# EFFECT OF CHEMICAL COMPOSITION ON THE MICROSTRUCTURE, HARDNESS AND ELECTRICAL CONDUCTIVITY PROFILES OF THE BI-CU-GE, BI-GA-GE AND BI-GE-ZN ALLOYS

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## Abstract

The microstructure, hardness and electrical conductivity of the tested ternary systems based on Bi and Ge have not been studied so far. Three ternary systems were examined: Bi-Cu-Ge, Bi-Ga-Ge and Bi-Ge-Zn. The paper presents the results of experimental and analytical testing for given ternary systems. Among the experimental techniques were used: optical microscopy (LOM), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), X-ray diffractometric analysis (XRD), Brinell hardness measurements and electrical conductivity meaurements. Among the analytical methods, the Calphad method and the thermodynamic program were used (Pandat ver. 8.1). In all three tested ternary systems, one isothermal section at 25 °C was investigation. The results obtained experimentally were compared with the results of thermodynamic calculations. Based on thermodynamic parameters for constitutive binary systems, the calculation was performed. Good agreement was obtained between experiments and calculations. Also, in all three tested systems, hardness and electrical conductivity were measured, and with the help of an appropriate mathematical model, the properties in the entire range of the composition were guided. The results include calculated isothermal sections, structure, electrical conductivity and mechanical properties.

**Key words:** *Isothermal sections, mechanical properties, electrical conductivity, mathematical model.*

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## Introduction

The use of germanium-based alloys is multiple due to its useful thermal and electrical properties [1-3]. Adding Bi to the Ge-based alloys can further improve these properties, especially as semiconductors. In recent times, ternary alloys based on Bi and Ge are attracting more and more attention. Therefore, in this paper, systems based on Bi and Ge were examined due to multiple benefits, and a small number of studies in this regard [4-7]. In this paper, three ternary systems: Bi-Cu-Ge, Bi-Ga-Ge and Bi-Ge-Zn were investigated. These ternary systems have been previously tested by our group [8, 9]. Since a reliable set of thermodynamic data was obtained in previous study [8, 9], the same thermodynamic parameters were used in this paper for the calculation of the isothermal section at 25 °C. The ternary alloys tested in all three ternary systems are from isothermal sections at 25 °C and three vertical sections from each angle elements. Used experimental techniques are: optical microscopy (LOM), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), X-ray diffractometric analysis (XRD), hardness and electrical conductivity meaurements. The reason for testing these properties is due to the contribution to the further development of the field of application. Based on experimental results and using an appropriate mathematical model, these properties are predicted along the entire range of the composition. Experimental results for alloys from ternary sistems Bi-Cu-Ge, Bi-Ga-Ge and Bi-Ge-Zn were compared with calculated phase diagrams of isothermal section at 25 ° C and vertical sections and a reasonable agreement was obtained between calculated phase diagrams and experimental data.

## Experimental procedure

All ternary samples with total mass of 3 g were prepared from high purity Bi, Ge, Cu, Ga and Zn produced by Alfa Aesar (Germany). Samples were melted in an arc furnace under high-purity argon atmosphere and slowly cooled to the room temperature. The average weight loss of the samples during induction melting was abouth 0.5 mass %. Such prepared samples are subjected to all experimental tests.

## Results and Discussions

### Microstructural analysis

For each ternary system twelve ternary samples were selected for experimental tests. Compositions of chosen samples were from three different vertical sections: Bi-X(Ga,Cu,Zn)Ge, X(Ga,Cu,Zn)-BiGe and Ge-BiX(Ga,Cu,Zn). Four samples were prepared for each vertical section. Phases presented in each microstructure were determined with XRD method. While microstructures were recorded with LOM and SEM. Experimental results were compared with calculated isothermal section at 25 °C.

At calculated isothermal section were marked composition of the prepared samples for experimental tests.

Twelve ternary samples of the Bi-Cu-Ge system were observed with ligh optical microscopy. Figure 1 presents calculated isothermal section at 25 °C for a ternary Bi-Cu-Ge system. On figure 1 were marked and nominal composition of samples.

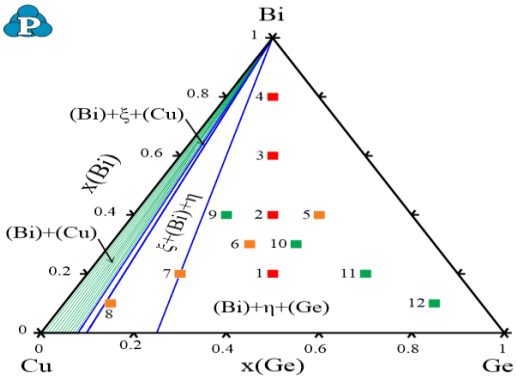


Figure 1. Predicted isothermal section at 25 °C of the ternary Bi-Cu-Ge system with marked compositions of tested alloys.

Four phase regions are visible on the calculated isothermal section at 25 °C. One region is two-phase region (Bi)+(Cu) on the Bi-Cu rich side and three are three-phase regions: (Bi)+η+(Ge), ξ+(Bi)+η and (Bi)+ξ+(Cu). From the four calculated phase regions, the existence of three have been experimentally confirmed. The confirmed phase regions are: (Bi)+η+(Ge) with samples 1-6 and 9-12, ξ+(Bi)+η with sample 7 and (Bi)+ξ+(Cu) with sample 8. It is clear that the experimentally determined phase compositions are very close to the calculated phase compositions. From this it can be concluded that the experiments support the calculated isothermal section at 25 ° C quite well.

Twelve microstructure of the ternary Bi-Ga-Ge system are observed with scanning electron microscope. Samples are numbered with numbers 1 to 12. The compositions of ternary samples are positioned along three vertical sections: Bi-GaGe (samples 1-4), Ga-BiGe (samples 5-8) and Ge-BiGa (samples 9-12). Figure 2 presents calculated isothermal section at 25 °C. Also, in the picture are marked and composition of prepared samples.

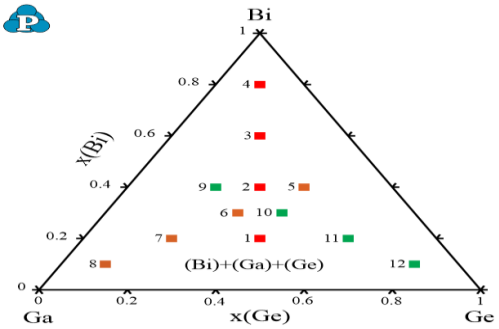


Figure 2. Predicted isothermal section at 25 °C of the ternary Bi-Ga-Ge system with marked compositions of tested alloys.

At the calculated isothermal section at 25 °C just one three-phase region is presented (Bi)+(Ga)+(Ge). All investigated samples should have three phases in their microstructures: (Bi), (Ga) and (Ge). XRD test of each samples detected three phases, same as predicted by calculation.
Twelve ternary samples of the ternary Bi-Ge-Zn system are observed and examined with scanning electron microscope. The compositions of ternary samples are positioned along three vertical sections: Bi-GeZn, Ge-BiZn and Zn-BiGe. From every section four samples were prepared and marked with numbers from 1 to 12. Figure 3 presents calculated isothermal section at 25 °C with marked composition of prepared samples.

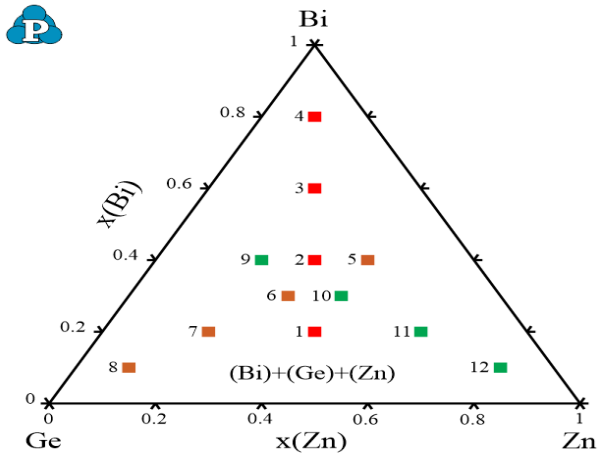


Figure 3. Predicted isothermal section at 25 °C of ternary Bi-Ge-Zn system with marked compositions of tested alloys.

According to the calculated isothermal section (fig. 3) all investigated samples should have three phases (Bi), (Ge) and (Zn) in microstructures. From isothermal section at 25 °C only one three-phase region is visible, and all tested samples belong to that region. By using XRD method it is determined that three phases correspond to the (Bi), (Ge) and (Zn), same as calculated.

## Mechanical properties

Mechanical properties were determined by using Brinell hardness test. Same samples as for microstructural teste were used for determination of the hardness values. In additional to the ternary samples three binary samples per each ternary system were added to examination. Hardness was measured at three different positions and based on experimental results mean value were calculated. Beside experimental results, experimental result of hardness for pure elements are used from literature [10].
A graphical representation of the results is given in figure 4. Presented is relationship between the hardness of the tested alloys and the composition of the alloys.

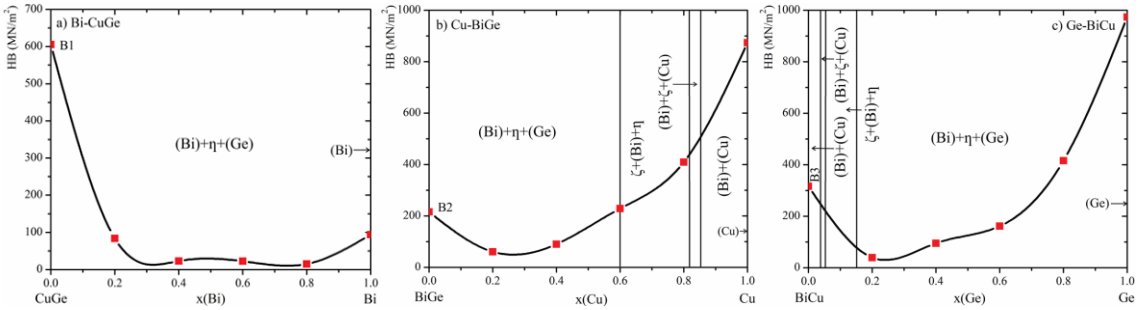


Figure 4. Graphical presentation of Brinell hardness of the investigated Bi-Cu-Ge alloys with overall compositions along vertical sections: a) Bi-CuGe, b) Cu-BiGe and c) Ge-BiCu.

Based on the obtained results graphically shown in figure 4, it can be seen that the highest value of hardness was recorded on sample 12 (415.56 MN/m²). The lowest Brinell hardness value was recorded on sample 4 (15.13 MN/m²). Figure 4a) shows the hardness of alloys by increasing the bismuth content. As the bismuth content of the alloys increases, the hardness of the alloy constantly declining. Figure 4b) shows the hardness behavior of alloys by increasing the copper content. Experimental results show that the addition of copper increases the hardness. The hardness showed the highest values in the alloy with 80 at.% of Cu, 408.93 MN/m². Figure 4c) shows the hardness of alloys with increasing germanium content and the results show that the addition of germanium increases the hardness of alloys.

A graphical representation of results of Brinell hardness of the ternary Bi-Ga-Ge alloys is given in figure 5. Presented is relationship between the hardness of the tested alloys and the composition of the alloys.

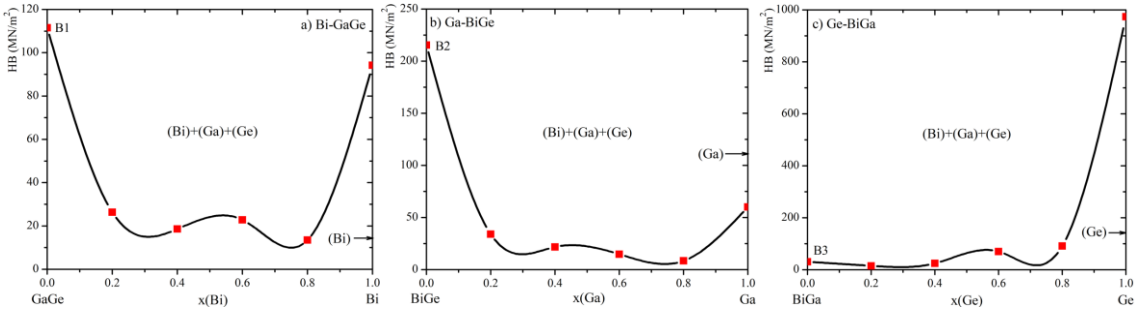


Figure 5. Graphical presentation of Brinell hardness of the investigated Bi-Ga-Ge alloys with overall compositions along vertical sections: a) Bi-GaGe, b) Ga-BiGe, and c) Ge-BiGa.

It can be seen from figure 5 that the hardness of the ternary Bi-Ga-Ge samples is in range from 8.33 MN/m² (sample 8) to the 90.60 MN/m² (sample 12). In microstructure of all tested sample same three phases are visible but difference of the detected hardness is clear. This difference is related to the different percentage of phases. So a high hardness of the sample 12 is associated with a very high germanium content in this alloy (80 at.%) and percent of (Ge) phase is 80 %, 10% of the (Bi) phase and 10 %

of the (Ga). With an increase of germanium content inside samples, the hardness increased from 15.06 MN/m² (sample 9, 20 % of (Ge) phase) to the 90.60 MN/m² (sample 12, 80 % of the (Ge) phase). The low value of the hardness of sample 8 is related to the high content of gallium in the alloy (80 at.% of the gallium, 80 % of the (Ga) phase, 10 % of the (Ge) phase and 10 % of the (Bi) phase). By increasing of the gallium content in the alloys, the hardness decreased, 33.93 MN/m² (sample 5) to 8.33 MN/m² (sample 8).

A graphical representation of results of Brinell hardness of the ternary Bi-Ge-Zn alloys is given in figure 6. Presented is relationship between the hardness of the tested alloys and the composition of the alloys.

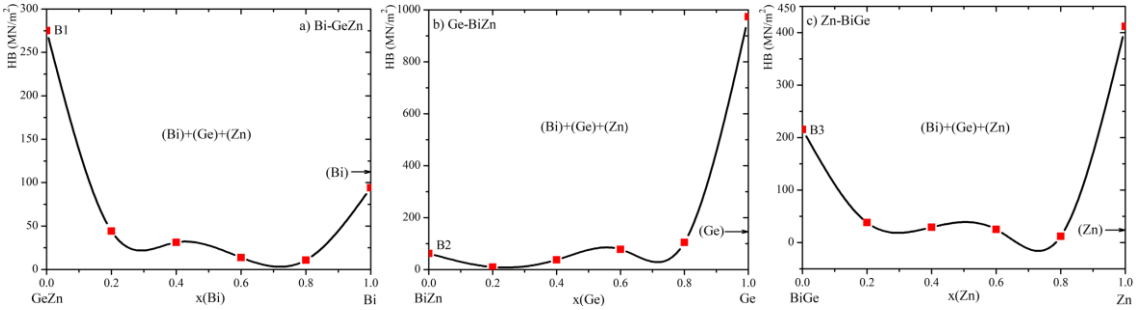


Figure 6. Graphical presentation of Brinell hardness of the investigated Bi-Ge-Zn alloys with overall compositions along vertical sections: a) Bi-GeZn, b) Ge-BiZn, and c) Zn-BiGe.

Based on the obtained results, graphically shown in figure 6, it can be seen that binary samples B1 and B3 have highest hardness 275.20 MN/m² and 215.40 MN/m². For the ternary samples, the highest hardness was recorded in sample 8 (80 at. % Ge) of the 105.30 MN/m², which is understandable due to the high presence of Ge in the alloy. Also, it can be noticed that with increasing Bi and Zn in ternary alloys the hardness decreases slightly, while increasing Ge in ternary samples leads to a slight increasement of the hardness.

## Electrical properties

On the same group of the samples on which mechanical properties were measured, electrical conductivity were determined. Electrical conductivity was measured at four different positions. Beside measured experimental values, tables 1-3 includes calculated mean values based on those four experimental values and, literature values of electrical conductivity for pure elements [11]. Table 1, presents results of the electrical conductivity of ternary Bi-Cu-Ge alloys.

Table 1. Electrical conductivity of the ternary Bi-Cu-Ge alloys.

| N. | Alloy nominal composition (at %) | | | Value (MS/m) | | | Mean value (MS/m) |
|---|---|---|---|---|---|---|---|
| | x(Bi) | x(Cu) | x(Ge) | 1 | 2 | 3 | |
| B1 | **0** | 0.5 | 0.5 | 5.643 | 5.345 | 5.543 | 5.510 |
| 1 | **0.2** | 0.4 | 0.4 | 3.481 | 3.512 | 3.466 | 3.486 |
| 2 | **0.4** | 0.3 | 0.3 | 0.338 | 0.352 | 0.352 | 0.347 |
| 3 | **0.6** | 0.2 | 0.2 | 1.109 | 1.133 | 1.108 | 1.117 |
| 4 | **0.8** | 0.1 | 0.1 | 0.231 | 0.211 | 0.276 | 0.239 |
| Bi | **1** | 0 | 0 | | | | 0.77 [11] |
| B2 | 0.5 | **0** | 0.5 | 0.341 | 0.353 | 0.344 | 0.346 |
| 5 | 0.4 | **0.2** | 0.4 | 0.748 | 0.761 | 0.788 | 0.765 |
| 6 | 0.3 | **0.4** | 0.3 | 0.969 | 0.978 | 0.912 | 0.953 |
| 7 | 0.2 | **0.6** | 0.2 | 1.519 | 1.442 | 1.491 | 1.484 |
| 8 | 0.1 | **0.8** | 0.1 | 2.380 | 2.362 | 2.376 | 2.373 |
| Cu | 0 | **1** | 0 | | | | 59 [11] |
| B3 | 0.5 | 0.5 | **0** | 7.215 | 7.569 | 7.289 | 7.357 |
| 9 | 0.4 | 0.4 | **0.2** | 1.373 | 1.350 | 1.331 | 1.351 |
| 10 | 0.3 | 0.3 | **0.4** | 1.235 | 1.218 | 1.237 | 1.230 |
| 11 | 0.2 | 0.2 | **0.6** | 0.319 | 0.313 | 0.387 | 0.339 |
| 12 | 0.1 | 0.1 | **0.8** | 0.287 | 0.246 | 0.254 | 0.262 |
| Ge | 0 | 0 | **1** | | | | 0.002 [11] |

The chemical composition of alloys has a strong influence on electrical conductivity. The experimentally determined value of electrical conductivity in all ternary samples is close to each other. The highest value of electrical conductivity was recorded in sample 1 (3.486 MS/m) of the $Bi_{0.2}Cu_{0.4}Ge_{0.4}$ composition. In addition to the composition of the alloy, the microstructure and amount of the phases inside samples are significantly affect on the electrical conductivity. The highest value of electrical conductivity of the binary alloys, was recorded on the $Bi_{50}Cu_{50}$ alloy, 7.357 MS/m. Also, it can be seen from the picture that with the increase of the copper content, the electrical conductivity increases, while with the increasement of the germanium content, electrical conductivity decreases. Electrical conductivity of the samples from the ternary Bi-Ga-Ge system are given in table 2.

Table 2. Electrical conductivity of the ternary Bi-Ga-Ge alloys.

| N. | Alloy nominal composition (at %) | | | Value (MS /m) | | | | Mean value |
|---|---|---|---|---|---|---|---|---|
| | x(Bi) | x(Ga) | x(Ge) | 1 | 2 | 3 | 4 | (MS/m) |
| B1 | **0** | 0.5 | 0.5 | 1.6520 | 1.6536 | 1.6521 | 1.7230 | 1.6701 |
| 1 | **0.2** | 0.4 | 0.4 | 0.5807 | 0.5789 | 0.5492 | 0.5483 | 0.5642 |
| 2 | **0.4** | 0.3 | 0.3 | 0.5998 | 0.5899 | 0.6234 | 0.6025 | 0.6039 |
| 3 | **0.6** | 0.2 | 0.2 | 0.6954 | 0.7325 | 0.7105 | 0.6988 | 0.7093 |
| 4 | **0.8** | 0.1 | 0.1 | 0.4073 | 0.409 | 1.4116 | 0.6896 | 0.7293 |
| Bi | **1** | 0 | 0 | | | | | 0.77 [11] |
| B2 | 0.5 | **0** | 0.5 | 0.3430 | 0.3410 | 0.3530 | 0.3440 | 0.3452 |
| 5 | 0.4 | **0.2** | 0.4 | 0.4359 | 0.4562 | 0.4499 | 0.4478 | 0.4474 |
| 6 | 0.3 | **0.4** | 0.3 | 0.9695 | 0.8563 | 0.8964 | 0.1253 | 0.7118 |
| 7 | 0.2 | **0.6** | 0.2 | 1.2350 | 1.2380 | 1.1810 | 1.2350 | 1.2220 |
| 8 | 0.1 | **0.8** | 0.1 | 2.512 | 2.349 | 2.265 | 2.457 | 2.3957 |
| Ga | 0 | **1** | 0 | | | | | 7.1 [11] |
| B3 | 0.5 | 0.5 | **0** | 0.2125 | 0.2930 | 0.2011 | 0.2351 | 0.2354 |
| 8 | 0.4 | 0.4 | **0.2** | 0.6411 | 0.6159 | 0.6649 | 0.6458 | 0.6419 |
| 10 | 0.3 | 0.3 | **0.4** | 0.3569 | 0.5785 | 0.4989 | 0.5233 | 0.4894 |
| 11 | 0.2 | 0.2 | **0.6** | 0.2838 | 0.3922 | 0.1746 | 0.2887 | 0.2848 |
| 12 | 0.1 | 0.1 | **0.8** | 0.1125 | 0.0965 | 0.0148 | 0.1283 | 0.0880 |
| Ge | 0 | 0 | **1** | | | | | 0.002 [11] |

The experimentally determined value of electrical conductivity in all ternary samples is close to each other. The electrical conductivity mainly increases with the increasement of the gallium content. The highest electrical conductivity was obtained on sample 8, with the highest content of the Ga, 2.3957 MS/m. Table 3, presents experimentally determined values of the electrical conductivity of the Bi-Ge-Zn alloys.

Table 3. Electrical conductivity of the ternary Bi-Ge-Zn alloys.

| N. | Alloy nominal composition (at %) | | | Value (MS /m) | | | | Mean value |
|---|---|---|---|---|---|---|---|---|
| | x(Bi) | x(Ge) | x(Zn) | 1 | 2 | 3 | 4 | (MS/m) |
| B1 | **0** | 0.5 | 0.5 | 1.8922 | 2.0152 | 1.9521 | 1.8787 | 1.9345 |
| 1 | **0.2** | 0.4 | 0.4 | 0.1258 | 0.1025 | 0.0968 | 0.0764 | 0.1003 |
| 2 | **0.4** | 0.3 | 0.3 | 0.2158 | 0.1996 | 0.2058 | 0.2187 | 0.2099 |
| 3 | **0.6** | 0.2 | 0.2 | 0.2598 | 0.2458 | 0.2149 | 0.2698 | 0.2475 |
| 4 | **0.8** | 0.1 | 0.1 | 0.3517 | 0.3509 | 0.3856 | 0.3625 | 0.3626 |
| Bi | **1** | 0 | 0 | | | | | 0.77 [11] |
| B2 | 0.5 | **0** | 0.5 | 1.9560 | 1.8640 | 1.9021 | 1.9020 | 1.9060 |
| 5 | 0.4 | **0.2** | 0.4 | 0.6254 | 0.6625 | 0.6419 | 0.6715 | 0.6503 |
| 6 | 0.3 | **0.4** | 0.3 | 0.3269 | 0.3127 | 0.2897 | 0.3025 | 0.3079 |
| 7 | 0.2 | **0.6** | 0.2 | 0.1258 | 0.1987 | 0.2108 | 0.1698 | 0.1762 |
| 8 | 0.1 | **0.8** | 0.1 | 0.0236 | 0.0189 | 0.3698 | 0.2158 | 0.1570 |
| Ge | 0 | **1** | 0 | | | | | 0.002 [11] |
| B3 | 0.5 | 0.5 | **0** | 0.3430 | 0.3410 | 0.3530 | 0.3440 | 0.3452 |
| 8 | 0.4 | 0.4 | **0.2** | 0.3079 | 0.3085 | 0.3065 | 0.3058 | 0.3071 |
| 10 | 0.3 | 0.3 | **0.4** | 0.3316 | 0.3046 | 0.3492 | 0.3322 | 0.3294 |
| 11 | 0.2 | 0.2 | **0.6** | 0.3596 | 0.3658 | 0.3469 | 0.3698 | 0.3605 |
| 12 | 0.1 | 0.1 | **0.8** | 0.3987 | 0.3898 | 0.4125 | 0.3874 | 0.3971 |
| Zn | 0 | 0 | **1** | | | | | 17 [11] |

Based on the obtained results of the electrical conductivity, the $Ge_{50}Zn_{50}$ binary alloy has the highest value of electrical conductivity, 1.9345 MS/m. It is known that the chemical composition, phase and percentage of the phase in the samples have a strong influence on electrical conductivity. In all tested ternary samples same three phases are detected in microstructure while, the values of electrical conductivity deviated in

range from 0.1003 MS/m to the 0.6503 MS/m, which is connected to the percentage of present phases inside samples.

## Mathematical modeling of the mechanical and electrical properties

By using experimentally determined values of the Brinell hardness and the electrical conductivity (Tables 1-3) and appropriated mathematical models it is developed unique equation for calculation of those properties along all composition ranges. Response Surface Methodology - RSM was used to quantify the relationship between independent input parameters and the dependent variable. Data processing was done in the software package Design Expert v.9.0.6.2 for each ternary and each properties. Iso-lines contour plot for Brinell hardness of Bi-Cu-Ge alloys is shown in figure 7.

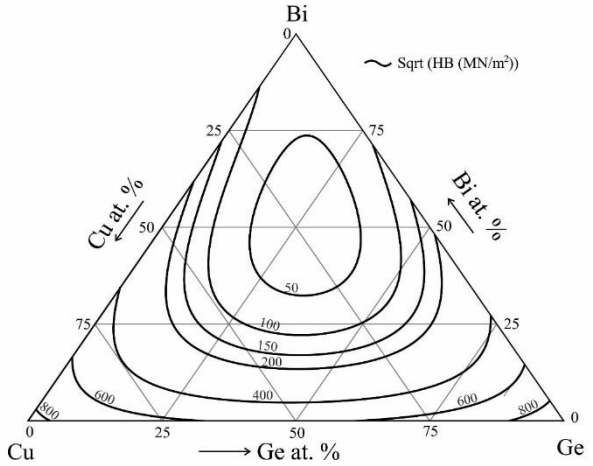


Figure 7. Calculated iso-lines of Brinell hardness in ternary Bi-Cu-Ge system with R2 =0.963.

The same methodology was applied in the process of obtaining models for electrical conductivity. Iso-lines contour plot for electrical conductivity of Bi-Cu-Ge alloys is shown in figure 8.

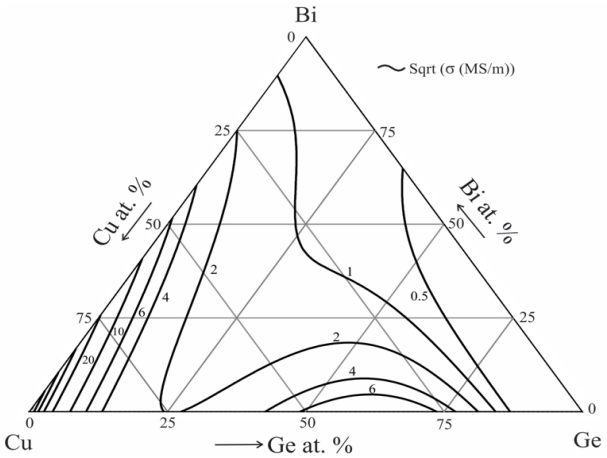


Figure 8. Calculated iso-lines of electrical conductivity in ternary

Bi-Cu-Ge system with R2 =0.929.

Mathematical model of the dependence of the Brinell hardness on composition for the Bi-Ga-Ge alloys was developed. Iso-lines contour plot for Brinell hardness of Bi-Ga-Ge alloys is shown in figure 9.

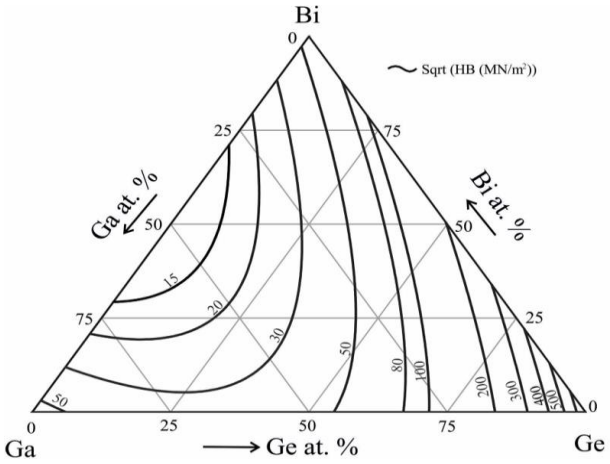


Figure 9. Calculated iso-lines of Brinell hardness in ternary Bi-Ga-Ge system with R2 =0.724.

Iso-lines contour plot for electrical conductivity of Bi-Ga-Ge alloys is shown in figure 10.

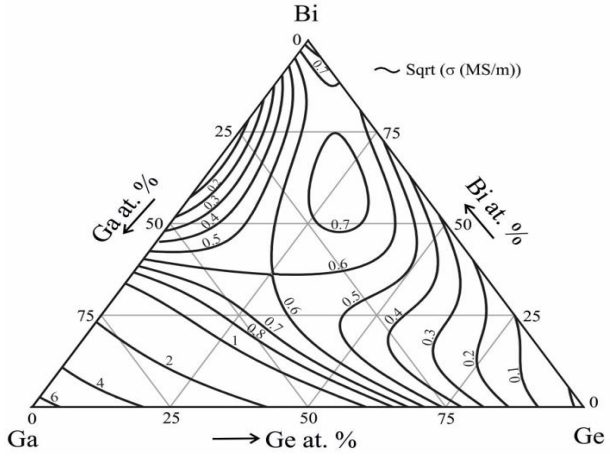


Figure 10. Calculated iso-lines of electrical conductivity in ternary Bi-Ge-Ga system with R2 =0.987.

The same methodology as for the previous two systems was applied in the process of obtaining a model for Brinell hardness of the Bi-Ge-Zn system. Iso-lines contour plot for Brinell hardness of Bi-Ge-Zn is shown in figure 11.

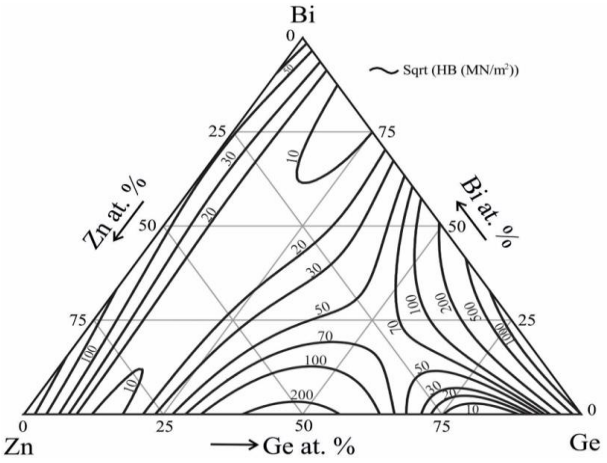


Figure 11. Calculated iso-lines of Brinell hardness in ternary Bi-Ge-Zn system with R2 =0.99.

Iso-lines contour plot for electrical conductivity of Bi-Ge-Zn alloys defined by equation 6 is shown in figure 12.

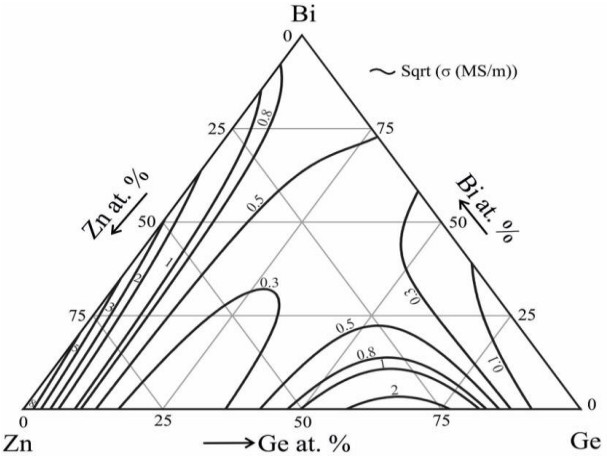


Figure 12. Calculated iso-lines of Electrical conductivity in ternary Bi-Ge-Zn system with R2 =0.901.

## Conclusions

In this paper, three ternary systems based on Bi and Ge: Bi-Ge-Cu, Bi-Ge-Ga and Bi-Ge-Zn were investigated. Ternary systems were tested experimentally using SEM-EDS, XRD, LOM, hardness tests and electrical conductivity tests. Isothermal section at 25 ° C were calculated by using Calphad method and calculated results are compared with tested samples. The phases that were experimentally determined by the XRD analysis were compared with the calculated isothermal section na 25 ° C and good agreement was reached between the results of the calculation and the experiments. Microstructure, hardness and electrical conductivity were tested on twelve ternary samples per each ternary system. In general, can be concluded that content of germanium influence strongly on hardness of ternary alloys because in all three system alloys with highest content of germanium have highest hardness. While for

electrical conductivity content of bismuth and germanium do not play important role. For electrical conductivity value can be concluded that alloying element gallium and copper play important role. At the end of result an appropriate mathematical model for calculations of hardness and electrical properties along all compositions range were predicted.

## References

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