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Mechanical and electrical properties of the ternary Ag-Ge-In alloys

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ABSTRACT: Mechanical (Brinell hardness test) and electrical properties of some selected ternary Ag-Ge-In alloys have been investigated in this study. By using obtained results for properties and ANOVA analysis it is suggested mathematical model for calculation properties for every composition of alloys. Microstructures of alloys have been carried out by using optical microscopy and scanning electron microscopy (SEM). Phases presented in microstructures have been detected by x-ray diffraction (XRD) analysis and compositions by energy dispersive spectrometry (EDS). Experimentally determined results are compared with calculated data. Calculation of isothermal section at 25 °C was carried out by using optimized thermodynamic parameters for the constitutive binary systems. Good overall agreement between experimental and calculated values was obtained.

KEYWORDS: Hardness properties; Electrical properties; Microstructures; Ternary alloys of the Ag-Ge-In system

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RESUMEN: *Propiedades mecánicas y eléctricas de las aleaciones ternarias de Ag-Ge-In*. En este estudio se investigaron las propiedades mecánicas (prueba de dureza Brinell) y eléctricas de algunas aleaciones de Ag-Ge-In ternarias seleccionadas. Los resultados obtenidos para las propiedades mecánicas y el análisis ANOVA, se sugiere un modelo matemático de cálculo para las propiedades de cada composición de aleaciones. Las microestructuras de aleaciones se han llevado a cabo mediante microscopía óptica y microscopía electrónica de barrido (SEM). Las fases presentadas en las microestructuras se han detectado mediante análisis de difracción de rayos X (XRD) y las composiciones mediante espectrometría de dispersión de energía (EDS). Los resultados determinados experimentalmente se comparan con los datos calculados. El cálculo de la sección isotérmica a 25 °C se realizó utilizando parámetros termodinámicos optimizados para los sistemas binarios constitutivos. Se obtuvo una buena concordancia general entre los valores experimentales y los calculados.

PALABRAS CLAVE: Aleaciones ternarias del sistema Ag-Ge-In; Microestructuras; Propiedades de dureza; Propiedades eléctricas

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1. INTRODUCTION

Alloying presents an important and a time consuming task for researchers all over word. Since the properties of materials can be change by adding other elements it is encouraging to study different alloys in way to get alloys with good properties. In our group we are focusing on Ge alloys and their properties (Premovic *et al.*, 2014; Premovic *et al.*, 2015; Premovic *et al.*, 2016; Premovic *et al.*, 2017a; Premovic *et al.*, 2017b) due to the technical importance of the systems based on Ge (Chen *et al.*, 2006; Raoux and Wuttig, 2009) and their special application as a phase change memory material (PCM materials) (Lacaita and Wouters, 2008; Ou *et al.*, 2011; Ielmini and Lacaita, 2011; Nemec *et al.*, 2012). Electrical and mechanical properties of ternary Ag-Ge-In system have not been investigated before. The reason for this study is experimental investigation of electrical and mechanical properties of the ternary Ag-Ge-In alloys at room temperature (≈25 °C). Phase equilibria in the ternary Ag-Ge-In system have been experimentally investigated before by our group Milisavljevic *et al.* (2018). Milisavljevic *et al.* (2018) have been experimentally investigated ternary alloys from three vertical sections Ag-GeIn, Ge-AgIn, and In-AgGe and two isothermal sections at 200 and 400 °C. By combining experimental results and thermodynamic parameters for the constitutive binary systems proposed in the literature (Chevalier, 1989; Kroupa *et al.*, 2007; Wang *et al.*, 2011) reliable thermodynamic data set has been proposed by Milisavljevic *et al.* (2018). Thermodynamic data set proposed by Milisavljevic *et al.* (2018) has been used in our study for the calculation of isothermal section at 25 °C. In the current study phase equilibria of the isothermal section at 25 °C have been investigated by using scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS) and x-ray diffraction (XRD). Ternary Ag-Ge-In alloys have been tested with Brinell hardness test and test for electrical conductivity. Experimental results of Brinell hardness and electrical conductivity have been used for obtaining mathematical model for estimation of those properties for every composition of alloys at room temperature (≈25 °C). Obtained results aimed to provide better insight into properties of alloys which should contribute to further expansion of their application possibilities.

2. MATERIALS AND METHODS

All ternary and three binary samples with total masses of about 3 g were prepared from high purity (99.999 at.%) Ag, Ge, and In produced by Alfa Aesar (Germany). Samples were melted in an induction furnace under high-purity argon atmosphere and slowly cooled to the room temperature. The average weight loss of the samples during induction melting was about 0.5 mass%. Such prepared samples are subjected to all experimental tests.

The compositions of samples and coexisting phases were determined by using JEOL JSM-6460 scanning electron microscope with energy dispersive spectroscopy (EDS) (Oxford Instruments X-act). Powder XRD data for phase identification of samples were recorded on a D2 PHASER (Bruker, Karlsruhe, Germany) powder diffractometer equipped with a dynamic scintillation detector and ceramic X-ray Cu tube (KFL-Cu-2K) in a 2θ range from 10° to 75° with a step size of 0.02°. The patterns were analyzed using the Topas 4.2 software, ICDD databases PDF2. Hardnesses of the samples were measured using Brinell hardness tester INNOVATEST, model NEXUS 3001. Electrical conductivity measurements were carried out using Foerster SIGMATEST 2.069 eddy current instrument.

3. RESULTS AND DISCUSSION

The isothermal section at 25 °C of the Ag-Ge-In ternary system has been thermodynamically predicted using optimized thermodynamic parameters for the constitutive binary systems. Optimized thermodynamic parameters are used from Wang *et al.* (2011) for the Ag-Ge binary system, Kroupa *et al.* (2007) for the Ag-In binary system and from Chevalier (1989) for the Ge-In binary system. Based on the literature information for binary sub-systems crystallographic data for solid phases in the ternary Ag-Ge-In system are summarized and presented in Table 1 (Jette and Foote, 1935; Cooper, 1962; Ridley, 1965; Campbell *et al.*, 1970; Havinga *et al.*, 1972).

Figure 1 presents calculated isothermal section of the Ag-Ge-In ternary system at 25 °C. Selected alloys samples experimental investigated are also marked on Fig. 1.

Compositions of the selected alloy samples lie along three vertical sections red squares Ag-$Ge_{50}In_{50}$, orange squares Ge-$Ag_{50}In_{50}$ and violet squares In-$Ag_{50}Ge_{50}$. Eight different phase regions are calculated at isothermal section at 25 °C. Four are two-phase regions (Ge)+$AgIn_2$, (Ge)+γ(Ag_2In), (Ge)+ζ(Ag_3In) and (Ge)+(Ag) and another four are three-phase regions (Ge)+$AgIn_2$+(In), (Ge)+$AgIn_2$+γ(Ag_2In), (Ge)+ζ(Ag_3In)+γ(Ag_2In), and (Ge)+ζ(Ag_3In)+(Ag). From eight predicted phase regions four are experimentally confirmed by EDS and XRD analyses.

EDS and XRD results confirmed existence of same phases. In microstructures of samples 3, 9, and 13 three phases (Ge), $AgIn_2$ and γ(Ag_2In) are detected. According to the calculated phase diagram Fig. 1 it is visible that examined samples 3, 9, and 13 belongs to the same three phase region (Ge)+$AgIn_2$+γ(Ag_2In), and by experiments same phases are experimentally detected. Samples 4 and

TABLE 1. Crystal structure data for the solid phases of the Ag-Ge-In system

Thermodynamic database name	Phase	Pearson symbol	Space group	Lattice parameters (Å)		Ref.
				a=b	*c*	
FCC_A1	(Ag)	*cF4*	$Fm\bar{3}\,m$	4.0861		Jette and Foote (1935)
DIAMOND_A4	(Ge)	*cF8*	$Fd\bar{3}m$	5.65675		Cooper (1962)
TETRAG_A6	(In)	*tI2*	*I4/mmm*	3.2523	4.9461	Ridley (1965)
BCC_A2	β(Ag_3In)	*cP2*	$Pm\bar{3}m$	4.144(4)		Campbell *et al.* (1970)
HCP_A3	ζ(Ag_3In)	*hP2*	$P6_3/mmc$	2.961(2)	4.778(4)	Campbell *et al.* (1970)
CUIN_GAMMA	γ(Ag_2In)	*cP52*	$P\bar{4}\,3m$	9.887(4)		Campbell *et al.* (1970)
AGIN2	$AgIn_2$	*tI12*	*I4/mcm*	6.881(4)	5.620(4)	Havinga *et al.* (1972)

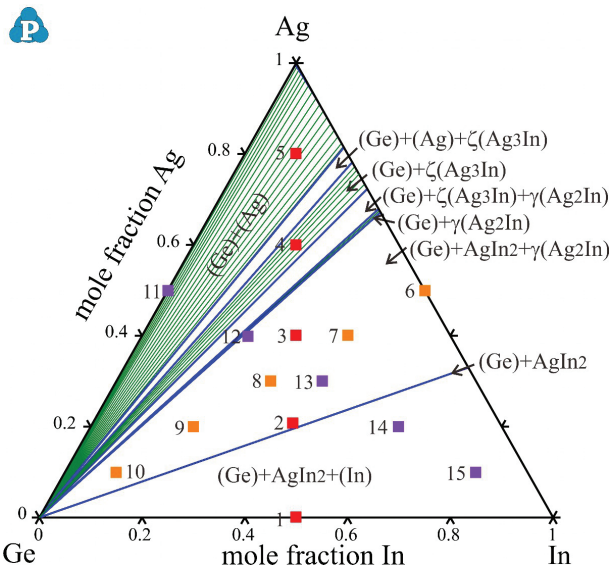

FIGURE 1. Predicted isothermal section of the ternary Ag-Ge-In system at 25 °C with marked compositions of the studied samples.

5, detected two phases. Sample 4, by calculation belongs to the two-phase region (Ge)+ζ(Ag_3In), same phase region are experimentally detected by EDS and XRD tests. Sample 5, detected another two-phase region (Ge)+(Ag), same phase region as predicted by calculation. Last tested sample 14, according to the calculation belong to the three-phase region (Ge)+$AgIn_2$+(In), by experiments same phases are detected. Three SEM micrographs of selected samples 3, 4 and 5 are given in Fig. 2.

SEM micrograph of sample 3, given on Fig. 2.a, have three phases in equilibrium. Dark phase is (Ge) solid solution, gray phase is intermetallic compound $AgIn_2$, and light gray phase is γ(Ag_2In) intermetallic compound. Sample 4 is from (Ge)+ζ(Ag_3In) two-phase region and on SEM micrograph (see Fig. 2.b), (Ge) solid solution is dark phase and ζ(Ag_3In) intermetallic compound gray phase. Last microstructure on Fig. 2 is for sample 5, and two phases are detected, dark phase is (Ge) solid solution and gray phase (Ag) solid solution. Figure 3 presents a three LOM micrographs of selected samples 9, 13 and 14.

Samples 9 and 13, have a same phases in microstructure. Detected phases are marked at the microstructures in Fig. 3a, sample 9, and Fig. 3b, sample 13, with related name of the phase. Three phases Ge, $AgIn_2$ and γ(Ag_2In) are visible in the microstructures. Figure 3c, presents a microstructure of the sample 14, and three phases are visible. Phases are (Ge), (In), and $AgIn_2$.

3.1. Mechanical properties

Twelve ternary samples and three binary (marked on Fig. 1) are experimentally tested with Brinell hardness test. Hardness of alloys were measured at three different position on the samples. Based on obtained results mine value of three measurements were calculated and given graphic form in Fig. 4. For easier visualization of the results mine value as a function of compositions are presented in graphic form in Fig. 4. Figure 4a presents hardness of alloys by increasing of the silver composition. With increasing of silver hardness of alloys increase to the point where silver is 0.4 mol in alloys, by adding more silver hardness of alloys decries. Figure 4b presents behaviors of hardness by increasing of germanium composition. From experimental results it is visible that by adding of the germanium, hardness of alloys decries to the alloys with 0.6 mol of Ge, while alloys with 0.8 mol of Ge hardness start to increase. Figure 4c presents hardness of alloys with increasing of indium and results shows that by adding indium, hardness decries.

By using this measurement and mathematical model, mathematical equation for calculation of Brinell hardness, were proposed. In order to define a mathematical model for the dependence of Brinell hardness vs composition for ternary alloys the Design Expert v.9.0.3.1 software package was used. Out of a possible canonical or Scheffe model (Cornell, 2002; Lazić, 2004; Kolarević *et al.*, 2011)

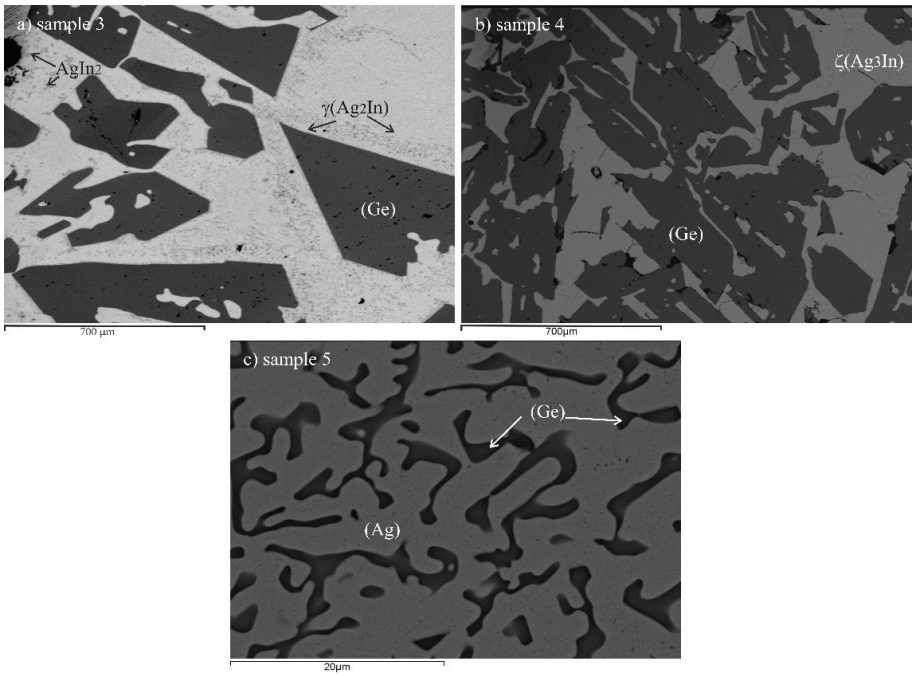

FIGURE 2. SEM micrographs of some samples: a) sample 3, b) sample 4 and c) sample 5.

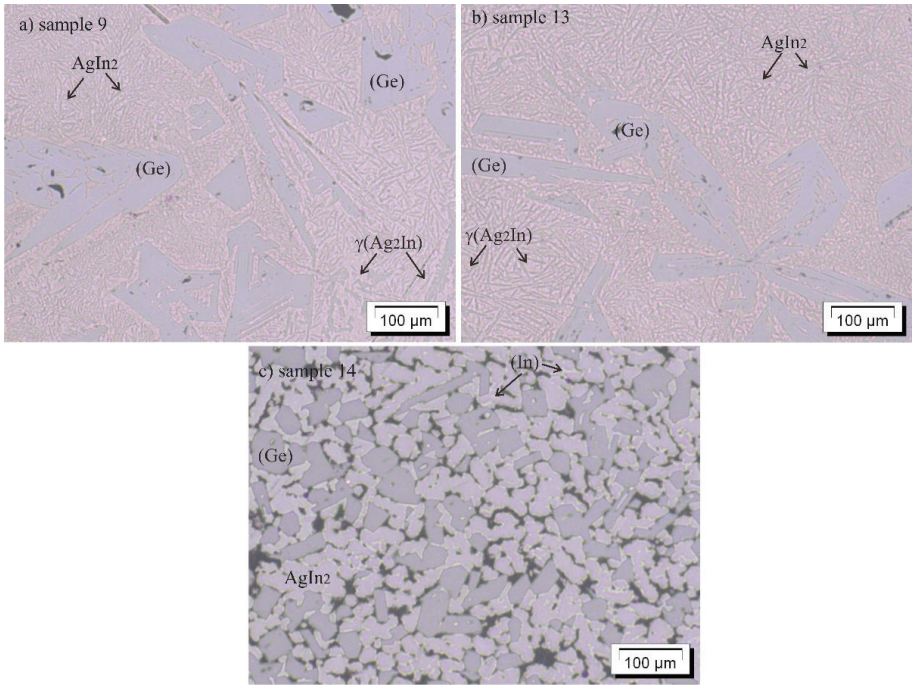

FIGURE 3. LOM micrographs of some samples: a) sample 9, b) sample 13, and c) sample 14.

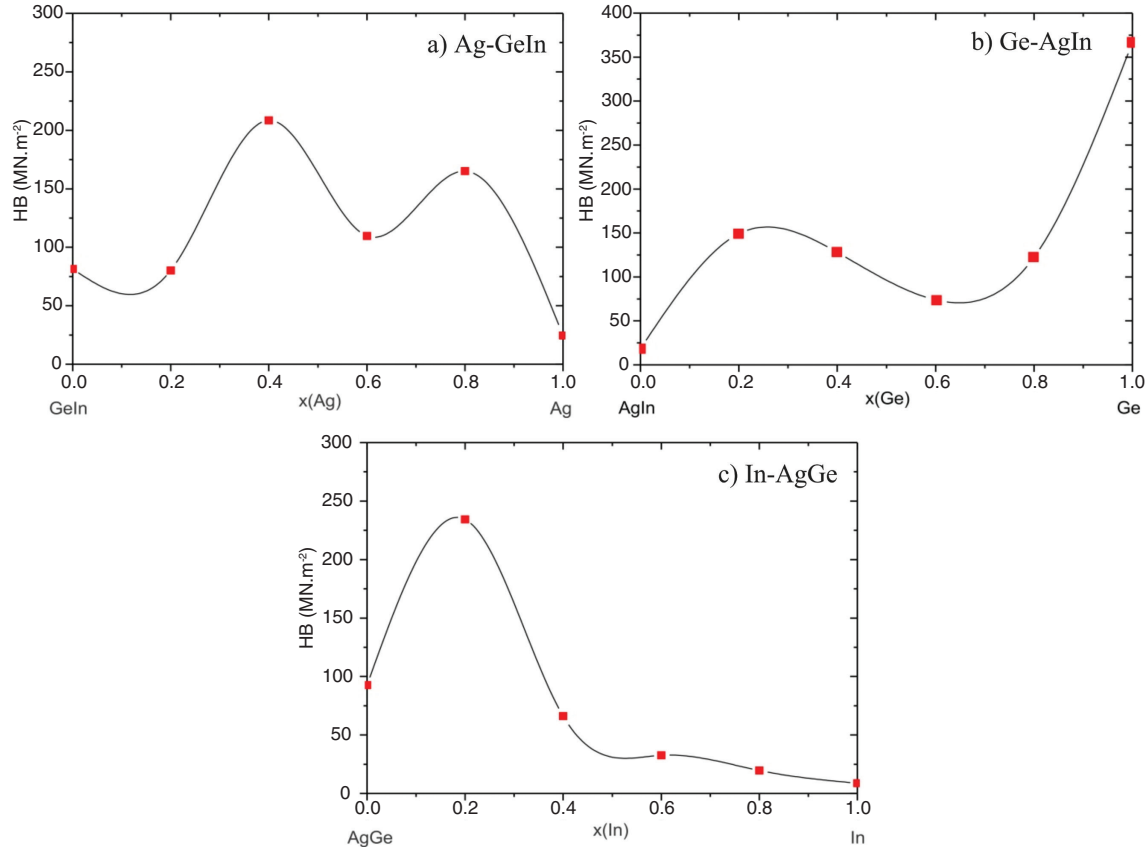

FIGURE 4. Brinell hardness of the investigated Ag-Ge-In alloys with overall compositions along cross-sections: a) Ag-Ge50In50, b) Ge-Ag50In50, and c) In-Ag50Ge50.

that meet the requirements of adequacy a Special Quartic model was recommended, Eq. (1):

$$\hat{y} = \sum_{i-1}^{q}\beta_i x_i + \sum_{i<j}^{q-1}\sum_{j}^{q}\beta_{ij}x_i x_j + \sum_{i<j}^{q-2}\sum_{j<k}^{q-1}\sum_{k}^{q}\beta_{iijk}x_i^2 x_j x_k + \sum_{i<j}^{q-2}\sum_{j<k}^{q-1}\sum_{k}^{q}\beta_{ijjk}x_i x_j^2 x_k + \sum_{i<j}^{q-2}\sum_{j<k}^{q-1}\sum_{k}^{q}\beta_{ijkk}x_i x_j x_k^2 \quad (1)$$

High value of F parameter (F=65.88) and small p, (p<0,0001) shows that in the Analysis of variance (ANOVA) chosen model is satisfactory. The final equation of the predictive model in terms of actual components is:

$$1/(HB)^2 = 0.05813x(Ge)+0.17328x(Ag)+0.31658x(In)-0.04916x(Ge)x(Ag)-0.32222x(Ge)x(In)-0.0814x(Ag)x(In)+3.92744x(Ge^2)x(Ag)x(In)-7.25474x(Ge)x(Ag^2)x(In) \quad (2)$$

Two-dimensional contour diagrams for Brinell hardness of alloys in ternary Ag-Ge-In system, calculated based on Eq. (2), is shown in Fig. 5.

3.2. Electrical properties

On same samples electrical conductivity were measurements in four points. Figure 6, presents graphic correlation between electrical conductivity and mole fraction of components for the all investigated samples. Electrical conductivity of alloys was measured at four different point and main value based on those four results were presented in Fig. 6 and used for graphic presentation and future calculation.

By using same procedure as for description of Brinell hardness mathematical equation for calculation of electrical conductivity, were proposed. Chosen mathematical model was Special Quartic. High value of F parameter (F=34.11) and small p, (p<0,0001) shows that in the Analysis of variance (ANOVA) chosen model is satisfactory. The final equation of the predictive model in terms of actual components is:

$$Ln(\sigma) = 0.69591x(Ge)+3.02351x(Ag)+2.66519x(In)+1.38301x(Ge)x(Ag)-3.91755x(Ge)x(In)-0.76495x(Ag)x(In)+175.22616x(Ge^2)x(Ag)x(In)-159.8468x(Ge)x(Ag^2)x(In)-137.19795x(Ge)x(Ag)x(In^2) \quad (3)$$

Iso-lines contour plot of electric conductivity defined by Eq. (3) is shown in Fig. 7.

4. CONCLUSIONS

- Some characteristic alloys with different composition were experimentally tested with SEM-EDS, XRD, LOM, Brinell hardness test and electrical conductivity test. By using thermodynamic data set, isothermal section at 25 °C was calculated and eight different phase fields were predicted. By prepared samples four of eight phase region were confirmed with EDS and XRD results.
- With SEM and LOM microstructures of tested alloys were observed. All samples are tested

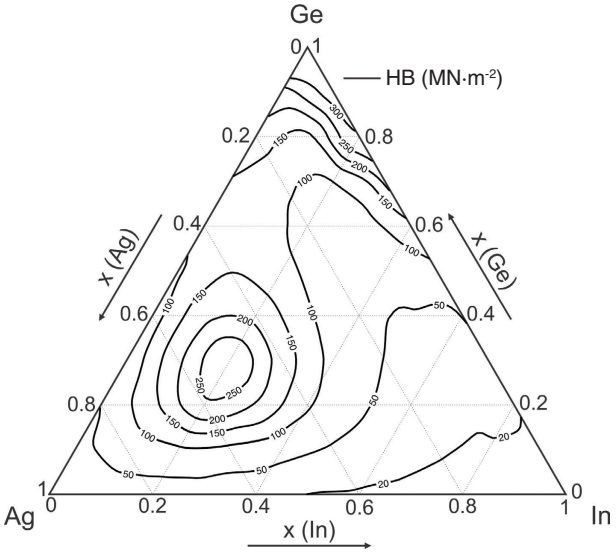

FIGURE 5. Calculated iso-lines of Brinell hardness in ternary Ag-Ge-In system.

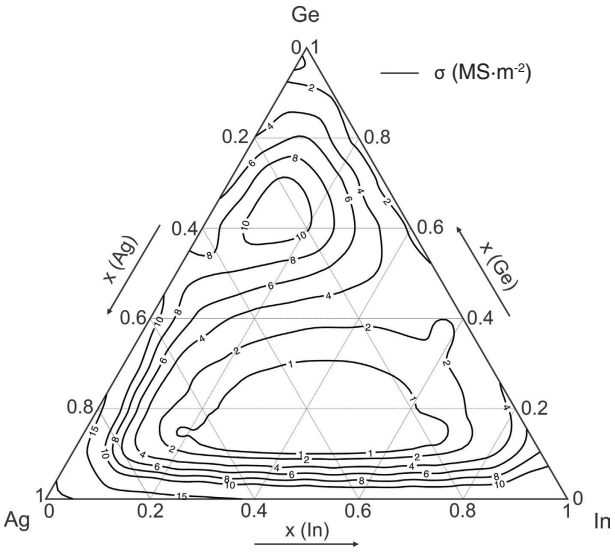

FIGURE 7. Calculated iso-lines of electric conductivity defined in ternary Ag-Ge-In system.

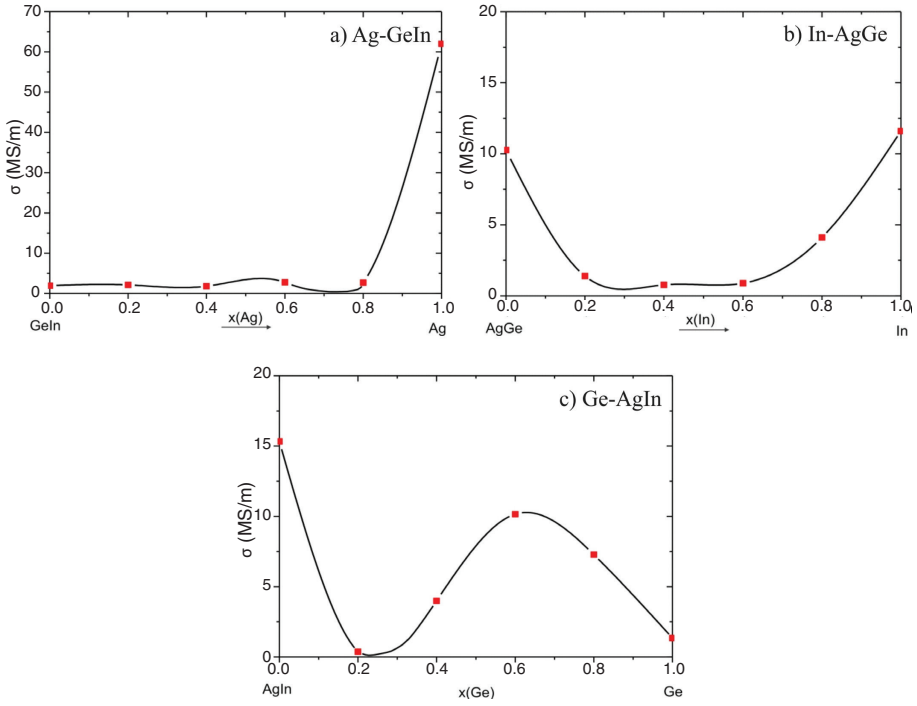

FIGURE 6. Electrical conductivity of the investigated Ag-Ge-In alloys with overall compositions along cross-sections: a) Ag-Ge50In50, b) In-Ag50Ge50, and c) Ge-Ag50In50.

with Brinell hardness test and electrical conductivity and results were used for predicting a mathematical model for calculation of those properties along all composition range.

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