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EFFECT OF CHEMICAL COMPOSITION ON THE MICROSTRUCTURE, HARDNESS, AND ELECTRICAL CONDUCTIVITY PROFILES OF THE Bi-Ge-X (Ga, Cu, Zn) ALLOYS

The microstructure, hardness, and electrical conductivity of the alloys from ternary systems based on Bi and Ge have not been studied so far. This paper presents the results of experimental and analytical investigation of Bi-Cu-Ge, Bi-Ga-Ge, and Bi-Ge-Zn ternary systems. Following experimental techniques were applied: optical microscopy (LOM), scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS), X-ray diffractometric analysis (XRD), Brinell hardness measurements and electrical conductivity measurements. Among the analytical methods, the Calphad method and the software Pandat ver. 8.1 were used. In all three investigated ternary systems an isothermal section at 25°C was selected for experimental testing. Based on the optimized thermodynamic parameters for the constitutive binary systems, the calculation was performed. The experimentally obtained results were compared with the results of thermodynamic calculations and good agreement was noticed. Also, in all three tested systems hardness and electrical conductivity were measured and using appropriate mathematical models these properties were guided in the entire range of the composition. The obtained results include determination of isothermal sections, identification of co-existing phases, electrical conductivity and hardness measurements and development of mathematical models for prediction of electrical conductivity and hardness.

Keywords: Bi-Cu-Ge; Bi-Ga-Ge; Bi-Ge-Zn; mechanical and electrical properties; mathematical model

1. 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 a previous study [8,9], the same thermodynamic parameters were used in this paper for the calculation of the isothermal sections 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 measurements. 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 at 25°C and a reasonable agreement was obtained between calculated phase diagrams and experimental data.

2. 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

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melting was abouth 0.5 mass %. Such prepared samples were subjected to all experimental tests. Scheme of experimental procedure has been presented on TABLE 1.

TABLE 1

Experimental procedure

Ternary systems	Groups of alloys	Experimental test	Device model
Bi-Cu-Ge alloys	one piece	XRD	D2 PHASER (Bruker) 2θ: 5 to 75° step 0.02°
	second piece	LOM	OLIPMUS GX-41
		Electrical conductivity	Foerster SIGMATEST 2.069
		Brinell hardness	INOVATEST NEXUS 3001 indenter diameter 2.5 mm pressing load 306.4 N
Bi-Ga-Ge alloys	one piece	XRD	D2 PHASER (Bruker) 2θ: 5 to 75° step 0.02°
	second piece	SEM-EDS	JEOL JSM-6460 with (EDS) (Oxford Instruments X-act)
		Electrical conductivity	Foerster SIGMATEST 2.069
		Brinell hardness	INOVATEST NEXUS 3001 indenter diameter 2.5 mm pressing load 306.4 N
Bi-Ge-Zn alloys	one piece	XRD	D2 PHASER (Bruker) 2θ: 5 to 75° step 0.02°
	second piece	SEM-EDS	JEOL JSM-6460 with (EDS) (Oxford Instruments X-act)
		Electrical conductivity	Foerster SIGMATEST 2.069
		Brinell hardness	INOVATEST NEXUS 3001 indenter diameter 2.5 mm pressing load 306.4 N

3. Results and discussions

3.1. Microstructural analysis

For each ternary system twelve ternary samples were selected for experimental study. 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 using the XRD method. The microstructures were recorded with LOM and SEM. Experimental results were compared with a calculated isothermal section at 25°C. The isothermal sections presented in Figs. 1, 3 and 5 were calculated using the program Pandat ver. 8.1 and optimized thermodynamic data from the literature for the binary subsystems. Composition of the prepared samples were marked at calculated isothermal sections.

Twelve ternary samples from the Bi-Cu-Ge system were observed using the light optical microscopy. Fig. 1 shows calculated isothermal section at 25°C for the ternary Bi-Cu-Ge system with marked nominal compositions of the investigated samples.

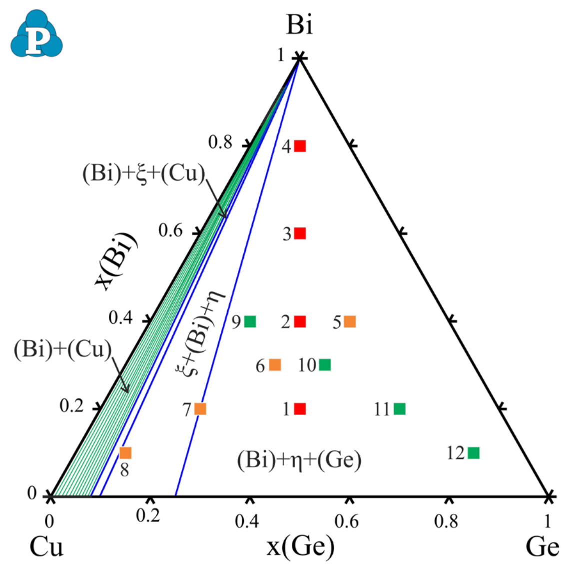

Fig. 1. Calculaced isothermal section at 25°C of the ternary Bi-Cu-Ge system with marked compositions of tested alloys

Four phase regions are visible on the calculated isothermal section at 25°C. One of them is (Bi) + (Cu) two-phase region on the Bi-Cu rich side and the rest 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. Experimentally 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.

The microstructures of the two tested alloy samples (samples 3 and 8) are shown in Fig. 2 as an illustration. The composition of all phases marked in Fig. 2 was determined by the EDS method, and based on the obtained results, they were marked on the presented LOM microstructures.

Fig. 2a) shows the microstructure of the sample 3 in which three phases are visible: (Bi) phase appearing as a light phase, (Ge) phase as a gray phase and η phase as a similar gray phase, only with a different shape than (Ge). Fig. 2b) shows the microstructure of sample 8 in which three phases are visible: (Bi) phase appearing as a light phase, (Cu) and ξ phases as gray phases.

Twelve microstructures 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

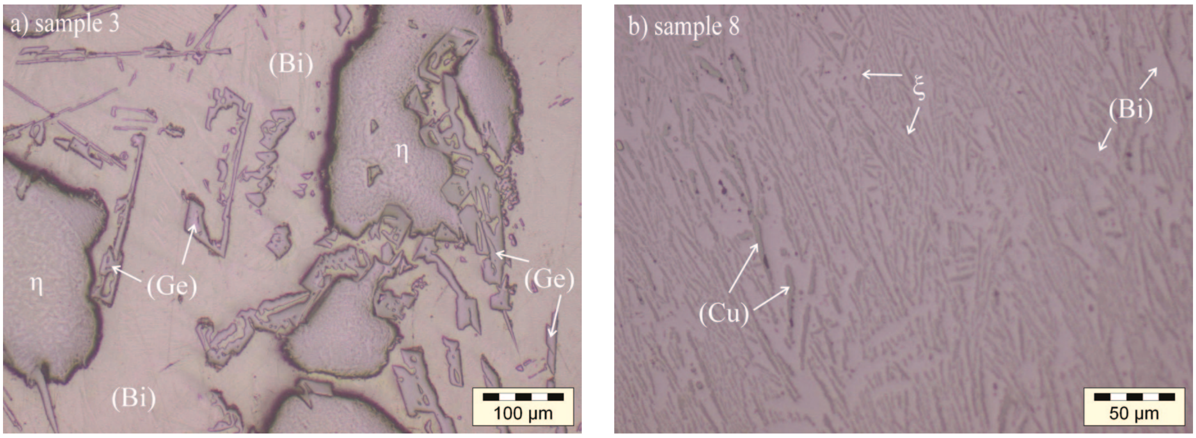

Fig. 2. LOM micrographs of the samples a) 3 and b) 8 of the ternary Bi-Cu-Ge system

(samples 9-12). Fig. 3 presents calculated isothermal section at 25°C with marked compositions of the prepared samples.

At the calculated isothermal section at 25°C only (Bi) + (Ga) + (Ge) three-phase region is presented. All investigated samples should have three phases in their microstructures: (Bi), (Ga) and (Ge). XRD test of each sample detected three phases, same as predicted by calculation. Two SEM images of microstructure for samples 3 and 6 are presented as an illustration in Fig. 4.

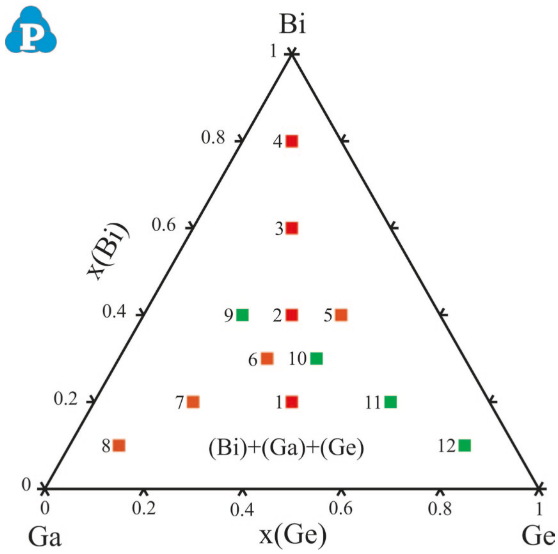

Fig. 3. Calculaced isothermal section at 25°C of the ternary Bi-Ga-Ge system with marked compositions of tested alloys

From Fig. 4 it is clear that the same phases in the microstructures are visible in both samples. Three phases can be noticed: solid solution (Bi) as a light phase, solid solution (Ga) as a grey phase and solid solution (Ge) as a dark phase.

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. Fig. 5 presents calculated isothermal section at 25°C with marked composition of prepared samples.

According to the calculated isothermal section (Fig. 5) all investigated samples should have (Bi), (Ge), and (Zn) phases in their microstructures. On isothermal section at 25°C only one three-phase region is visible, and all tested samples belong to that region. By using the XRD method it is determined that three phases correspond to the (Bi), (Ge) and (Zn) solid solution phases. Two microstructures of samples 4 and 11 are presented as an illustration in Fig. 6.

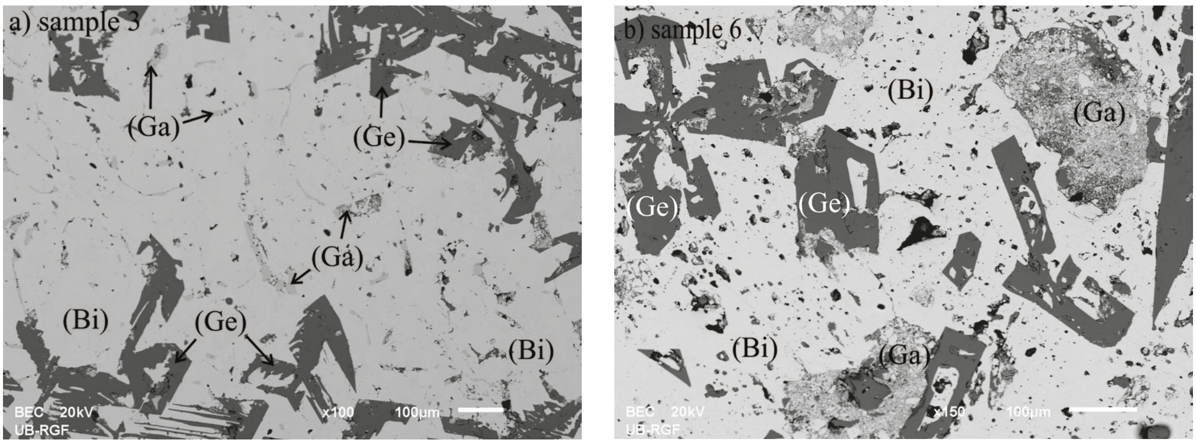

Fig. 4. SEM micrographs of the samples a) 3 and b) 6 of the ternary Bi-Ga-Ge system

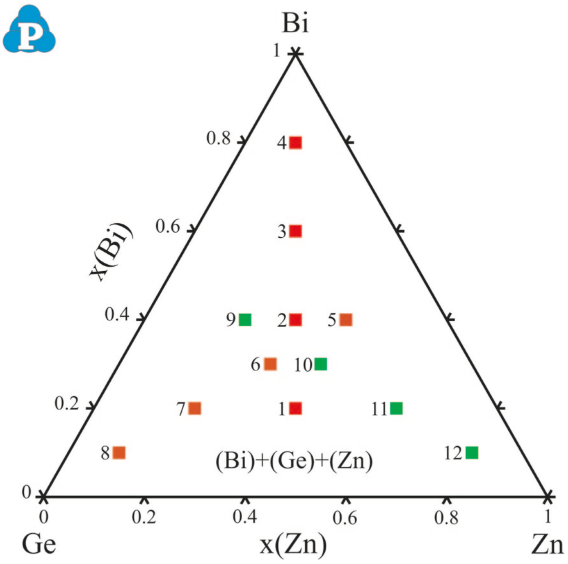

Fig. 5. Calculaced isothermal section at 25°C of ternary Bi-Ge-Zn system with marked compositions of tested alloys

In given SEM images three phases are noticed. (Bi) solid solution occurs as a light phase, (Ge) solid solution as a grey phase and (Zn) solid solution as a dark phase in the shape of needles.

3.2. Mechanical properties

Mechanical properties were determined using Brinell hardness test. Samples used for microstructural investigation were used for determination of the hardness values. In addition to the ternary samples, three binary samples per each ternary system were added to examination. For the Brinell hardness test, a steel ball with a diameter of 2.5 mm was used, and a load force of 306.4 N was applied for 20 seconds. Hardness was measured at three different positions and based on experimental results the mean value was calculated. Beside experimental results, experimental results of hardness for pure elements are used from literature [10].

A graphical representation of the results of the Brinell hardness for the ternary Bi-Cu-Ge system is given in Fig. 7.

Based on the obtained results shown in Fig. 7, it can be seen that the highest value of hardness was obtained for the sample 12 (415.56 MN/m^2). The lowest Brinell hardness value was obtained for the sample 4 (15.13 MN/m^2). Fig. 7a) shows variation of hardness of alloys with increasing bismuth content. As the bismuth content of the alloys increases, the hardness of the alloy is constantly declining. Fig. 7b) shows variation of hardness with increasing 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/m^2. Fig. 7c) shows the variations of alloy hardness upon increasing

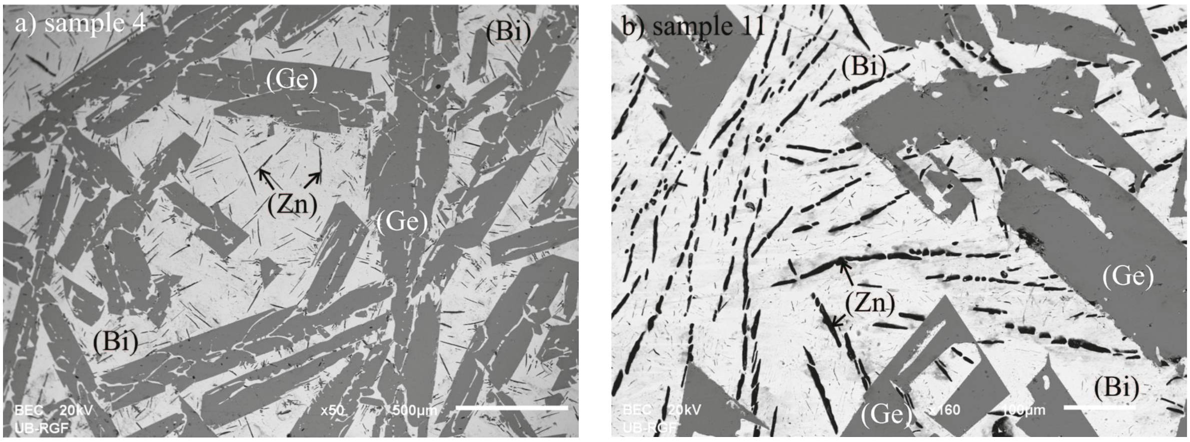

Fig. 6. SEM micrographs of the samples a) 4 and b) 11 of the ternary Bi-Ge-Zn system

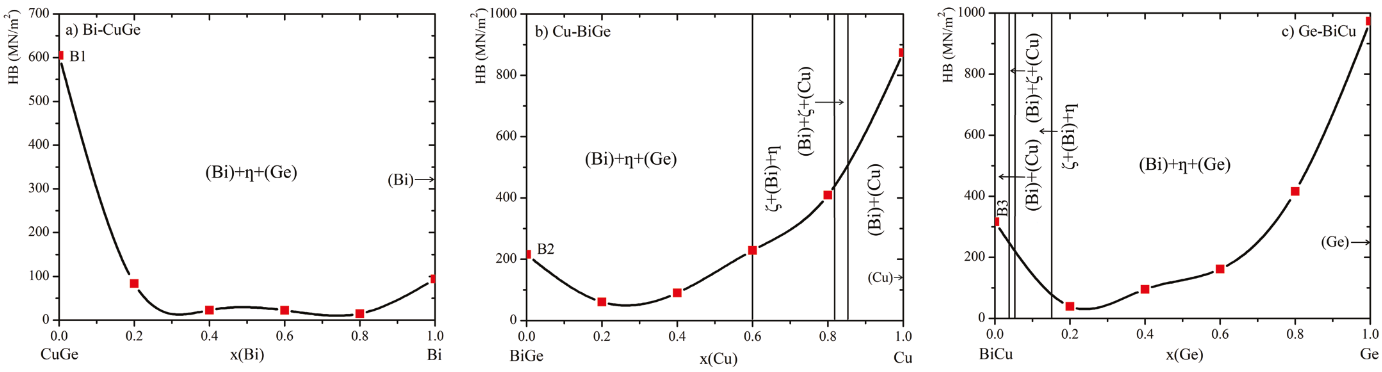

Fig. 7. Graphical presentation of Brinell hardness of the investigated Bi-Cu-Ge alloys with overall compositions along vertical sections: a) Bi-CuGe, b) Cu-BiGe and c) Ge-BiCu

germanium content and the results reveal that the addition of germanium increases the hardness of alloys.

A graphical representation of the results of the Brinell hardness measurements for the ternary Bi-Ga-Ge system is given in Fig. 8.

It can be seen from Fig. 8 that the hardness of the ternary Bi-Ga-Ge samples is in range from 8.33 MN/m^2 (sample 8) to 90.60 MN/m^2 (sample 12). In the microstructure of all tested samples the same three phases are visible but the difference of the detected hardness is clear. This difference is related to the different percentages 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/m^2 (sample 9, 20% of (Ge) phase) to 90.60 MN/m^2 (sample 12, 80% of the (Ge) phase). The low value of the hardness for the 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 the gallium content in the alloys, the hardness decreased from 33.93 MN/m^2 (sample 5) to 8.33 MN/m^2 (sample 8).

A graphical representation of the results of the Brinell hardness for the ternary Bi-Ge-Zn system is given in Fig. 9.

Based on the obtained results shown in Fig. 9, it can be seen that binary samples B1 and B3 have high hardness 275.20 MN/m^2 and 215.40 MN/m^2. For the ternary samples, the highest hardness was recorded in sample 8 (80 at.% Ge) of the 105.30 MN/m^2, 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 increase of the hardness.

3.3. Electrical properties

Germanium is a metalloid with very low electrical conductivity, almost electrically non-conductive. Therefore, the aim was to study the effect of the alloying elements (Bi, Ga, Cu and Zn) on electrical conductivity of germanium alloys. Electrical conductivity was obtained on the same group of the samples on which mechanical properties were measured. Electrical conductivity was measured on a Foerster SIGMATEST 2.069 device with eddy current. The measurements were repeated at four different positions. Beside measured experimental values, Figs. 10-12 includes calculated mean values based on those four experimental values and, literature values of electrical conductivity for pure elements [11].

A graphical representation of the results of the electrical conductivity for the ternary Bi-Cu-Ge system is given in Fig. 10. The relationships between the electrical conductivity of the tested alloys and the composition of the alloys are presented in the following graphs.

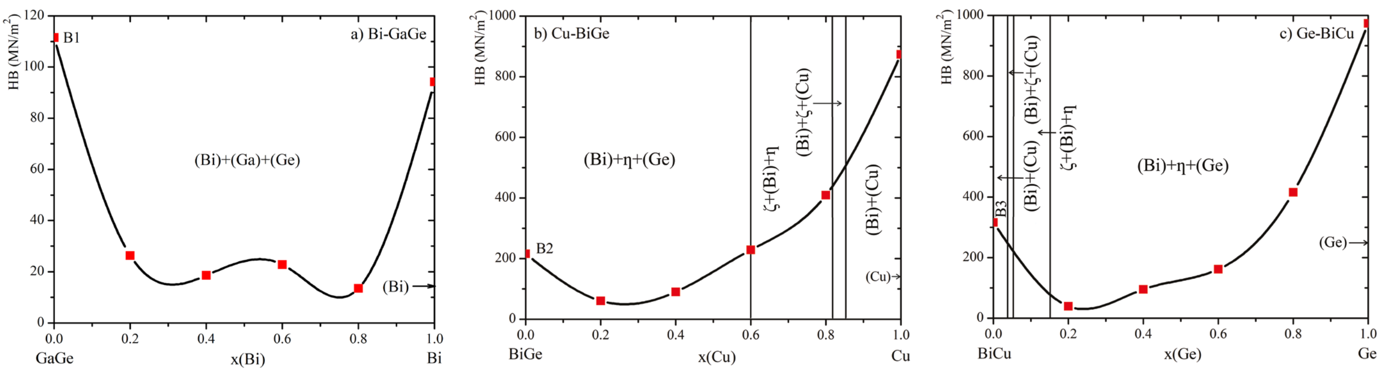

Fig. 8. Graphical presentation of Brinell hardness of the investigated Bi-Ga-Ge alloys with overall compositions along vertical sections: a) Bi-GaGe, b) Ga-BiGe, and c) Ge-BiGa

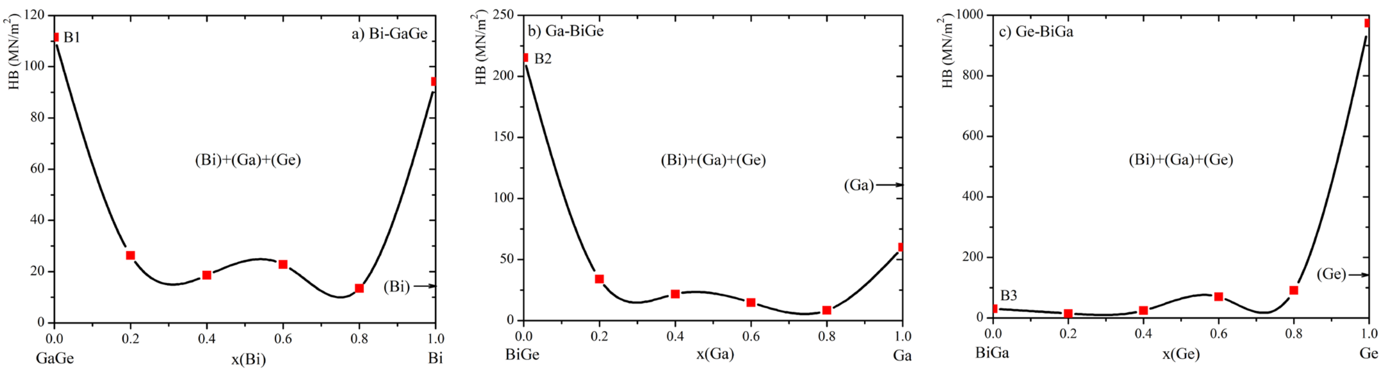

Fig. 9. Graphical presentation of Brinell hardness of the investigated Bi-Ge-Zn alloys with overall compositions along vertical sections: a) Bi-GeZn, b) Ge-BiZn, and c) Zn-BiGe

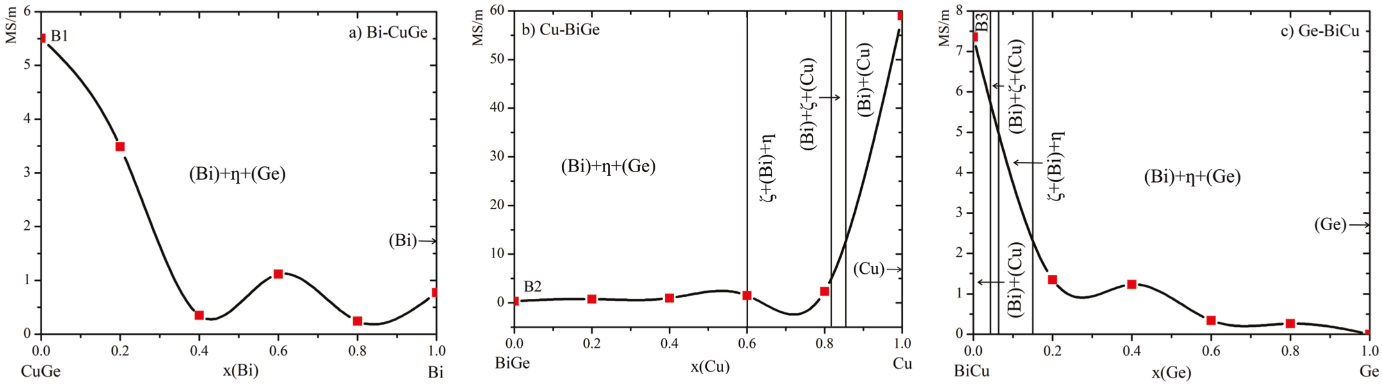

Fig. 10. Graphical presentation of the electrical cnductivity of the investigated Bi-Cu-Ge alloys with overall compositions along vertical sections: a) Bi-CuGe, b) Cu-BiGe and c) Ge-BiCu

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 obtained for the sample 1 (3.486 MS/m) with 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 significantly affect the electrical conductivity. The highest value of electrical conductivity of the binary alloys was obtained for the $Bi_{50}Cu_{50}$ alloy, 7.357 MS/m. Also, it can be seen that with the increase of the copper content, the electrical conductivity increases, and while with the increasement of the germanium content, electrical conductivity decreases.

A graphical representation of the results of the electrical conductivity measurements for the ternary Bi-Ga-Ge system is given in the Fig. 11.

The experimentally determined value of electrical conductivity in all ternary samples is close to each other. The electrical conductivity mainly increases with the increase of the gallium content. The highest electrical conductivity was obtained for the sample 8 with the highest content of the Ga, 2.3957 MS/m.

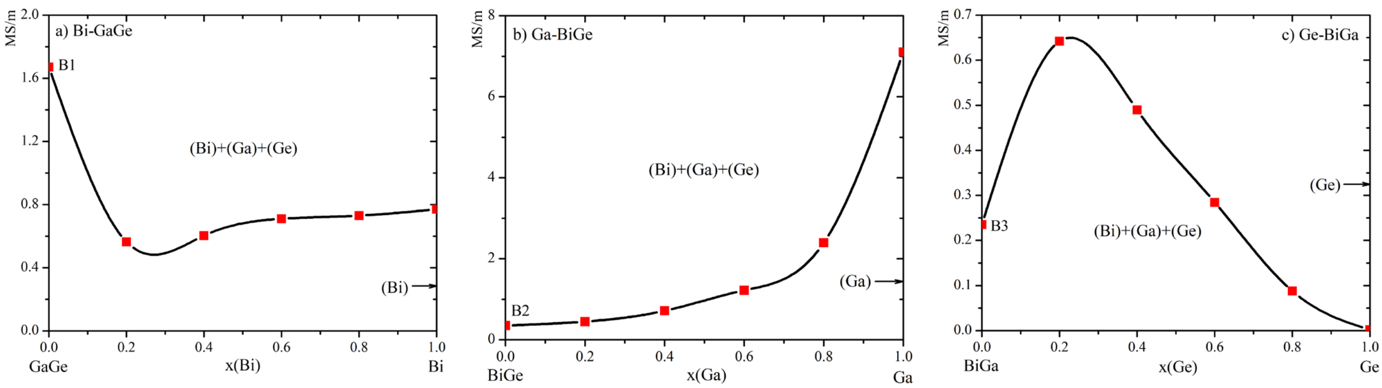

Fig. 11. Graphical presentation of the electrical conductivity of the investigated Bi-Ga-Ge alloys with overall compositions along vertical sections: a) Bi-GaGe, b) Ga-BiGe and c) Ge-BiGa

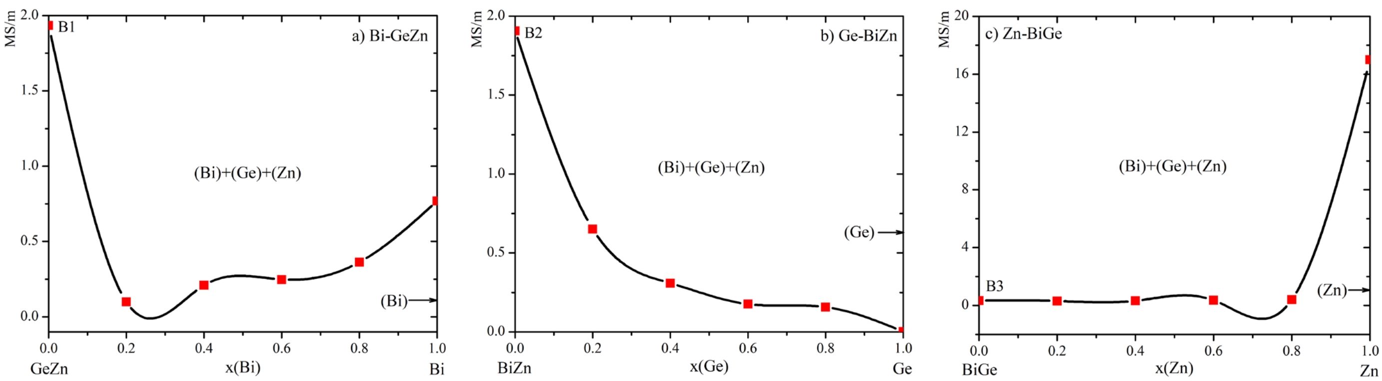

Fig. 12. Graphical presentation of the electrical cnductivity of the investigated Bi-Ge-Zn alloys with overall compositions along vertical sections: a) Bi-GeZn, b) Ge-BiZn and c) Zn-BiGe

A graphical representation of the results of the electrical conductivity for the ternary Bi-Ge-Zn system is given in Fig. 12. Relationship between the electrical conductivity of the tested alloys and the composition of the alloys is presented.

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 the same three phases are detected in microstructure while, the values of electrical conductivity deviated in range from 0.1003 MS/m to 0.6503 MS/m, which is connected to the percentage of present phases inside the samples.

3.4. A Mathematical modeling of the mechanical and electrical properties

Using experimentally determined values of the Brinell hardness and the electrical conductivity and appropriated mathematical models, the unique equations for calculation of those properties along all composition ranges have been developed. Response Surface Methodology – RSM was used to quantify the relationship between independent input parameters and the dependent variable [12-16]. Data processing was done in the software Design Expert v.9.0.6.2 for each ternary system and each property.

By utilizing experimentally determined values of hardness mathematical model of the dependence of the Brinell hardness on composition for the Bi-Cu-Ge alloys was developed. The "Special Cubic Mixture model" was proposed. Since the residues are not distributed according to the law of normal distribution, it was necessary to transform the model. The mathematical model was transformed using the "Square Root" function. ANOVA analysis (TABLE 2) confirmed the adequacy of the transformed model.

TABLE 2

ANOVA for Special Cubic Mixture model

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	1154.2052	6	192.3675	47.6213	3.08E-07
Linear Mixture	572.5796	2	286.2898	70.8722	5.2E-07
AB	3.1503	1	3.1503	0.7799	0.396069
AC	22.4367	1	22.4367	5.5543	0.038031
BC	24.0304	1	24.0304	5.9488	0.032880
ABC	111.9965	1	111.9965	27.7252	0.000266
Residual	44.4348	11	4.0395		
Cor Total	1198.6400	17			

The F-value of the Model is 47.62 and it implies that the model is significant. Model statistics have good values, which confirms the justification of the choice of the selected mathematical model (TABLE 3).

TABLE 3

Computational values of statistics for the evaluation of a mathematical model

Std. Dev.	2.01	R-Squared	0.96
Mean	13.99	Adj R-Squared	0.94
C.V. %	14.36	Pred R-Squared	0.78
PRESS	268.24	Adeq Precision	19.85

The final equation of the predictive model in terms of real components is (1):

$$\mathrm{Sqrt(HB)} = 7.913x(\mathrm{Bi}) + 29.102x(\mathrm{Cu}) + 30.505x(\mathrm{Ge}) - 8.451x(\mathrm{Bi})x(\mathrm{Cu}) - 22.553x(\mathrm{Bi})x(\mathrm{Ge}) - 23.340x(\mathrm{Cu})x(\mathrm{Ge}) - 266.202x(\mathrm{Bi})x(\mathrm{Cu})x(\mathrm{Ge}) \quad (1)$$

The diagnosis of the statistical properties of the assumed model found that the distribution of residuals are normal. After the applied Box-Cox procedure, the value of λ is 0.5, the optimum value of λ is 0.55 and the 95% confidence interval for λ (Low C.I. = 0.32, High C.I. = 0.78) contains the value 0.5, thus proving the justification of the model transformation (Fig. 13).

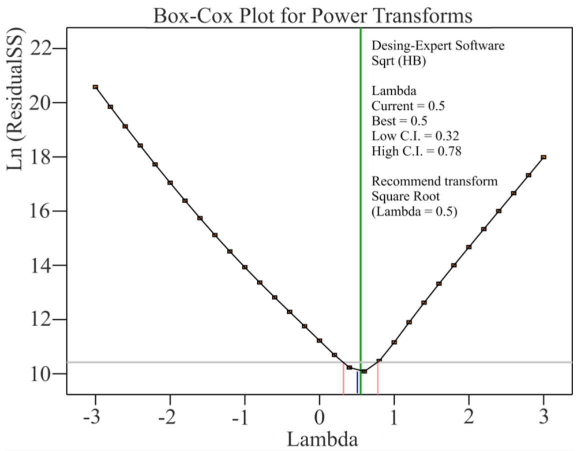

Fig. 13. The Box-Cox plot for power transforms

Iso-lines contour plot for Brinell hardness of alloys defined by Eq. (1) is shown in Fig. 14.

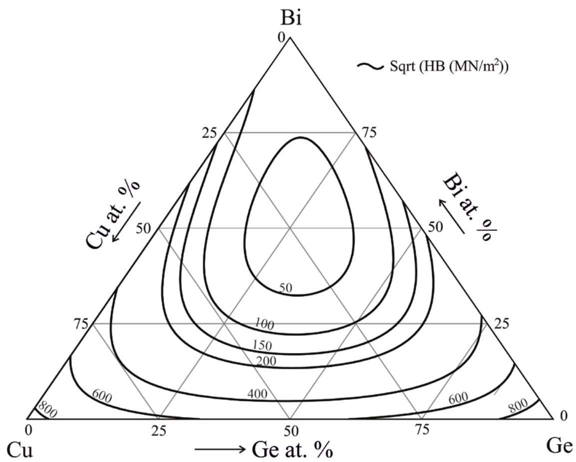

Fig. 14. Calculated iso-lines of Brinell hardness in ternary Bi-Cu-Ge system with $R^2 = 0.963$

The same methodology was applied in the process of obtaining models for electrical conductivity. The so-called Slack-Variable mixture models were used [17,18]. "Cubic Slack Mixture model" was suggested as a final equation for prediction of electrical conductivity. The diagnosis of the statistical properties of the assumed model found that the distribution of residuals is not normal and that it is necessary to transform the mathematical model in order to meet the conditions of normality. The Box-Cox diagnostics recommends the "Natural Log" transformation for the variance stabilization. ANOVA analysis (TABLE 4) confirmed the adequacy of the transformed model.

TABLE 4

ANOVA for Reduced Cubic Slack Mixture model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	66.83753	6	11.13959	23.97684	0.00001
B-Cu	1.10765	1	1.10765	2.38411	0.15084
C-Ge	0.24210	1	0.24210	0.52109	0.48544
BC	4.45516	1	4.45516	9.58928	0.01016
B^2	0.00138	1	0.00138	0.00298	0.95745
C^2	3.39311	1	3.39311	7.30334	0.02057
BC^2	9.32679	1	9.32679	20.07497	0.00093
Residual	5.11058	11	0.46460		
Cor Total	71.94811	17			

The F-value of the Model is 23.98 and it implies that the model is significant. R-squared and other statistics after the ANOVA have good values which confirm the justification of the choice of the adopted mathematical model (TABLE 5).

TABLE 5

Computational values of statistics for the evaluation of a mathematical model

Std. Dev.	0.682	R-Squared	0.923
Mean	–0.103	Adj R-Squared	0.891
C.V. %	662.558	Pred R-Squared	0.775
PRESS	16.211	Adeq Precision	23.810

The final equation of the predictive model in terms of actual components is:

$$\text{Ln(EP)} = -0.704 + 4.819x(\text{Cu}) + 2.089x(\text{Ge}) - 28.810x(\text{Cu})x(\text{Ge}) - 0.160x(\text{Cu}^2) - 7.551x(\text{Ge}^2) + 64.215x(\text{Cu})x(\text{Ge}^2) \quad (2)$$

The diagnosis of the statistical properties of the assumed model found that the distribution of residuals are normal. After the applied Box-Cox procedure, the value of λ is 0.0, the optimum value of λ is 0.02 and the 95% confidence interval for λ (Low C.I. = –0.14, High C.I. = 0.18) contains the value 0, thus proving the justification of the model transformation (Fig. 15).

Iso-lines contour plot for electrical conductivity of Bi-Cu-Ge alloys defined by equation (2) is shown in Fig. 16.

By utilizing experimentally determined values of hardness, mathematical model of the dependence of the Brinell hardness on composition for the Bi-Ga-Ge alloys was developed. The "Quadratic Mixture model" was proposed. Since the residues are not distributed according to the law of normal distribution, it was necessary to transform the model. The mathematical model was transformed using the "Natural Log" function. ANOVA analysis (TABLE 6) confirmed the adequacy of the transformed model.

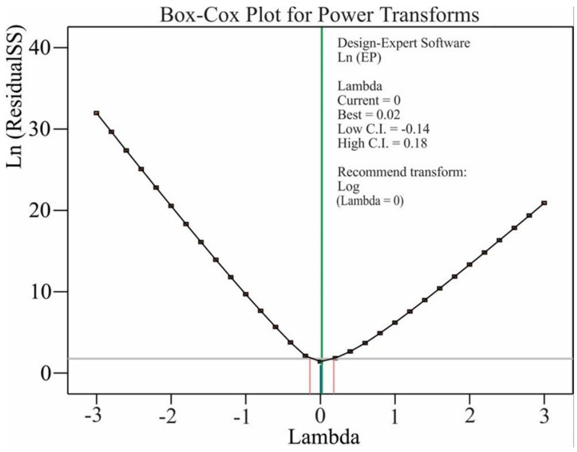

Fig. 15. The Box-Cox plot for power transforms

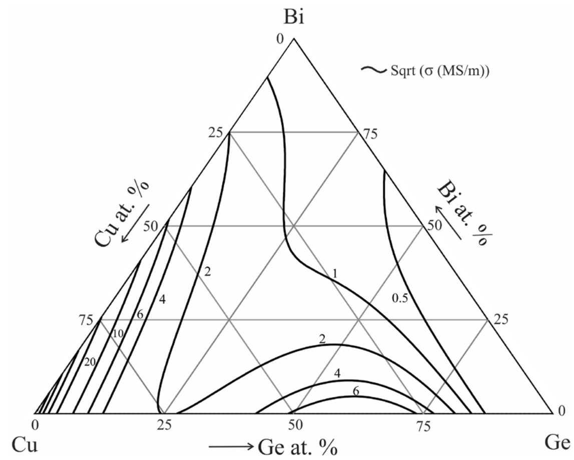

Fig. 16. Calculated iso-lines of electrical conductivity in ternary Bi-Cu-Ge system with R^2 = 0.929

TABLE 6

ANOVA for Quadratic Mixture model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	16.8649	4	4.2162	8.5064	0.00134
Linear Mixture	11.0544	2	5.5272	11.1513	0.00151
AC	2.8076	1	2.8076	5.6644	0.03331
BC	2.3175	1	2.3175	4.6756	0.04982
Residual	6.4435	13	0.4957		
Cor Total	23.3084	17			

The F-value of the Model is 8.51 and it implies that the model is significant. Model statistics have good values, which confirms the justification of the choice of the selected mathematical model (TABLE 7).

TABLE 7

Computational values of statistics for the evaluation of a mathematical model

Std. Dev.	0.704	R-Squared	0.724
Mean	3.724	Adj R-Squared	0.638
C.V. %	18.905	Pred R-Squared	0.452
PRESS	22.807	Adeq Precision	11.098

The final equation of the predictive model in terms of real components is:

$$\text{Ln(HB)} = 3.866x(\text{Bi}) + 6.311x(\text{Ge}) + 3.892x(\text{Ga}) - 6.747x(\text{Bi})x(\text{Ga}) - 6.130x(\text{Ge})x(\text{Ga}) \quad (3)$$

The diagnosis of the statistical properties of the assumed model found that the distribution of residuals are normal. After the applied Box-Cox procedure, the value of λ is 0.0, the optimum value of λ is –0.11 and the 95% confidence interval for λ (Low C.I. = –0.54, High C.I. = 0.22) contains the value 0.0, thus proving the justification of the model transformation (Fig. 17).

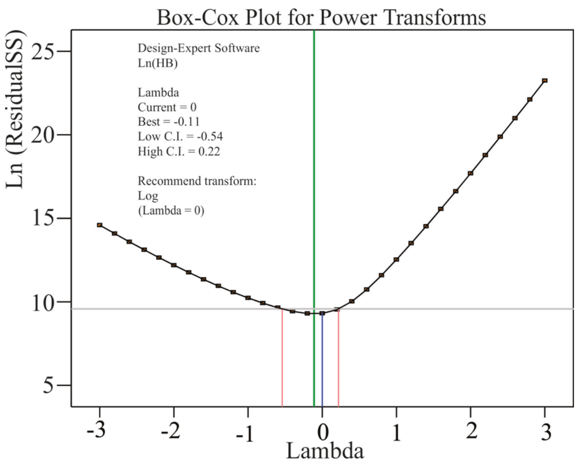

Fig. 17. The Box-Cox plot for power transforms

Iso-lines contour plot for Brinell hardness of alloys defined by Eq. (3) is shown in Fig. 18.

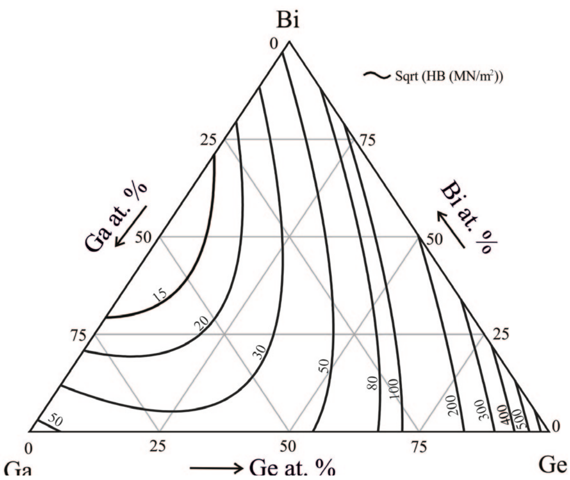

Fig. 18. Calculated iso-lines of Brinell hardness in ternary Bi-Ga-Ge system with $R^2 = 0.724$

The same methodology was applied in the process of obtaining models for electrical conductivity of the ternary Bi-Ga-Ge alloys. The "Special Quartic Mixture model" was adopted. The mathematical model was transformed using the "Square Root" function. ANOVA analysis (TABLE 8) confirmed the adequacy of the transformed model.

TABLE 8

ANOVA for Special Quartic Mixture model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	3.60805	7	0.51544	105.21181	1.4762E-08
Linear Mixture	2.44837	2	1.22418	249.88299	2.9050E-09
AB	0.00166	1	0.00166	0.33839	5.7364E-01
AC	0.78789	1	0.78789	160.82503	1.7347E-07
BC	0.05383	1	0.05383	10.98779	7.8160E-03
A^2BC	0.11832	1	0.11832	24.15246	6.0981E-04
ABC^2	0.03589	1	0.03589	7.32679	2.2054E-02
Residual	0.04899	10	0.00490		
Cor Total	3.65704	17			

The F-value of the Model is 105.21 and it implies that the model is significant. R-squared and other statistics after the ANOVA have good values which confirm the justification of the choice of the adopted mathematical model (TABLE 9).

TABLE 9

Computational values of statistics for the evaluation of a mathematical model

Std. Dev.	0.069	R-Squared	0.987
Mean	1.163	Adj R-Squared	0.977
C.V. %	6.017	Pred R-Squared	0.885
PRESS	0.419	Adeq Precision	43.166

The final equation of the predictive model in terms of actual components is:

$$\text{Sqrt(EP} + 0.50) = 1.168x(\text{Bi}) + 0.688x(\text{Ge}) + 2.702x(\text{Ga}) - 0.191x(\text{Bi})x(\text{Ge}) - 4.305x(\text{Bi})x(\text{Ga}) - 1.087 \times (\text{Ge})x(\text{Ga}) + 25.108x(\text{Bi}^2)x(\text{Ge})x(\text{Ga}) - 13.829\, x(\text{Bi})x(\text{Ge})x(\text{Ga}^2) \quad (4)$$

The diagnosis of the statistical properties of the assumed model found that the distribution of residuals are normal. After the applied Box-Cox procedure, the value of λ is 0.5, the optimum value of λ is 0.17 and the 95% confidence interval for λ (Low C.I. = –0.45, High C.I. = 0.54) contains the value 0.5, thus proving the justification of the model transformation (Fig. 19).

Iso-lines contour plot for electrical conductivity of Bi-Ga-Ge alloys defined by Eq. (4) is shown in Fig. 20.

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. The „Quartic Slack Mixture model" was selected. Since the residues are not distributed according to the law of normal distribution, it was necessary to

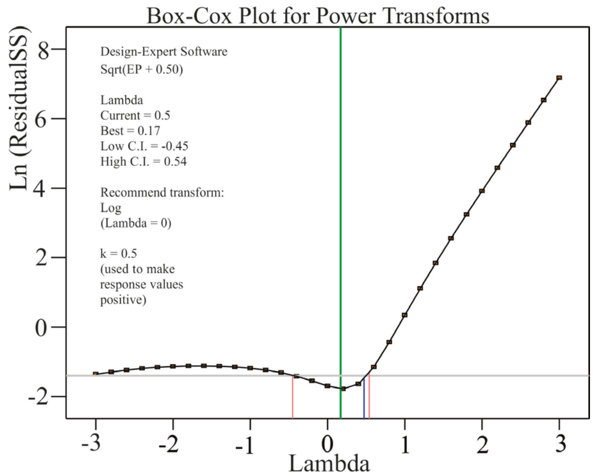

Fig. 19. The Box-Cox plot for power transforms

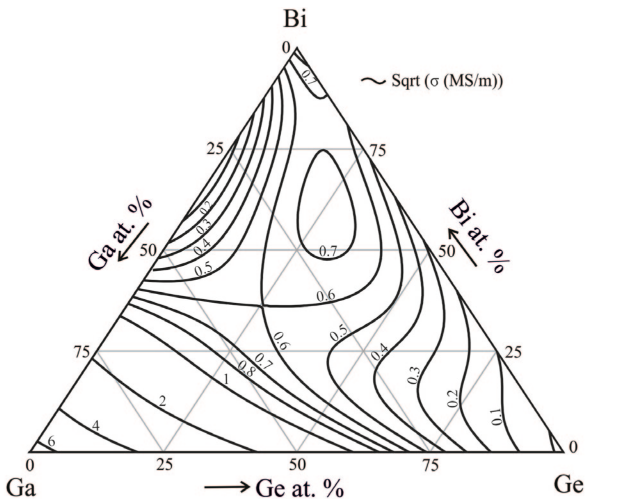

Fig. 20. Calculated iso-lines of electrical conductivity in ternary Bi-Ga-Ge system with $R^2 = 0.987$

transform the model using the "Natural Log" function. ANOVA analysis (TABLE 10) confirmed the adequacy of the transformed model.

TABLE 10

ANOVA for Reduced Quartic Slack Mixture model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	12.00854	9	1.33428	87.18875	0.000001
B-Ge	0.46902	1	0.46902	30.64789	0.000550
C-Zn	0.19215	1	0.19215	12.55575	0.007582
BC	0.34754	1	0.34754	22.71004	0.001417
B^2	0.61357	1	0.61357	40.09379	0.000225
C^2	0.50700	1	0.50700	33.12984	0.000426
B^2C	0.81470	1	0.81470	53.23669	0.000084
BC^2	0.90588	1	0.90588	59.19470	0.000058
B^3	0.57059	1	0.57059	37.28501	0.000288
B^2C^2	2.49301	1	2.49301	162.90573	0.000001
Residual	0.12243	8	0.01530		
Cor Total	12.13097	17			

The F-value of the Model is 87.19 and it implies that the model is significant. Model statistics have good values, which confirms the justification of the choice of the selected mathematical model (TABLE 11).

TABLE 11

Computational values of statistics for the evaluation of a mathematical model

Std. Dev.	0.124	R-Squared	0.989
Mean	4.734	Adj R-Squared	0.978
C.V. %	2.613	Pred R-Squared	0.833
PRESS	2.029	Adeq Precision	32.689

The final equation of the predictive model in terms of real components is:

$$\begin{gathered}Ln(HB + 40.00) = 4.871 - 12.372x(Ge) - \\ 2.187x(Zn) + 30.859x(Ge)x(Zn) + 40.497x(Ge^2) + \\ 3.412x(Zn^2) - 84.575x(Ge^2)x(Zn) - 49.539 \\ x(Ge)x(Zn^2) - 26.072x(Ge^3) + 151.280 \\ x(Ge^2)x(Zn^2)\end{gathered} \tag{5}$$

The diagnosis of the statistical properties of the assumed model found that the distribution of residuals are normal. After the applied Box-Cox procedure, the value of λ is 0.0, the optimum value of λ is 0.01 and the 95% confidence interval for λ (Low C.I. = –0.78, High C.I. = 0.58) contains the value 0.0, thus proving the justification of the model transformation (Fig. 21).

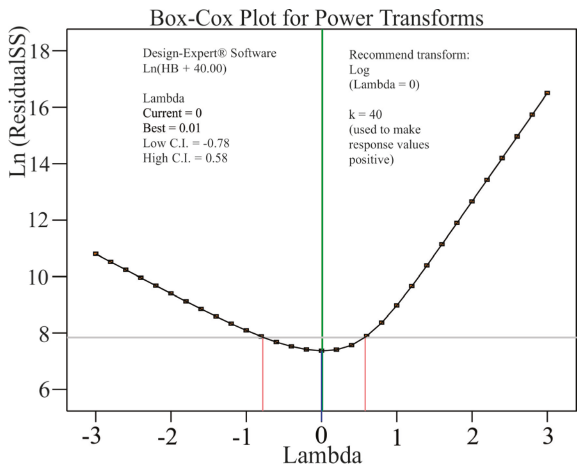

Fig. 21. The Box-Cox plot for power transforms

Iso-lines contour plot for Brinell hardness of alloys defined by Eq. (5) is shown in Fig. 22.

The same methodology was applied in the process of obtaining the electrical conductivity model. The „Cubic Slack Mixture model" was selected. The mathematical model was transformed using the „Natural Log" function. ANOVA analysis (TABLE 12) confirmed the adequacy of the transformed model.

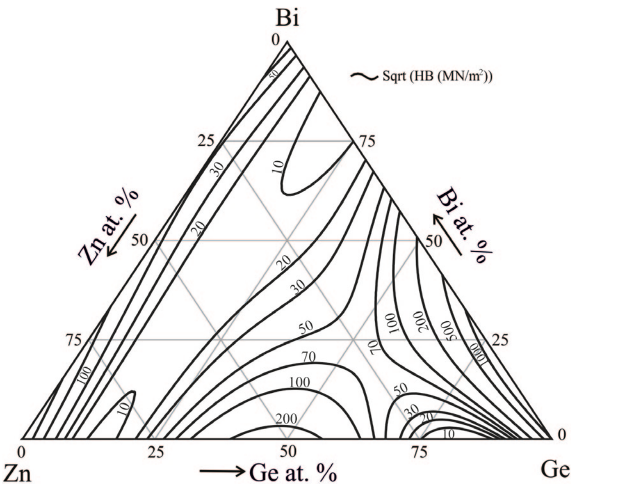

Fig. 22. Calculated iso-lines of Brinell hardness in ternary Bi-Ge-Zn system with $R^2 = 0.99$

TABLE 12

ANOVA for Reduced Cubic Slack Mixture model

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	46.571958	5	9.31439	21.95014	1.1776E-05
B-Ge	0.04895	1	0.04895	0.11535	0.74001
C-Zn	6.44622	1	6.44622	15.19105	0.00212
BC	10.26741	1	10.26741	24.19601	0.00035
B^2	2.48841	1	2.48841	5.86414	0.03222
B^2C	13.40383	1	13.40383	31.58725	0.00011
Residual	5.09212	12	0.42434		
Cor Total	51.66408	17			

The F-value of the Model is 21.95 and it implies that the model is significant. R-squared and other statistics after the ANOVA have good values which confirm the justification of the choice of the adopted mathematical model (TABLE 13).

TABLE 13

Computational values of statistics for the evaluation of a mathematical model

Std. Dev.	0.651	R-Squared	0.901
Mean	–1.061	Adj R-Squared	0.860
C.V. %	61.377	Pred R-Squared	0.713
PRESS	14.811	Adeq Precision	23.176

The final equation of the predictive model in terms of real components is:

$$\mathrm{Ln(EP)} = -0.6631 + 0.9383x(\mathrm{Ge}) + 3.1951x(\mathrm{Zn}) - 36.0586x(\mathrm{Ge})x(\mathrm{Zn}) - 6.4598x(\mathrm{Ge}^2) + 72.4346x(\mathrm{Ge}^2)x(\mathrm{Zn}) \quad (6)$$

The diagnosis of the statistical properties of the assumed model found that the distribution of residuals are normal. After the applied Box-Cox procedure, the value of λ is 0.0, the optimum value of λ is –0.01 and the 95% confidence interval for λ (Low C.I. = –0.19, High C.I. = 0.16) contains the value 0.0, thus proving the justification of the model transformation (Fig. 23).

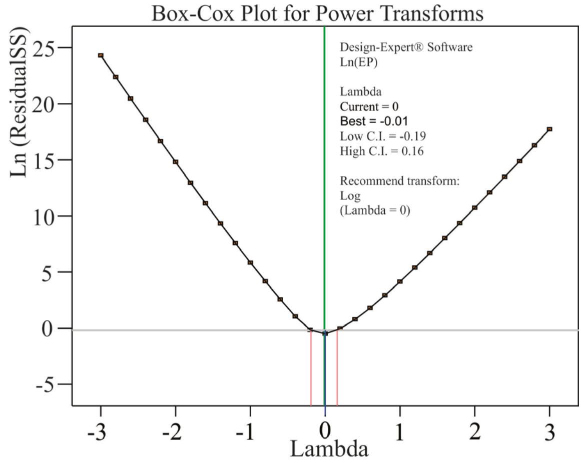

Fig. 23. The Box-Cox plot for power transforms

Iso-lines contour plot for electrical conductivity of Bi-Ge-Zn alloys defined by Eq. (6) is shown in Fig. 24.

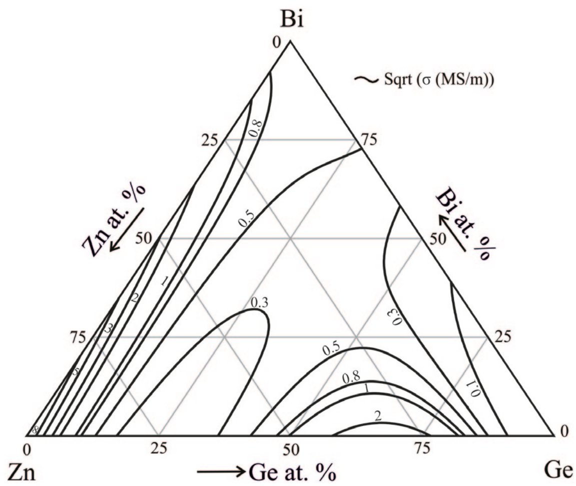

Fig. 24. Calculated iso-lines of electrical conductivity in ternary Bi-Ge-Zn system with $R^2 = 0.901$

4. Conclusion

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 sections at 25°C were calculated using the 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 studied on twelve ternary samples per each ternary system.

In microstructure of tested samples from Bi-Cu-Ge system, three different phase regions were detected. Ten samples were confirmed (Bi) + η + (Cu) phase region, sample 7 detected ξ + (Bi) + η phase region while sample 8 confirmed (Bi) + ξ + (Cu) phase region. Alloy 12, $Bi_{10}Cu_{10}Ge_{80}$ has highest hardness 415.46 MN/m^2 in comparison with other ternary samples. In this alloy 12, three phases are presented in microstructure (Bi) solid solution, η and (Cu) solid solution. Alloy $Bi_{10}Cu_{80}Ge_{10}$ has highest electrical conductivity 2.373 MS/m in this sample three phases are presented (Bi), ξ and (Cu).

In all samples of the ternary Bi-Ga-Ge system three phases are detected in microstructure. Detected phases are (Bi), (Ge) and (Ga) solid solutions. Different composition of phases reflected on different percentages of phases in the alloys. So, different percent of phases reflect the properties of alloys. Alloy with composition $Bi_{10}Ga_{10}Ge_{80}$ has highest hardness 90.60 MN/m^2 (sample 12) while sample 8, $Bi_{10}Ga_{80}Ge_{10}$ has highest electrical conductivity 2.3957 MS/m.

In each microstructure of the Bi-Ge-Zn alloys the same three phases were detected. Detected phases were (Bi), (Ge) and (Zn) solid solutions. Sample 8 ($Bi_{10}Ge_{80}Zn_{10}$) is alloy with the highest hardness 105.30 MN/m^2. Sample 5 with composition $Bi_{40}Ge_{20}Zn_{40}$ is alloy with the highest electrical conductivity (0.6503 MS/m) in comparison with other ternary alloys of this system.

In general, it can be concluded that the content of germanium influences strongly on the 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 an important role. For electrical conductivity value can be concluded that alloying elements gallium and copper play an important role.

In addition, mathematical models for prediction of hardness and electrical conductivity along the entire composition range were obtained.

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