Structural studies of the Ge-Se-Bi System

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Abstract

A study of the effect of bismuth dopant on the structural properties of Ge_{33} Se_{67-x} Bi_x (x=0,5,10,15 and 20) semiconductor system of X-ray diffraction analysis is presented . The measurement shows that the system consists of crystals of Bi_2 Se_3. At large concentration of Bi (x>10%) it implies a change in the number of Bi_2 Se_3 crystals . No evidence for the Ge-Bi bond was found.

X-ray analysis of thin deposited films of the $Ge_{33}Se_{67-X}Bi_x$ systems shows that they are amorphous for all values of x.

Key words: Structural study , Ge – Se -Bi systems , doping , Thin Films , X- ray diffraction , Amorphous structure.

Introduction

Germanium chalcogenide glassy semiconductors are an interesting and unique class of amorphous materials. They have a widely different lattice structure in crystalline and non-crystalline form [4]. There is generally p-type with positive Seebeck coefficients describing the thermoelectric power. This case is not only for binary, but also ternary and multicomponent glass forming alloys of S, Se and Te with metalloid elements such as Si , Ge, -Sun, As and Sb . The addition of Bi to certain chalcogenide glasses changed the conductivity type from p to n [3,6]. The question so far unresolved is why Ge-Bi-Se chalcouenide glasses, prepared by quenching from the melt show n-type conductivity at higher concentrations of Bi. Different explanations have been proposed [9] e.g,the lack of Ge-Bi bonds at higher Bi concentration. EXAFS measurements have recently been perfomed from the Ge K edge and BiL_{III} edge on GeSBi glass with 6, 8 and 16 Bi at %(atomic percent) and on crytalline Bi_2S_3[10]. The purpose of the present paper is to determine the structural properties of Ge_{33} $Se_{67-x}Bi_x$ system using X-ray diffraction analysis.

Materials and Methods

The purity of the materials used were (99.999%), and are weighed in proportion to their atomic percentages and sealed in an evacuated quartz tube at ~ 10^{-2} Torr and kept in a furnace whose temperature was raised to 950°C. The ampoules were rocked frequently for (8)h in order to ensure a homogeneous melt and the melt is then quenched in water. The glassy nature of the samples were investigated using X-ray diffraction type siemens D-500. The intensity recorded as a function of angle was used under the following- condition, Source copper Ka radiation of wavelength 1.5404°A. voltage 40kV and current 40mA. The composition of the ingots was determined by wavelength disperse spectroscopy (WDS). Thin films of the $Ge_{33}Se_{67-x}Bi_x$ system have been deposited at pressure=10^{-6} torr by thermal evaporation at the room temperature substrates T_S=R.T. and of thickness (~300±5) nm.

Results and Discussion

Table 1 shows the error between the experimental composition and that calculated from WDS was less than 5% except for the $Ge_{33}Se_{52}Bi_{15}$ alloy where the error in Bi concentration was ~ 8% , and this is due to some weight approximations during the mixing process.

Table I: Analysis of the $Ge_{33}Se_{52}Bi_{15}$ alloys by (WDS)

Sample No.	Alloys	Actual wt%			Calculate wt%			Error (%)		
		Ge	Se	Bi	Ge	Se	Bi	Ge	Se	Bi
1.	$Ge_{33}Se_{62}Bi_5$	28.92	59.04	12.05	28.8	58.0	13.0	0.4	1.8	7.4
2.	$Ge_{33}Se_{57}Bi_{10}$	26.7	50.96	23.25	26.2	51.0	22.8	1.9	0.08	2
3.	$Ge_{33}S_{52}Bi_{15}$	25.0	41.7	33.3	25.5	43.8	30.5	2	5	8.4
4.	$Ge_{33}Se_{47}Bi_{20}$	23.53	37.25	39.22	23.0	37.0	40.0	2.2	0.7	2

Figure 1 shows the x-ray analysis for the alloy which contains 33% Ge and 67% Se. It is in good agreement with the ASTM (American Society For Testing Materials) structure cards of crystals of $GeSe_2$

The X-ray analysis for $Ge_{33}Se_{62}Bi_5$ alloy is presented in figure 2. It represents the crystals of GeSe and few crystals of Bi_2Se_3.

Figure (3 a,b,c) illustrates the patterns for different Bi content (X=10,15 . 20) respectively . From the figure, we found the composition that results was few crystals of $GeSe_2$ with an increasing number of Bi_2Se_3 crystal due to the increase of Bi concentration . No evidence for the Ge-Bi bond was observed. From the composition dependence of Seebeck coefficients [2], it was proposed that the appearance of n-type conduction was related to the formation of a sufficient number of Bi-Se bonds and the disappearance of some of the Ge-Se bonds, where Se has two nearest neighbours when replaced by Bi which have 3-valence electron, leaves free electrons. Thus it render the structure n-type.

Table II summarizes the X-ray analysis of $Ge_{33}Se_{67-X}Bi_X$ system for x=5,10.15 and 20.

Our results in Table II are in agreement with the results found by Agnihotri etal [1,2] , Philips [7], Elliot and Steel [5] who found that the Bi forms Bi --Se bonds at low concentration of Bi (2 at%) while at a higher concentration (10 at %) Ge-Bi bonds are favoured.

Our results are in agreement with previous measurements mentioned by Polcik etal [8] who studied the system $Ge_{20}Bi_X\ Se_{80-X}$ (for x=7-13) via measurements of the X – ray $Ge_{(K)}$ and $Bi_{(L)}$ absorption bands. The measurements yield no evidence for the presence of of Ge-Bi bonds at higher Bi concentration.

It is found by X-ray analysis that the structure of these thin films are amorphous for all values of x (figure 4)

Table 11 : X-ray diffraction analysis of the $Ge_{33}Se_{67-X}Bi_X$

GeSeBi alloy	2θ	
	$GeSe_2$	Bi_2Se_3
$Ge_{33}Se_{62}Bi_5$	22.4	
From fig. (2)	25.42	
	26.36	
	27.7	
	29.1	
	30.38	
	30.72	
	31:36	
	33.12	35.42
		37.74
	41.42	
		42.94
	45	
		51.14
	55.8	
$Ge_{33}Se_{57}Bi_{10}$		25.6
From fig (3-a)	25.6	
	27.2	
	29.28	27.8
	31.42	
	45	
	55.8	
	27.1	
$Ge_{33}Se_{52}Bi_{15}$	31.28	29.38
From fig. (3-b)		40.52
		43.6
	45	
		53.4
	55.8	
$Ge_{33}Se_{47}Bi_{20}$	20.52	
From fig. (3 – c)	27.24	
		29.34
	31.32	
		40.48
	45	43.6
		53.4
	55.8	

Conclusion

The X-ray diffraction patterns of $Ge_{33}Se_{67-x}Bi_x$ with x=0,5,10,15 and 20 have been studied. The results indicate that the addition of low concentration of Bi forms BiSe bonds while, at a high concentration (x>10%), an increase in BiSe bonds was observed with no evidence for the Ge-Bi bonds. These results are in agreement with the recent measurements for the Ge-Bi-Se system.

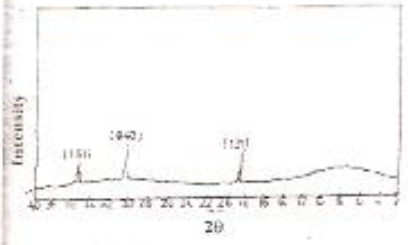

Fig.(1) : X-ray spectrum of $Ge_{10}Se_{90}$ system

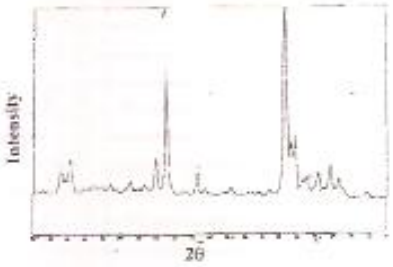

Fig.(2) : X-ray spectrum of $Ge_{10}Se_{80}Bi_{10}$ system

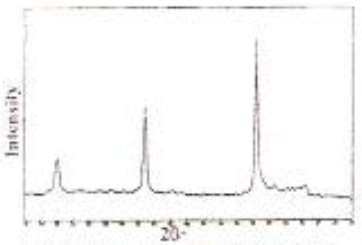

Fig.(3-a) : X-ray spectrum of $Ge_{10}Se_{70}Bi_{20}$ system

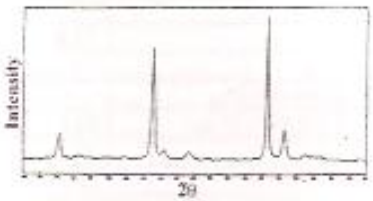

Fig.(3-b) : X-ray spectrum of $Ge_{10}Se_{60}Bi_{30}$ system

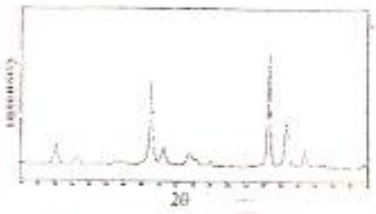

Fig.(3-c) : X-ray spectrum of $Ge_{10}Se_{50}Bi_{40}$ system

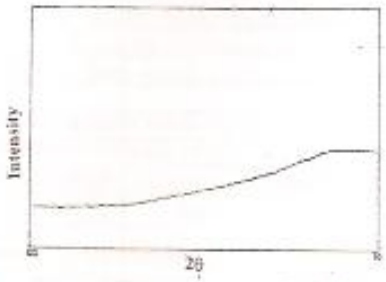

Figure (4) : X-ray diffraction pattern for $Ge_xSe_{(1-x)}Bi_x$ thin films prepared at Ta=R.T.

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دراسات تركيبية لنظام الجرمانيوم والسلينيوم والبزموث

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الملخص

لقد تم دراسة تأثير نسب تطعيم (x) البزموث على الخواص التركيبية لنظام شبه الموصل $Ge_{33} Se_{67-x} Bi_x$ لقيم x = 0,5,10,15, 20 من خلال قياسات حيود الأشعة السينية . أوضحت هذه القياسات احتواء النظام على بلورات $Bi_2 Se_3$. وعند التراكيز العالية للبزموث (x > 10 %) فإن ذلك يتضمن تغيراً في عدد بلورات $Bi_2 Se_3$. كما أنه لم يتم الكشف عن وجود إصرة Ge – Bi . كما أظهرت تحاليل الأشعة السينية للأغشية المرسبة الرقيقة لأنظمة $Ge_{33} Se_{67-x} Bi_x$ بأنها عشوائية التركيب لكافة قيم x .

كلمات مفتاحة : دراسات تركيبية ، أنظمة الجرمانيوم السلينيوم البزموث ، التطعيم ، أغشية رقيقة ، حيود الأشعة السينية ، عشوائية التركيب .