

RAPIDLY SOLIDIFIED SEMICONDUCTING Bi-Ag ALLOYS PRODUCED USING MELT-SPINNING TECHNIQUE

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Two alloys, bismuth based, of compositions Bi-1Ag and Bi-2Ag (in atomic percent) have been produced by rapid solidification using melt-spinning technique. The results show that these alloys are single phase semiconducting at room temperature. The energy gap was calculated for both to be 0.2251 eV for Bi-1Ag, and 0.2411 eV for Bi-2Ag.

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1. Introduction

Bismuth is semimetal belong to group V, with the A7 rhombohedral structure, it is poor conductor and has a small overlap between its filled and energy zones, which leads to a small number of free electrons and holes and these sufficient to provide a small conductivity [1]. The details of the electronic structure of Bi are given by [2].

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, they found that the addition of antimony changes the electrical behavior from semimetal to semiconductor at certain range of concentration of Sb [3-5]. It was found by [6] the alloying of Bi with Sn led to high increase in resistivity with zero temperature coefficients.

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 an element with low valency so as to change the valence electron concentration. So that silver has been chosen because it has valency +1. According to the equilibrium phase diagram of the Ag-Bi system, no intermediate phase was formed and the eutectic temperature is 535 K. Also there is no solubility of Ag in Bi [7].

The aim of the present work is to study the effect of alloying Bi with low concentration of Ag (1 and 2 at. %) on the structure and electrical properties. Rapid solidification has 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 fragments and Ag wires, the starting purity were better than 99.99%. Bi-xAg ($x = 0, 1, \text{ and } 2$ at. %) alloys was 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 $_{\alpha}$ radiation ($\lambda = 1.5406 \text{ \AA}$). Differential Scanning Calorimetry (DSC) was carried out in a Shimadzu (DSC-60) with heating rate 10 K min^{-1} . The temperature dependence of resistivity

(TDR) was measured using the double bridge method with heating rate 5 K min^{-1} . The detail of the double bridge method was described elsewhere [8].

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 and Bi-2at.%Ag alloys. The crystal structure of pure Bi (Fig. 1) was found to be rhombohedral-hexagonal (S.G.: $R\bar{3}m$) with $a = 4.5491$, $c = 11.9485 \text{ \AA}$. There is no any precipitation of Ag found in Bi-1Ag and Bi-2Ag alloys, i.e. there is complete solid solubility in these systems at these concentrations. 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. However, both the lattice parameters a and c are decreased to $a = 4.5447$, $c = 11.9181$. The decrease in both a and c leads to the contraction of the volume of the unit cell from 214.13 to 213.18 \AA^3 , also the axial ratio is decreased from 2.6265 to 2.6224 . The particle size of Bi was calculated using Debye-Scherrer formula [9], to be 185.7175 \AA , and due to the addition of Ag to be 340.5108 \AA for Bi-1at. % Ag, and 314.3176 \AA for Bi-2at. % Ag (see Table.2). According to Hume-Rothery rules [10] for substitution solid solution the atomic radii of the solute and solvent atoms must differ by no more than 15%. In this case for Bi-Ag alloy the difference is about 21% so that the structure of this alloy will be interstitial solid solution.

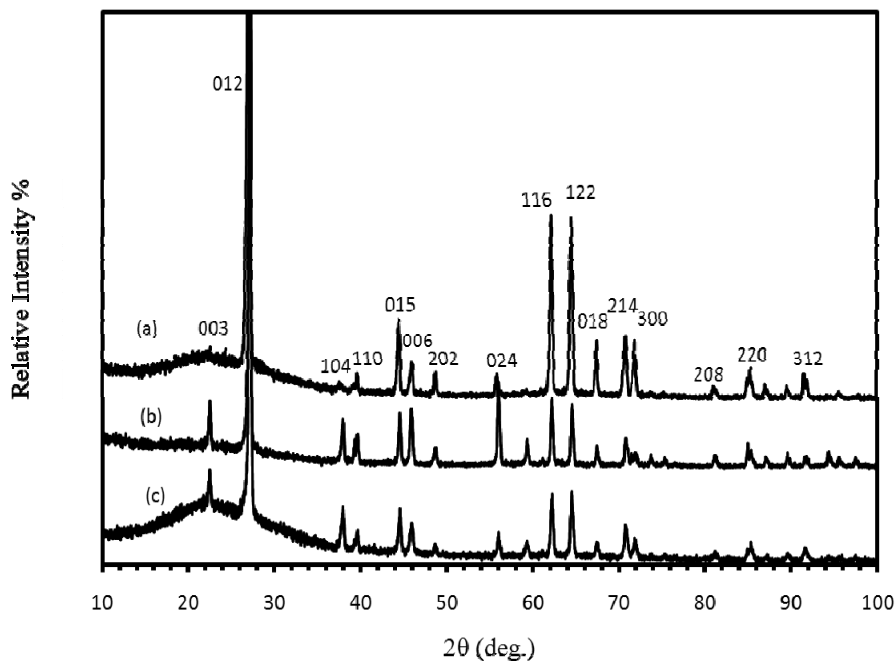


Fig.1: The x-ray diffraction patterns of as-quenched melt spun (a) pure Bi, (b) Bi-1at. % Ag and (c) Bi-2at. %Ag.

Table.1: The x-ray diffraction patterns details for as-quenched melt spun.

Alloy	Phases present	$2\theta^\circ$	d (Å°)	hkl	I/I_0	System
Bi	Bi	22.51	3.9466	003	7.03	Rhomb. (hex) S.G.: $R3^- m$
		27.09	3.2889	012	100	
		62.15	1.4923	116	23.79	
		64.49	1.4437	122	23.46	
		67.35	1.3875	018	7.83	
		71.83	1.3131	300	7.91	
		Bi-1at.% Ag	Bi	22.47	3.9536	
27.13	3.2841			012	100	
62.21	1.4910			116	8.98	
64.53	1.4429			122	8.22	
67.39	1.3875			018	2.99	
71.89	1.3122			300	2.17	
Bi-2at.% Ag	Bi			22.45	3.9571	003
		27.13	3.2841	012	3.28	
		62.25	1.4902	116	9.04	
		64.47	1.4441	122	9.28	
		67.39	1.3875	018	2.93	
		71.83	1.3131	300	3.41	

Table.2: The lattice parameter details for conventional Bi, as-quenched melt spun.

Alloy	a (Å°)	c (Å°)	c/a	v (Å ³)	t (Å°)
Bi(Conv.)	4.547	11.861	2.6085	212.3742	-
Bi(RS)	4.5491	11.9485	2.6265	214.1386	185.7175
Bi-1%Ag	4.5447	11.9181	2.6224	213.1808	340.5108
Bi-2%Ag	4.5447	11.9181	2.6224	213.1808	314.3176

3.2 Thermal analysis

Fig. 2 shows the DSC curves for as-quenched melt-spun pure Bi, Bi-1Ag, and Bi-2Ag 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 and Bi-2Ag alloys no phase transformation is observed before melting which starts at the eutectic temperature 535 K and complete melting occurred at 545 K for Bi-1Ag and at 543 K for Bi-2Ag. The enthalpy of fusion is decreased due to rapid solidification from 54.07 to 52.22 Jg⁻¹ for pure Bi. For Bi-1Ag and Bi-2Ag the enthalpy of fusion was found to be 52.73 and 51.33 Jg⁻¹ respectively. The details of DSC are shown in Table 3.

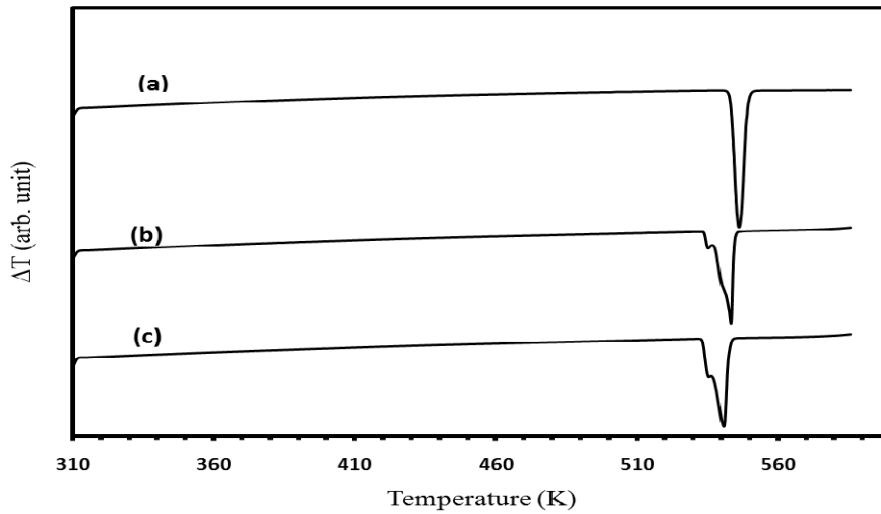


Fig. 2: The differential Scanning Calorimetry (DSC) of as-quenched melt spun (a) pure Bi, (b) Bi-1at. % Ag and (c) Bi-2at. %Ag.

Table.3: The differential Scanning Calorimetry (DSC) details for as-quenched.

Alloy	T_m (K)	T_s (K)	T_l (K)	ΔH (J/g)
Bi (Conv.)	544	-	-	54.07
Bi (RS)	544	-	-	52.22
Bi-1%Ag	-	535	545	52.73
Bi-2%Ag	-	535	543	51.33

3.3 Electrical properties

Fig. 3 shows the temperature dependence of resistivity obtained for as-quenched melt-spun Bi in the temperature range from 300 to 520 K. The resistivity is increased due to rapid solidification from 117 to 192×10^{-8} ohm.m. The behavior is metallic with temperature coefficient of resistivity $0.317 \times 10^{-3} \text{ K}^{-1}$. The resistivity is increased due to the addition of Ag to Bi from 192 to 305 for Bi-1Ag and to 760 for Bi-2Ag. The temperature dependence of resistivity for as-quenched melt-spun Bi-1Ag and Bi-2Ag alloys in the temperature range from 300 to 520 K is shown in Fig. 4. The behavior is semiconducting for the two alloys up to 428 K for Bi-1Ag and 456 for Bi-2Ag. The energy gap is calculated to be 0.2251 eV for Bi-1Ag, and 0.2411 eV for Bi-2Ag (see Table 4.). This is a narrow energy gap semiconducting alloys and the energy gap is slightly increased in by increasing Ag concentration. To explain this behavior we suggest the following; the Ag atoms form a donor level beyond the conduction band by small amount of energy which is the energy gap. This donor level provides the conduction band by electrons as the temperature raises until all the electrons contribute to conduction. At this time the number of conduction electrons is independent of temperature and the conductivity drops because of the reduction of the mobility as temperature increases.

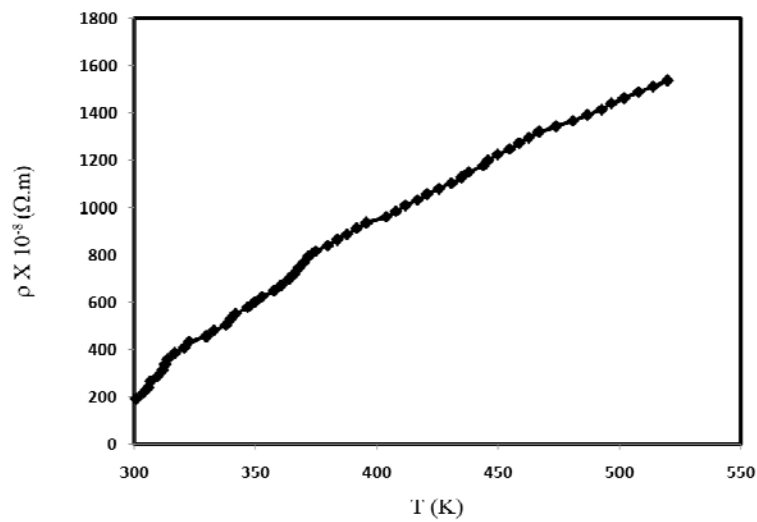


Fig. 3: The temperature dependence of resistivity for as-quenched melt-spun pure Bi.

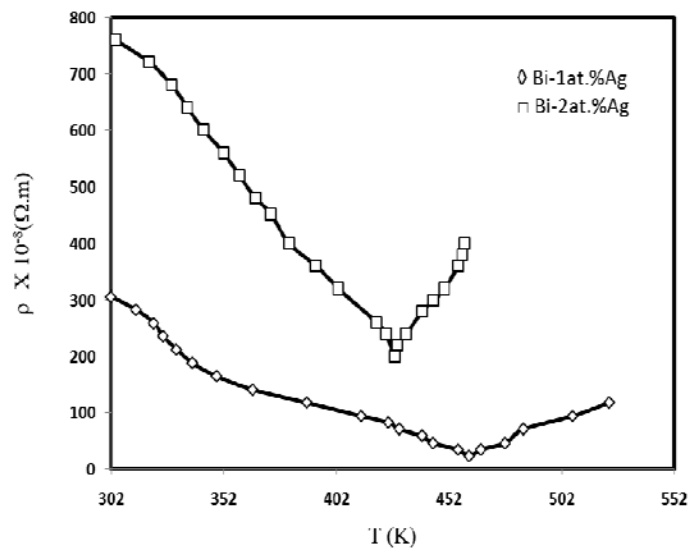


Fig.4: The temperature dependence of resistivity for as-quenched melt-spun for Bi-1at.%Ag and Bi-2at.%Ag alloys measured at different times after preparation.

Table.4: The electrical properties of as-quenched melt-spun for conventional Bi, as-quenched melt spun

Alloy	$\rho \times 10^{-8} (\Omega.m)$	$\sigma \times 10^3 (S.m^{-1})$	$TCR \times 10^{-3} (K^{-1})$	$\Delta E (eV)$
Bi (Conv.)	117	854.7	4.6	-
Bi (RS)	192	520.8	0.317	-
Bi-1%Ag	305	327.8	-	0.2251
Bi-2%Ag	760	131.5	-	0.2411

4. Conclusions

In this paper, the preparation and characterization (thermal and electrical properties) of Bi-Ag alloys have been discussed in detail. The rapidly solidified Bi-Ag was found to be semiconducting at room temperature. This work opened the way for the production of a metallic

alloys with semiconducting behavior without complicated process however. More investigations are needed in the future.

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