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ODD VALENCY DOPANTS CONVERT BISMUTH INTO SEMICONDUCTOR

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Five alloys Bi-1at.%Ag, Bi-1at.%Zn, Bi-1at.%Al, Bi-1at.%Sn and Bi-1at.%Sb are produced by rapid solidification using the melt-spinning technique. From x-ray diffraction analysis it was found that these alloys are single phase at room temperature. It is also found that all alloys containing odd valency dopants such as Ag (+1) , Al (+3) and Sb (+5) have semiconducting behavior and by contrast all alloys containing even valency dopants such as Zn (+2) and Sn (+4) have metallic behavior. The produced semiconductors are narrow band semiconductors. The band gap is decreased by increasing valency from 225.1 meV for Bi-Ag system to 12.7 meV for Bi-Sb system.

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1. Introduction

The rapidly solidified Bi-Ag was found to be semiconducting at room temperature. This work has opened the way for the production of a metallic alloys with semiconducting behavior without complicated process [1]. The electric properties of Bi can be changed by structure modification or by alloying with various elements. Several authors studied the effect of alloying on the electronic and the electrical properties of Bi, and they found that the addition of antimony changes the electrical behavior from semimetal to semiconductor at certain range of concentration of Sb [2-4]. It was found by [5] that the alloying of Bi with Sn has leadto high increase in resistivity with zero temperature coefficient.

The change in band structure is related to the change in the crystal structure which depends mainly on the valence electron concentration. Therefore the idea of this paper is to use elements with different valencies so as to change the valence electron concentration of Bi. The aim of the present work is to study the effect of alloying Bi with low concentration of elements with different valencies such as Ag +1, Zn+2, Al+3, Sn+4,and Sb+5. Rapid solidification and low concentration of alloying elements have been used in the present work to prevent rejection of extra solute atoms and thus prevent precipitation, from a solid solution.

2. Experimental procedures

The materials used in the present work are Bi, Zn, Sn , Sb fragments and Ag, Al wires, and the starting purity was higher than 99.99%. Five alloys Bi-1at.%Ag, Bi-1at.%Zn, Bi-1at.%Al, Bi-1at.%Sn and Bi-1at.%Sb are produced by a single copper roller (200 mm in diameter) melt spinning technique. The process parameters such as the ejection temperature, and the linear speed of the wheel were fixed at 873 K and 30.4 ms^{-1} respectively. X-ray diffraction analysis (XRDA) was carried out with a XPERT-PRO x-ray diffractometer, using Cu-K_α radiation (λ = 1.5406 Å). Differential Scanning Calorimetry (DSC) was carried out in a Shimadzu (DSC-60) with heating

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rate 10 K min^{-1}. The temperature dependence of resistivity (TDR) was measured by four probe method using microhmmeter of type BS407. The BS407 uses a four terminal measurement system via high quality Kelvin Clip leads with sensitivity is 1μΩ. The heating range starts from room temperature up to 530 K with heating rate about 5 K min^{-1}.

3. Results and discussion

3.1 Structure

Fig. 1 shows the x-ray diffraction patterns for as-quenched melt-spun pure Bi, Bi-1at.%Ag, Bi-1at.%Zn, Bi-1at.%Al, Bi-1at.%Sn and Bi-1at.%Sb alloys. The crystal structure of pure Bi (Fig. 1.a) was found to be rhombohedral-hexagonal (S.G.: $R\,\overline{3}\,m$) with $\boldsymbol{a}$ = 4.5491, $\boldsymbol{c}$ = 11.9485 Å. Fig. 1.b shows for Bi-1at.%Ag that, there is no precipitation of Ag in Bi-1Ag alloy, i.e. there is complete solid solubility of Ag in Bi at this concentration.

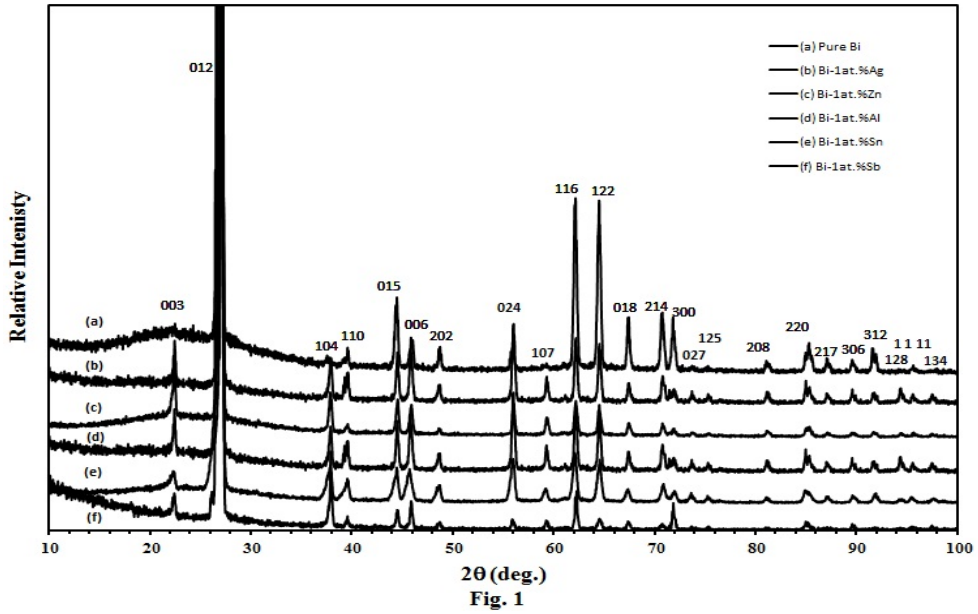

Fig.1: The x-ray diffraction patterns of as-quenched melt spun (a) pure Bi, (b) Bi-1at.%Ag, (c) Bi-1%Zn (d) Bi-1%Al (e) Bi-1%Sn and (f) Bi-1%Sb alloys.

The relative intensity from (166) and (122) planes is decreased from 23.79 and 23.46 to 8.98 and 8.22 respectively due to the addition Ag (see Table 1). This means that the Ag atoms dissolved in the Bi lattice lie in these planes. Therefore the structure of these alloys is single phase solid solution of Ag in Bi. Fig. 1.c shows for Bi-1at.% Zn that there is no precipitation of Zn is found in Bi-1at.% Zn.

There is complete solid solubility of Zn in Bi at this concentration. Fig. 1.d shows for Bi-1at.% Al that there is no precipitation of Al found in Bi-1at.% Al alloy. There is complete solid solubility of Al in Bi at this concentration. Fig. 1.e shows for Bi-1at.% Sn that there is no precipitation of Sn found in Bi-1at.% Sn alloy. There is complete solid solubility of Sn in Bi at this concentration. Fig. 1.f shows for Bi-1at.% Sb that there is complete solid solubility of Sb in Bi. Actually the Bi-Sb system is isomorphous. The variation of lattice parameters of the Bi unit cell is shown in Table 2.

Table.1: The x-ray diffraction details for as-quenched melt spun pure Bi, Bi-1at.%Ag, Bi-1%Zn, Bi-1%Al, Bi-1%Sn and Bi-1%Sb alloys.

Alloy	Phases present	2θ°	d (Å)	hkl	I/I_0	System
Pure Bi	Bi	22.51 27.09 62.15 64.49 67.35 71.83	3.9466 3.2889 1.4923 1.4437 1.3875 1.3131	003 012 116 122 018 300	7.03 100 23.79 23.46 7.83 7.91	Rhomb. (hex) S.G.: $R\bar{3}m$
Bi-1at%.Ag	Bi	22.47 27.13 62.21 64.53 67.39 71.89	3.9536 3.2841 1.4910 1.4429 1.3875 1.3122	003 012 116 122 018 300	8.65 100 8.98 8.22 2.99 2.17	Rhomb. (hex) S.G.: $R\bar{3}m$
Bi-1at%.Zn	Bi	22.45 27.11 62.19 64.51 67.39 71.91	3.957108 3.286562 1.491504 1.443352 1.388499 1.311931	003 012 116 122 018 300	9.72 100 5.03 4.49 2.07 1.36	Rhomb. (hex) S.G.: $R\bar{3}m$
Bi-1at%.Al	Bi	22.47 27.13 62.21 64.53 67.39 71.45	3.953631 3.284185 1.491072 1.442953 1.388499 1.319243	003 012 116 122 018 300	14.70 100 1.36 8.98 8.22 3.93	Rhomb. (hex) S.G.: $R\bar{3}m$
Bi-1%at.Sn	Bi	22.31 27.13 62.09 64.57 67.37 71.05	3.981622 3.284185 1.493666 1.442155 1.388862 1.325685	003 012 116 122 018 300	4.45 100 6.88 6.00 2.06 1.77	Rhomb. (hex) S.G.: $R\bar{3}m$
Bi-1at%.Sb	Bi	22.43 27.17 62.27 64.47 67.35 71.85	3.960591 3.27944 1.48978 1.444151 1.389226 1.312879	003 012 116 122 018 300	4.92 100 5.26 1.49 1.21 3.64	Rhomb. (hex) S.G.: $R\bar{3}m$

Table.2: The lattice parameter details for conventional Bi, as-quenched melt spun pure Bi, Bi-1at.%Ag, Bi-1%Zn, Bi-1%Al, Bi-1%Sn and Bi-1%Sb alloys.

Alloy	Lattice parameters			
	a (Å)	***c*** (Å)	***c/a***	***v*** (Å ^{3})
Bi (Conv.)	4.547	11.861	2.6085	212.3742
Bi (RS)	4.5491	11.9485	2.6265	214.1386
Bi-1at.%Ag	4.5447	11.9181	2.6224	213.1808
Bi-1at.%Zn	4.5469	11.9333	2.6244	213.6596
Bi-1at.%Al	4.5513	11.8656	2.6057	213.0718
Bi-1at.%Sn	4.5513	11.8786	2.6099	213.0985
Bi-1at.%Sb	4.5491	11.8357	2.6017	212.1170

3.2 Thermal analysis

Fig. 2 shows the DSC curves for as-quenched melt-spun pure Bi, Bi-1%Ag Bi-1%Zn Bi-1%Al, Bi-1%Sn and Bi-1%Sb alloys.

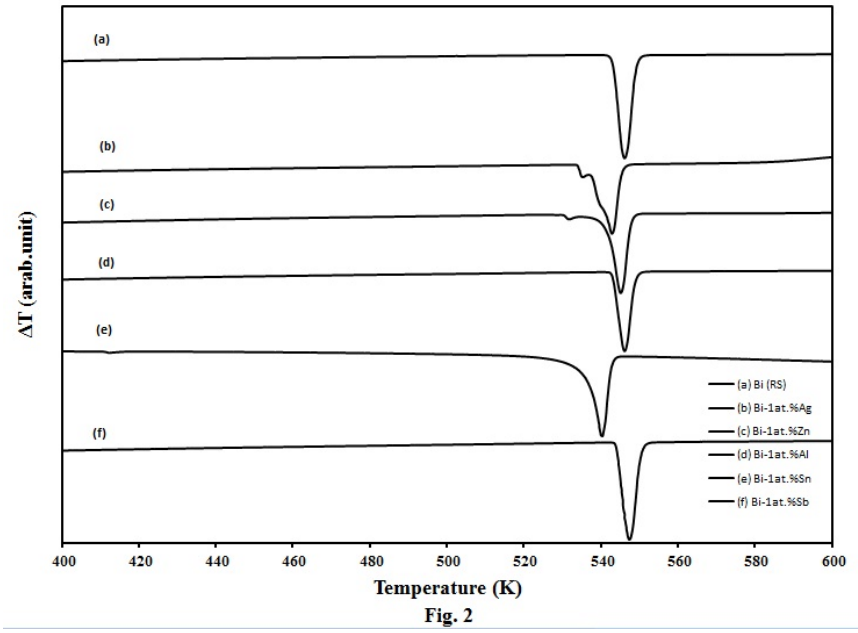

Fig. 2: The differential Scanning Calorimetry (DSC) of as-quenched melt spun (a) pure Bi, (b) Bi-1at.%Ag, (c) Bi-1%Zn (d) Bi-1%Al (e) Bi-1%Sn and (f) Bi-1%Sb alloys.

For Bi (Fig. 2.a) no phase transition was observed before melting and the melting temperature is found to be 544 K. Also for Bi-1Ag (Fig. 2.b) no phase transformation is observed before melting which starts at the eutectic temperature 535 K and complete melting occurred at 545 K (see Table 3).

Table.3: The differential Scanning Calorimetry (DSC) details for as-quenched melt spun pure Bi, Bi-1at.%Ag, Bi-1%Zn, Bi-1%Al, Bi-1%Sn and Bi-1%Sb alloys.

Alloy	T_m (K)	T_s (K)	T_l (K)	T_c (K)	ΔH_m (kJ/kg)
Bi (conv.)	544.2	544.2	544.2		54.07
Bi (RS)	544.1	544.1	544.1		52.22
Bi-1at. %Ag	537.8	535	545		52.73
Bi-1at%.Zn	542.2	541.2	549.1	531.5	55.65
Bi-1at.%Al	544.3	543.3	548.6		55.17
Bi-1at.%Sn	535.9	535	543.2	412.2	56.41
Bi-1at.%Sb	545	544	550.9		50.26

Fig. 2.c shows the DSC curves for as-quenched melt-spun Bi-1at. %Zn alloy. It is found that a small endothermic peak occurs at 531.5 K and the endothermic peak of melting occurs at 542.2 K, the enthalpy of fusion is found to be ΔH = -55.65 $kJ.kg^{-1}$. Fig. 2.d shows the DSC curves for as-quenched melt-spun Bi-1at. %Al alloy no phase transformation is observed before melting which occurred at 544.3 K. The enthalpy of fusion is found to be -55.173 $kJ.kg^{-1}$. Fig. 2.e shows the DSC curves for as-quenched melt-spun Bi-1at.%Sn alloy. It is found that a small endothermic peak occurs at 412.2 K and the endothermic peak of melting occurs at 535.9 K. This small endothermic peak is due to the beginning of eutectic reaction. The enthalpy of melting is found to be ΔH = -56.41 $kJ.kg^{-1}$. Fig. 2.f shows the DSC curves for as-quenched melt-spun Bi-1at.% Sb alloy. No phase transformation is observed before melting which occurred at 545 K. The enthalpy of fusion is found to be -50.26 $kJ.kg^{-1}$.

3.3 Electrical properties

Fig. 3 shows the temperature dependence of resistivity obtained for as-quenched melt-spun pure Bi, Bi-1at.%Ag, Bi-1at.%Zn, Bi-1at.%Al, Bi-1at.%Sn and Bi-1at.%Sb alloys in the temperature range from 300 to 520 K.

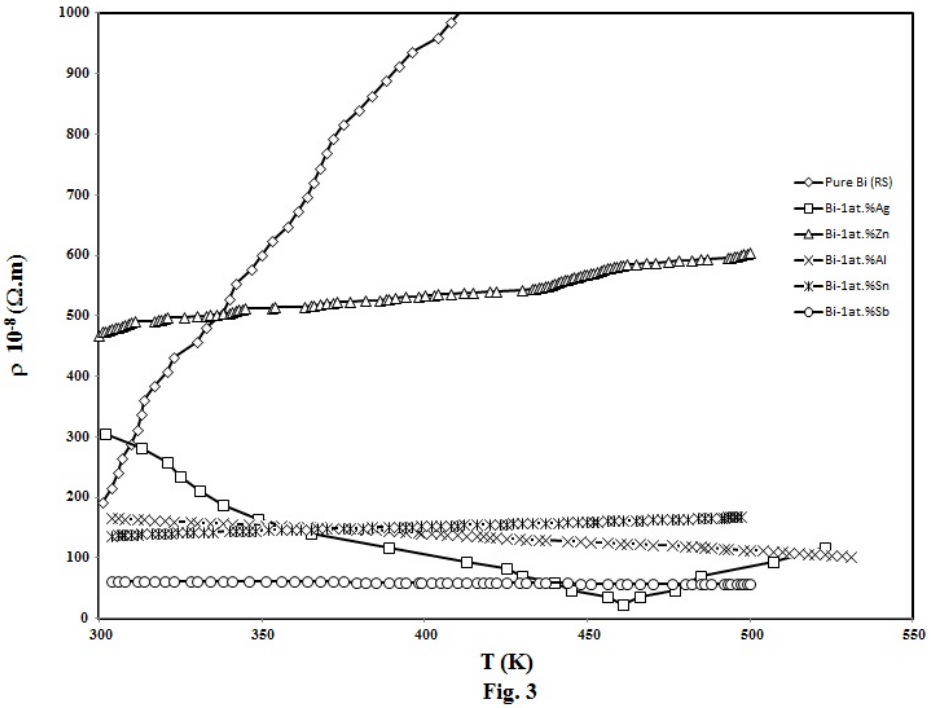

Fig. 3: The temperature dependence of resistivity of as-quenched melt-spun pure Bi, Bi-1at.%Ag, Bi-1%Zn, Bi-1%Al, Bi-1%Sn and Bi-1%Sb alloys.

For pure Bi the resistivity is increased due to rapid solidification from 117 to 192 x10^{-8} ohm.m. The behavior is metallic with temperature coefficient of resistivity 0.317 x10^{-3} K^{-1} .The resistivity is increased due to the addition of Ag to Bi from 192 to 305 x10^{-8} ohm.m. The behavior is semiconducting up to 428 K for Bi-1at.%Ag and then the resistivity is increased. The energy gap is calculated to be 0.2251 eV for Bi-1Ag, (see Table 4.).

Table.4: The electrical properties of as-quenched melt-spun for conventional Bi, as-quenched melt spun pure Bi, Bi-1at.%Ag, Bi-1%Zn, Bi-1%Al, Bi-1%Sn and Bi-1%Sb alloys.

Alloy	ρ X 10^{-8} (Ω.m)	Behavior	TCR X10^{-3} (K^{-1})	E_g(meV)
Bi (Conv.)	117	Metallic	4.6	
Bi (RS)	192	Metallic	0.317	
Bi-1at.%Ag	305	Semiconductor		225.1
Bi-1at.%Zn	465	Metallic	1.309	
Bi-1at.%Al	166	Semiconductor		56.04
Bi-1at.%Sn	136	Metallic	1.097	
Bi-1at.%Sb	62	Semiconductor		12.70

For as quenched melt-spun Bi-1at. %Zn alloy, the resistivity at room temperature is 465 x 10^{-8} Ω.m for Bi-1at.%Zn. The behavior is metallic with temperature coefficient of resistivity 1.309 × 10^{-3} K^{-1} (see Table 4). The temperature dependence of resistivity for as quenched melt-spun Bi-1at.%Al is shown in Fig. 3. It is evident that the behavior is semiconducting and the resistivity at room temperature is found to be 166 x 10^{-8} Ω.m. The band gap is calculated from Fig. 4. as 56.04 m eV. The temperature dependence of resistivity for as quenched melt-spun Bi-1at.% Sn is shown

in Fig. 3. The resistivity at room temperature is found to be 136 X 10^{-8} Ω.m. The behavior is metallic with temperature coefficient of resistivity 1.097 × 10^{-3} K^{-1}. (see Table 4).

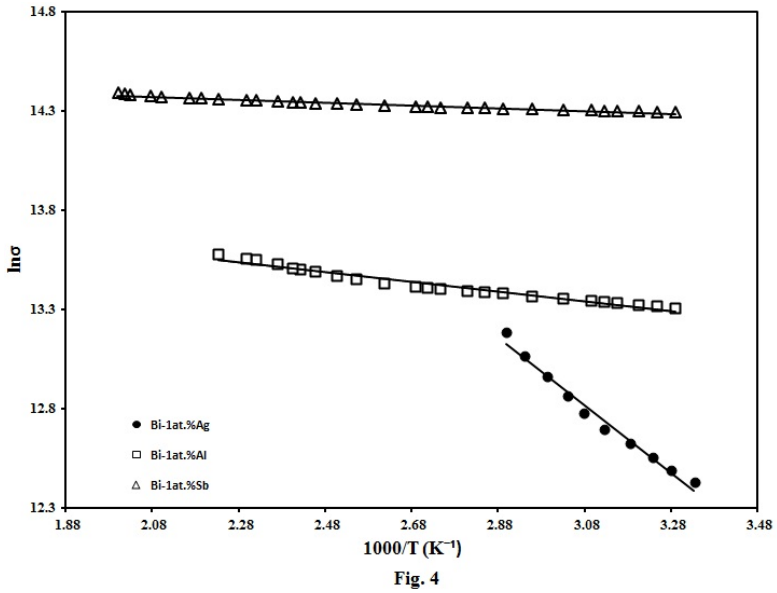

Fig.4: The electrical conductivity versus 1000/T as-quenched melt-spun for Bi-1at.%Ag, Bi- 2at.%Al and Bi-1%Sb alloys.

The temperature dependence of resistivity for as quenched melt-spun Bi-1at.%Sb is shown in Fig. 3. It is evident that the behavior is semiconducting for the two alloys. The resistivity at room temperature is found to be 62.008 X 10-8 Ω.m for Bi-1at. %Sb and 442 X 10-8 Ω.m for Bi-2at. %Sb. The energy gap is calculated from Fig. 3.31 to be 12.70 m eV for Bi-1at. %Sb, and 18.48 m eV for Bi- 2at. % Sb. The variation of resistivity at room temperature with valency is shown in Fig. 5. It shows that the resistivity increases by addition of Ag to maximum value in case of Zn and the decreases to minimum value in case of addition of Sb.

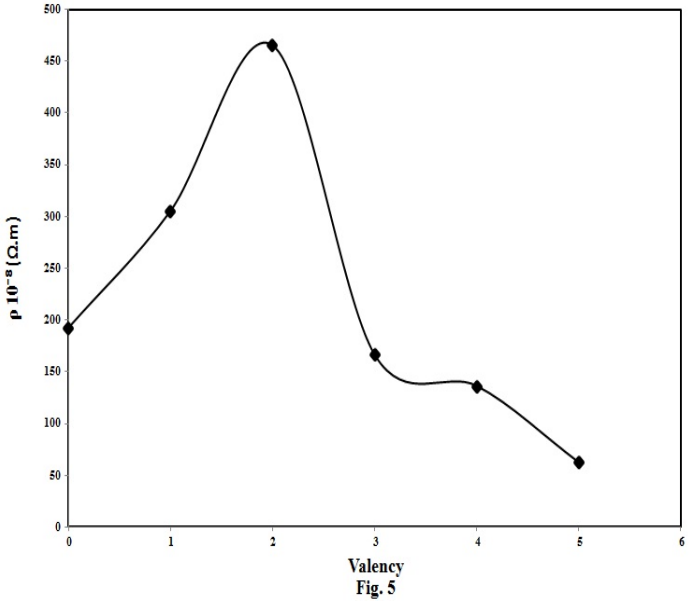

Fig.5: The variation of resistivity at room temperature with valency of dopants of Bi.

The semiconducting behavior can be explained by [6].When the impurity atoms are added to pure Bi, electrons in T_V and L_c go to impurity levels and, consequently, the Fermi level will

move to the lower energy to a position E_f^a and then the impurity atoms are ionized. If the concentration of impurity is increased, the impurity will take more electrons from the bands, and after a sufficient percentage of impurity, the Fermi level may enter into the region of the L_V band. As a result more holes will be created in T_V, L_v bands and L_C band will be devoid of electrons and this could lead to the semiconducting behavior which is observed experimentally. However, from Table 4 it is evident that odd valency dopants such as Ag (+1), Al (+3) and Sb (+5) convert Bi into semiconductor however, even valency dopants such as Zn (+2) and Sn (+4) keep the metallic behavior of Bi. This can be explained by considering the total number of electrons shared in formation of covalent bonds between the solvent atoms and the impurity atoms. The total number of valence electrons shared between the solvent and impurity atoms in case of odd valency dopants will be even, this means formation of covalent bonds and no electrons will be free for electrical conduction and the behavior becomes semiconducting. If the valency of the dopants is even, the total number of valence electrons shared between the solvent and impurity atoms is odd. This means formation of covalent bonds and an electron will be free which makes electrical conduction and the behavior becomes metallic.

4. Conclusions

From x-ray diffraction analysis it is found that all the produced alloys are single phase solid solution for 1 and 2 at.% concentrations. This means extension of solid solubility due to rapid solidification. No intermediate phases are formed and all the produced alloys have the rhombohedral structure of Bi.

From the Differential scanning calorimetry it is found that all the produce alloys are stable and the melting point is decreased by increasing valency**.**

From electrical measurements it is found that the resistivity at room temperature is increased by increasing valency up to maximum value 465 x 10^{-8} Ω.m in case of Bi-Zn system and then decreases by increasing valency to a minimum value 62 x 10^{-8} Ω.m in case of Bi-Sb system.

It is also found that all alloys containing odd valency dopants such as Ag (+1) , Al (+3) and Sb (+5) have semiconducting behavior by contrast to all alloys containing even valency dopants such as Zn (+2) and Sn (+4) that have metallic behavior.

The produced semiconductors are narrow band semiconductors. The band gap is decreased by increasing valency from 225.1 meV for Bi-Ag system to 12.7 meV for Bi-Sb system.

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