with temperature and stayed constant. Thus it can be said that the results convenient with the WFL. According to this, the K_e is proportional to the product of electrical conductivity with temperature. Because of electrical conductivity decreases with increasing temperature K_e stays constant according to the WFL. Also in Figure 4
and Figure 7 it is seen that $K_{\text{thermal}}$ and $K_{\text{ph}}$ values linearly decrease with increasing temperature. The percentages of $K_{\text{ph}}$ were found as 49-54 %, 49-57 %, 37-52 %, 23-39 %, 30-40 %, 49-52 %, 35-46 % for Bi-12 wt.% In, Bi-15 wt.% In, Bi-35.4 wt.% In, Bi-45 wt.% In, Bi-47.6 wt.% In, Bi-53 wt.% In and Bi-62 wt.% In alloys at between 313-373 K temperature, respectively.

**CONCLUSIONS**

The results that were obtained from the study summarized below;

(1) The microstructure of Bi-In intermetallic alloy systems was observed through SEM images and all phases on the samples were determined by EDX analyses. As shown in Figure 4, Bi, Bi$_3$In, Bi$_5$In, Bi$_2$In$_3$, Bi$_5$In$_3$, BiIn$_2$ and BiIn$_3$ phases have been detected. The phases obtained on the samples are compatible with the phases on the phase diagram reported in ASM (1992).

(2) The melting temperatures, the enthalpy of fusion and the specific heat change of Bi-In alloy systems were determined by using DSC measurements. As seen from the results, the measured melting temperatures are in good agreement with the values in Ref ASM (1992).

(3) For the studied systems, it was seen that electrical conductivity and thermal conductivity decrease linearly with increasing temperature between the values of 0.8524 and $2.8381 \times 10^6 /\Omega m$ and 14.50 and 35.93 W/Km, respectively. In addition, it mightily related with the composition of the elements in the system. As the amount of indium increases, the thermal conductivity value increases too.

(4) $K_e$ and $K_{ph}$ values for the systems were obtained with the measured $K_{\text{thermal}}$ and $\sigma$ values by using WFL. It is clearly seen that the $K_e$ values seem to be constant while the values of $K_{ph}$ decrease linearly with increasing temperature. In other words, since the electron mean free path is longer in pure materials, $K_e$ value is dominant at all temperatures. However, in impure materials, $K_{ph}$ approaches to the $K_e$ because of the reducing of the mean free path by collisions with impurities.

**AUTHOR CONTRIBUTIONS**

P. Ata Esener wrote the manuscript with contributions from Ü. Bayram, E. Öztürk and N. Maraşlı, P. Ata Esener, Ü. Bayram, E. Öztürk and S. Aksöz were

![Figure 7](image-url)
responsible for experimental and analysis periods. S. Aksöz supervised the work and contributed to the writing of the manuscript.

DECLARATION OF COMPETING INTEREST
The authors declare no conflict of interest.

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