The 56th International October Conference on Mining and Metallurgy
22-25 October 2025, Bor Lake, Bor, Serbia
www.ioc.tfbor.bg.ac.rs

DOI: 10.5937/IOC25511M *Original scientific paper*

EXPERIMENTAL CHARACTERIZATION OF THE Bi-Ge-Pb TERNARY ALLOYS

Veljko Minic[1a], Jelena Miladinovic[1b], Miljana Popovic[1c], Milena Zecevic[2a], Aleksandar Djordjevic[2b]

[1] University of Belgrade, Faculty of Technology and Metallurgy, Belgrade, Serbia
[2] University in Pristina, Faculty of Technical Science, Kos. Mitrovica, Serbia
[1a] veljkominic3@gmail.com, 0009-0002-0812-6460
[1b]duma@tmf.bg.ac.rs, 0000-0001-6259-8245
[1c]miljana@tmf.bg.ac.rs, 0000-0002-4691-0603
[2a] milena.premovic@pr.ac.rs, 0000-0003-0532-7048
[2b] aleksandar.djordjevic@pr.ac.rs, 0000-0002-2020-6976

Abstract
In this work, the ternary system Bi-Ge-Pb has been studied. Sixteen ternary samples were prepared for experimental tests. Selected samples were subjected to phase transition temperatures and phase equilibria tests. Used experimental techniques were differential thermal analysis (DTA), X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive spectrometry (EDS). Results of DTA detected temperatures of two invariant reactions, monovariant phase transition and liquidus curves.

***Keywords**: Bi-Ge-Pb ternary system, phase transition temperatures, experimental characterization.*

1. INTRODUCTION

Reason for choosing Bi-Ge-Pb ternary system is due to the possible application as a low-melting point alloys, (LMPA). These alloys are required for a wide variety of applications, including thermal fuse application, rapid prototyping, die casting, mercury replacement, thermal cooling, heating designs, and soft solder formulation [1]. They also represent promising candidates for metallic phase-change materials (PCMs) for thermal storage (TS) [2-3].

Ternary Bi-Ge-Pb alloys were prepared and tested experimentally for the first time. The knowledge of the ternary alloys is very important for future possible application of these alloys. The aim of this study was to investigate Bi-Ge-Pb ternary system using a combination of different experimental techniques (DTA, XRD, SEM/EDS). In total 16 ternary samples were prepared. Prepared alloys were are located along three vertical sections Bi-GePb, Ge-BiPb and Pb-BiGe and one isothermal section at 100 °C.

2. EXPERIMENTAL

Experimentally investigated samples with a wide range of compositions were prepared from high purity metals Bi, Ge and Pb (99.99 %) produced by Alfa Aesar, Germany. In total, 16 ternary samples were weighed, mixed and melted in an electric arc furnace under high-purity argon atmosphere. The samples were melted and re-melted five times until homogeneity was maintained. The average weight loss during melting and remelting was approximately 0.5 mass %.

The samples were divided into two groups (one group with 12 samples and the other group with 4 samples). The samples of the first group after melting, were left in furnace to slowly cool down to the room temperature. Those samples were used for DTA measurements. Second group of 4 alloy samples were placed in a quartz tube and annealed at 100 °C for four weeks (28 days). After annealing, the samples were quenched in ice-cold water. These samples were divided into two parts. One part was pulverized and used for the XRD measurement. The second part was metallographically prepared and used for SEM-EDS analysis.

The DTA measurements were performed with an SDT Q600 (TA Instruments). Alumina crucibles were used and measurements were performed under a flowing argon atmosphere with an empty alumina crucible as reference material. Samples weighing between 20 and 30 mg were analyzed at a heating rate of 5 °C/min with three heating and cooling cycles. The overall uncertainty of the determined phase transformation temperatures was estimated to be ±1 °C. Before realizing the DTA experiments temperature calibration of DTA were performed by measuring the melting temperature, of pure elements (In, Sn, Pb, Bi, Zn, Sb, Al, Ag and Ge) using the same working conditions.

TESCAN VEGA3 scanning electron microscope (SEM) with energy dispersive spectrometer (EDS) (Oxford Instruments X-act) was used for microstructural investigation. SEM-EDS analysis of the prepared ternary alloy was carried out at an accelerating voltage of 20 kV. Overall composition and compositions of coexisting phases were determined using EDS area and point analysis. All SEM images of the microstructures were taken on the polished surfaces of the studied alloy samples in backscattered electron mode.

Powder X-ray diffractometer D2 PHASER (Bruker, Karlsruhe, Germany), equipped with a dynamic scintillation detector and a ceramic X-ray Cu tube (KFL-Cu-2K) in a 2θ range from 10° to 75° with a step size of 0.02°. The samples were analyzed using Topas 4.2 software, ICDD databases.

3. RESULTS AND DISCUSSION

According to literature information, ternary Bi-Ge-Pb systems have not been studied previously. The available literature information are related to constitutive binary systems. The ternary Bi-Ge-Pb system consists of three binary systems. The constitutive binary phase diagrams (Bi-Ge [4], Ge-Pb [5] and Bi-Pb [6]) have been studied in the past [4-6]. According to the literature, the solid phases that could be expected in the ternary system are summarized in Table 1 [7-10].

Table 1. Considered phase, their crystallographic data and database names for the solid phases of the ternary Bi-Ge-Pb system [6-9].

Thermodynamic database name	Phase	Reference
RHOMBO_A7	(Bi)	[7]
DIAMOND_A4	(Ge)	[8]
FCC_A1	(Pb)	[9]
HCP_A3	ε	[10]

In total four solid phases and one liquid phase should be expected in ternary Bi-Ge-Pb system. Solid phases are (Pb), (Bi) and (Ge) solid solution and ε phase. Liquid phase is L and no information about ternary compound.

Experimental results of the DTA test are summarized in Table 2.

Table 2. Phase transition temperatures of the studied alloys from the ternary

Bi-Ge-Pb system determined by DTA.

Sample no. and nominal composition at. %	Temperatures of phase transformation in °C	
	Invariant reaction and Monovariant phase transition	Liquidus
Vertical section Bi-GePb		
Sample 1, $Bi_{20}Ge_{40}Pb_{40}$	55.20; 191.13	827.93

Sample 2, $Bi_{40}Ge_{30}Pb_{30}$	134.21; -	846.27
Sample 3, $Bi_{60}Ge_{20}Pb_{20}$	133.67; 209.66	810.41
Sample 4, $Bi_{80}Ge_{10}Pb_{10}$	134.58; 254.93	735.11
Vertical section Ge-BiPb		
Sample 5, $Bi_{40}Ge_{20}Pb_{40}$	127.32; 149.21	814.86
Sample 6, $Bi_{30}Ge_{40}Pb_{30}$	131.09; 148.11	865.13
Sample 7, $Bi_{20}Ge_{60}Pb_{20}$	130.19; 145.43	877.80
Sample 8, $Bi_{10}Ge_{80}Pb_{10}$	123.11; 144.51	881.75
Vertical section Pb-BiGe		
Sample 9, $Bi_{40}Ge_{40}Pb_{20}$	127.13; 173.87	867.81
Sample 10, $Bi_{30}Ge_{30}Pb_{40}$	126.62; 180.69	852.39
Sample 11, $Bi_{20}Ge_{20}Pb_{60}$	190.02; 246.62	789.69
Sample 12, $Bi_{10}Ge_{10}Pb_{80}$	298.95	753.38

According to the appearance of DTA peaks it is discovered existence of reactions, monovariant phase transition and liquidus transformation. So, determined temperatures of phase transitions are divided into two groups. The first group are the temperatures of the invariant reaction and the peak of the mono-variant phase transition. The last peak detected is described as a liquidus temperature. First detected temperature in samples 2 to 10 correspond to the ternary eutectic reaction L→(Ge)+ε+(Bi) while the temperature of 191.13 °C in sample 1 and 190.02 °C in sample 11 corresponds to the reaction L+(Pb)→(Ge)+ε. These conclusions are supported by construction of related vertical sections by using literature information of reference [4-6].

Samples annealed at 100 °C were experimentally tested and results of the experimental analyses are summarized in Table 3.

Table 3. Results of EDS and XRD tests of samples 13 to 16 annealed at 100 °C.

No.	Composition, at. %	Determined phases		Composition of phase, at. %			Lattice parameter, Å	
		EDS	XRD	Bi	Ge	Pb	a=b	c
13	4.75 Bi 51.70 Ge 43.55 Pb	(Ge) (Pb)	(Ge) (Pb)	0.52±0.3 9.67±0.1	99.35±0.5 0.31±0.8	0.13±0.8 90.02±0.1	5.6552±0.0002 4.9521±0.0003	5.6552±0.0002 4.9521±0.0003
14	10.59 Bi 69.17 Ge 20.24 Pb	(Ge) ε	(Ge) ε	0.52±0.8 35.51±0.5	99.05±0.2 0.29±0.7	0.43±0.8 64.20±0.2	5.6560±0.0004 3.2648±0.0002	5.6560±0.0004 5.3866±0.0001
15	38.16 Bi 39.67 Ge 22.17 Pb	(Ge) (Bi) ε	(Ge) (Bi) ε	0.52±0.8 99.01±0.4 39.50±0.2	98.77±0.2 0.86±0.9 0.89±0.7	0.71±0.8 0.13±0.7 59.61±0.1	5.6549±0.0002 4.5467±0.0001 3.2641±0.0001	5.6549±0.0002 11.8628±0.0003 5.3869±0.0004
16	63.24 Bi 12.21 Ge 24.55 Pb	(Ge) (Bi) ε	(Ge) (Bi) ε	0.16±0.9 98.71±0.1 39.81±0.7	99.08±0.1 1.14±0.5 0.46±0.3	0.76±0.7 0.15±0.7 59.73±0.1	5.6553±0.0003 4.5460±0.0003 3.2645±0.0004	5.6553±0.0003 11.8631±0.0001 5.3862±0.0005

Three different phase regions were experimentally investigated. In sample 13, the two phases that are defined are (Ge) and (Pb). In sample 14, two other phases are defined, (Ge) and ε. While in samples 15 and 16, three phases are present, (Ge), (Bi) and ε. The SEM microstructure of sample 14 is shown in Figure 1 as an illustration.

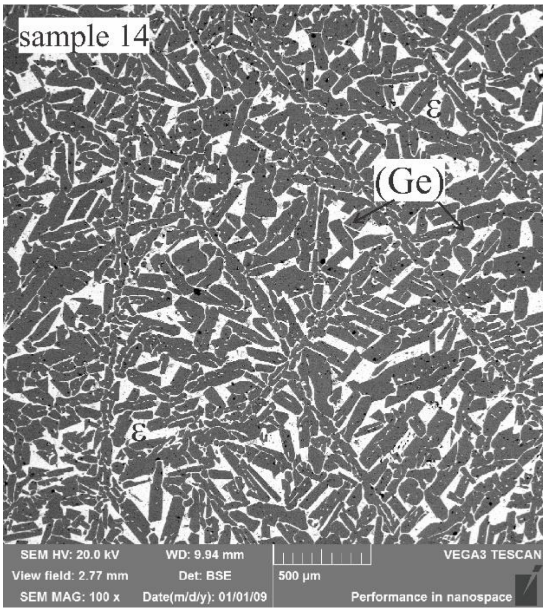

Figure 1. SEM micrograph of the sample 14 annealed at 100 °C.

4. CONCLUSION

In this paper ternary Bi-Ge-Pb system have been studied experimentally and theoretically, as the data about investigation of this system are not available in already published literature. The DTA analysis showed the existence of two reactions, one at a temperature in the range of 123.11 to 134.58 °C and the second at a temperature in the range of 190.02 °C to 191.13 °C. The first temperature is related to the ternary eutectic reaction $L \rightarrow (Ge) + \varepsilon + (Bi)$ and according to the calculation, this reaction is predicted at 124.985 °C. The second reaction is $+(Pb) \rightarrow (Ge) + \varepsilon$, which is predicted at 183.623 °C.

The phase regions of isothermal section at 100 °C were experimentally confirmed by 4 samples annealed at 100 °C for 28 days. Confirmed regions are (Ge)+(Pb), (Ge)+ε and (Ge)+ε+(Bi).

REFERENCES

[1] M. Kamal, A.-B. El-Bediwi, R.M. Shalaby, M. Younus, J. Adv. Phys., 7 (2) (2015) 1404-1414.
[2] X.H. Yang, S.C. Tan, J. Liu, Int. J. Heat Mass Transf., 100 (2016) 899–907.
[3] D. Manasijević, Lj. Balanović, V. Ćosović, D. Minić, M. Premović, M. Gorgievski, U. Stamenković, N. Talijan, Metall. Mater. Eng., 25 (4) (2019) 325-334.
[4] P.Y. Chevalier, Thermochim. Acta, 132 (1988) 111–116.
[5] P.Y. Chevalier, A thermodynamic evaluation of the Germanium-Indium, Germanium-Lead, Germanium-Antimony, Germanium-Thallium and Germanium Zinc systems, 155 (1989) 227-240.
[6] D. Boa, I. Ansara, Thermochim. Acta., 314(1) (1998) 79-86.
[7] P. Cucka, C.S. Barrett, Acta Crystallogr., 15 (1962) 865-872.
[8] A.S. Cooper, Acta Crystallogr., 15 (1962) 578-582.
[9] H.E. Swanson, E. Tatge, Natl. Bur. Stand. Circular, 539 (1953) 539A.
[10] T. Takahashi, H. K. Mao, W. A. Bassett, Science, 165 (1969) 1352-1353.