STRUCTURAL AND ELECTRICAL PROPERTIES OF THE CHALCOGENIDE GLASSES Bi_{30} $Se_{(70-x)}$ Te_x SYSTEM

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Samples with compositions Bi_{30} $Se_{(70-x)}$ Te_x (x = 35, 40, 45) were prepared by the melt quenching technique. X -ray diffraction patterns were obtained for the annealed characterization by X-ray samples in the powder form at room temperature. Structural diffraction indicates their rhombohedral structure with hexagonal lattice and a space group R3m. However, there is corresponding increase of the lattice parameters (a and c) as the Te content increase. The change of the electrical conductivity with temperature for annealed samples was also investigated. A sharp increase of the electrical conductivity and a corresponding decrease of the activation energy of conduction are detected as increasing Te content from 30 to 40.

1. Introduction

Amorphous materials especially the chalcogenide glasses (Se, Te and S) are the promising materials receiving increasingly attention in view of the fabrication of various solid state devices [1-3].

New applications of amorphous materials and optical recording have been possible due to recent in the technique improvements of preparations. The bonding arrangement in the amorphous materials is not well defined as they lack in long range order. Due to this, it is difficult to understand the conduction mechanism in these chalcogenide glasses.

Transport properties of chalcogenide glasses strongly depend on the nature and the degree of short range order and are not significantly affected by the loss of long range order. As chalcogenide glasses have poor thermo-mechanical properties, in order to enlarge their domain of applications, it is necessary to increase their softening temperature and mechanical strength. Researches [4-5] have been done in the domain transformation of chalcogenides. Often, attempts have been made by changing the compositions [6] and introducing some extra element [7] into binary alloy. The effect of the additives on the properties of binary system is, therefore, of great importance.

In the present work, we have studied the structural and electrical properties of Bi_{30} $Se_{(70-x)}$ Te_x system. Among all the chalcogens, Se is one of the most important chalcogen elements, as it has applications in electrophotography. The pure Se has some disadvantage due to its short life time and low sensitivity, which can be improved by incorporation of group III, IV, V, and VI elements such as Ga, In, Ge, As, Sb, Bi, Te, S, etc. .The work on binary Se-alloys have already been reported [8-12]. Se-Te has been used as a base material and incorporation of Bi as a third element has been studied [13]. The introduction of third element expands the glass forming area, and also, creates compositional and configurational disorder in the system.

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Generally, the binary alloys are covalent in nature and the addition of third element creates iono-covalent bonds and as a result the conduction increases .We have chosen Bi because of its special role on the type of conduction [14]. Tohge et al. [15] and Negels et al. [16] reported that the type of conduction changes from p to n-type when Bi ≥ 7 at %. This change is related to the chemistry of the system and consequently a change in the Fermi level [17]. Several workers have added different elements to Se-Bi system [18-22], and most of these materials exhibit a p-type transition [23-25].

Table 1. The values of d and I / I₀ for all the studied samples.

Composition	Lattice Parameter			$V(\AA)^3$	α^o
	$a_H(\AA)$	$a_R(\AA)$	$c(\AA)$		
$Bi_{30} Te_{35} Se_{35}$	4.152	9.769	28.412	424.16	24.538
$Bi_{30} Te_{40} Se_{30}$	4.165	9.834	28.607	429.754	24.451
$Bi_{30} Te_{45} Se_{25}$	4.193	9.916	28.847	439.206	24.412

To observe the influence of Bi on the transport properties in (Bi Te Se) alloys, we have decided to study the structural and electrical properties in ($Bi_{30} Se_{(70-x)} Te_x$) alloys (x =35, 40, 45). The study includes measurements of X–ray diffraction and dc electrical conductivity during heating – cooling consecutive cycle. The expected chemical bonds and cohesive energy is given.

2. Experimental techniques

High purity (99.999%) Bi, Te and Se in appropriate atomic percentages were weighted on a mono pan balance having an accuracy of ±0.0001 gm.

Table 2. Dependence of the lattice parameters a_H, a_R and c, and the volume of unit cell (V) on composition.

Composition	ΔE (eV)	log σ_o	log σ_{20}
$Bi_{30}Se_{35}Te_{35}$	0.52	-5.265	-6.2
$Bi_{30}Se_{30}Te_{40}$	0.45	-5.54	-5.9
$Bi_{30}Se_{25}Te_{45}$	0.37	-5.81	-5.7

The synthesis process of constituent elements was carried out in silica ampoules. The latter were sealed under vacuum (10^{-4} torr) and heated in a furnace where the temperature was raised to 800 °C for 10 hours for all the samples. During the synthesis, the molten was shacked to ensure a homogeneous mixture. The molten samples were then rapidly quenched in iced water to produce a glassy solid. The glassy nature of quenched ingots was confirmed by using

Philips X- ray diffractometer type (PW 1373) with CuKα radiation and Ni filter. The dc electrical conductivity measurements were carried out using a special design Pyrex cell supported with two fixed tungsten electrodes. A programmable electrometer model Keithly 617 was used to measure the ohmic resistance of the samples.

3. Results and discussion

3.1 X-ray diffraction

Powder X-ray diffraction patterns of the as prepared samples are shown in fig. (1).The absence of diffraction lines confirms the amorphous structure of the compounds. In order to investigate the crystalline structure of the compositions under study, all the samples were annealed at a temperature 200◦C for 8 hours and then slowly cooled down to room temperature. Fig. (2), presents the X-ray diffraction diagrams carried out for the annealing compositions at room temperature. The experimental X-ray data, the inter planer spacing (d) and the relative intensity (I / I_0), for the crystallized samples are given in table (1). For indexing the patterns of the investigated samples from the shape of the spectrum, many trails have been made. The best one was to assume the samples to have rhombohedral unit cell $Bi_2 Te_3$ type, tetradymite group [26], with space group symmetry R 3 m and consists of five stacked layers of atoms along the c-axis of the hexagonal lattice [27]. As observed from the X-ray diffraction patterns, all refractions obey the rhombohedral criteria [28]:

$$- h + k + l = 3n \qquad (1)$$

where n= 0, 1, 2…

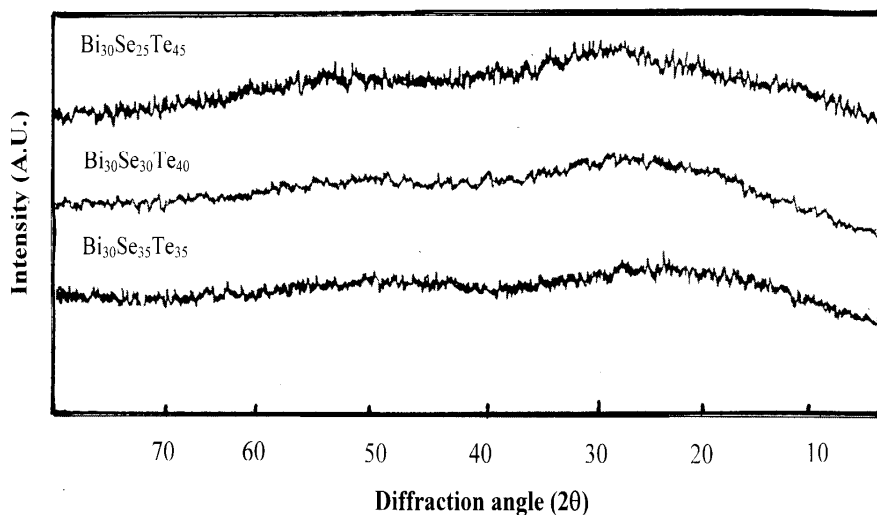*Fig.(1): X –ray diffraction pattern for $Bi_{30}Se_{(70-x)}Te_x$ samples.*

The hexagonal lattice parameters were determined. The unit cell dimensions, the volume of the unit cell and the angle α_R for the investigated compositions were calculated and listed in table (2) where [29]:

$$(2) \quad a_R = \frac{1}{3}(3 \, a_H^2 + c^2)^{\frac{1}{2}}$$

and
$$\sin \frac{\alpha}{2} = \frac{3}{2} \frac{1}{[3 + (\dfrac{c}{a_H})^2]^{\frac{1}{2}}} \qquad (3)$$

It is found that the lattice parameter (a) shows a slight increase with increasing Te content, gradually from 4.152 Å for the compound $Bi_{30} Se_{35} Te_{35}$ to 4.193 Å for the compound $Bi_{30} Se_{25} Te_{45}$. Also the calculated lattice parameter (c) shows a gradual increase form 28.412 Å for the compound $Bi_{30} Se_{35} Te_{35}$ to 28.847 Å for the compound $Bi_{30} Se_{25} Te_{45}$. According to the increase in the lattice parameters the calculated unit cell volume increases as the Te content increase.
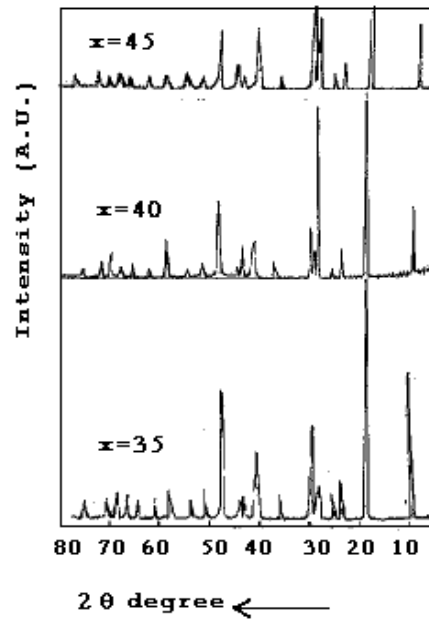

Fig. (2): X –ray diffraction pattern for the annealing samples.

Table (3): Electrical parameters of the studied samples.

$Bi_{30} Te_{35} Se_{35}$		$Bi_{30} Te_{40} Se_{30}$		$Bi_{30} Te_{45} Se_{25}$		h k l
d	I/I_0	d	I/I_0	d	I/I_0	
9.371	31	9.479	30	9.615	37	0 0 3
4.739	100	4.772	100	4.821	100	0 0 6
3.790	20	3.812	13	3.829	12	1 0 1
3.529	17	3.547	12	3.579	10	0 1 2
3.175	23	3.190	35	3.226	27	1 0 4
3.120	32	3.124	28	3.187	27	0 0 9
3.025	16	3.041	13	3.062	11	0 1 5
2.533	26	2.539	21	2.555	19	0 1 8
2.238	17	2.245	15	2.259	12	1 0 10
2.109	12	2.113	11	2.127	11	0 1 11
2.066	17	2.076	15	2.086	12	1 1 0
1.915	19	1.918	16	1.932	14	0 0 15
1.804	12	1.802	11	1.791	10	0 2 1
1.709	11	1.714	10	1.721	10	2 0 5

3.2. DC Electrical Conductivity:

The dc electrical conductivity σ $(\Omega$ cm$)^{-1}$ for crystallized samples has found to be negative function of temperature expressed by:

$$\sigma = \sigma_o \exp [- \Delta E / k_B T] \qquad (4)$$

where σ_o is the pre- exponential factor, ΔE is the activation energy of conduction, k_B is the Boltzmann's constant and T is the absolute temperature. Fig. (3), shows the temperature dependence of the dc electrical conductivity for all the studied samples. A least square fit is used to represent the experimental points. The activation energies of conduction were computed from the slope of the least square fit. Different values of electrical energy of conduction), log σ_o (the pre-exponential factor) and log parameters ΔE (activation σ_{20} (the conductivity at room temperature) are given in table (3). The bond energies D (A –B) for heteronuclear bonds have been calculated by Pouling [30] using the relation :

$$D (A\text{-}B) = [D (A\text{-}A) D (B\text{-}B)]^{\frac{1}{2}} + 30 (\chi_A\text{-} \chi_B)^{2} \qquad (5)$$

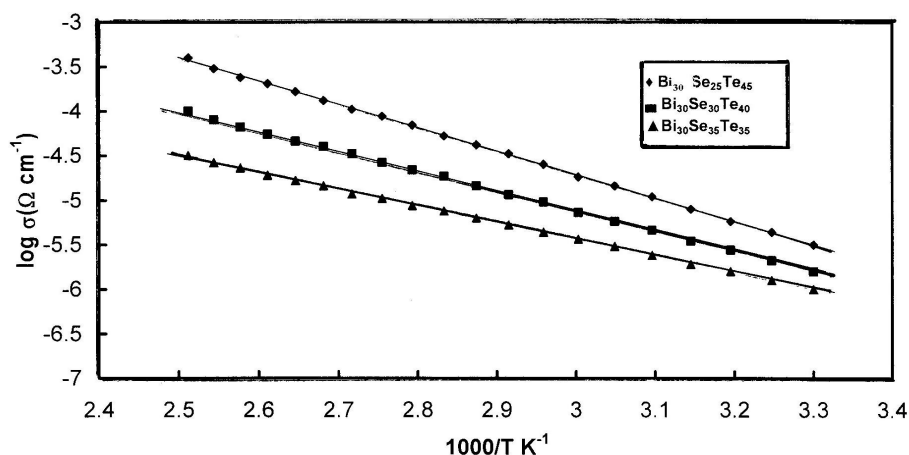*Fig. (3): Relation between logσ and 1000/T for all the studied samples.*

where D (A-A) and D (B-B) are the energies of the homonuclear bonds. The D (A-A) values are 47.9 for Bi, 33.0 for Te, and 44.0 for Se [31]. χ_A and χ_B are the electro negativities of the atoms involved where χ_A values used are 1.7 for Bi, 2.10 for Te and 2.4 for Se. The types of bonds expected to occur together with their bond energies as calculated using equation (5) are Se—Te (40.8 Kcal /mol) and Se—Se (44 Kcal /mol). It was found that the replacement of Se by Te leads to decrease the activation energy of conduction ΔE, this is because of the replacement of Se—Se bonds (energy bond 44 Kcal /mol) by Te—Se bonds which have a lower bond energy (40.8 Kcal /mol), so, the cohesive energy of the system decrease with increasing Te content and the conduction is easier and hence ΔE will decrease.

4. Conclusions

A study of the effect of Te addition to the system Bi$_{30}$ Se $_{(70-x)}$ Te$_x$ (x=35, 40, 45) on the structural and electrical properties has been followed. The results obtained show that:
1-All the prepared samples are in the amorphous state.

2- In the crystalline state, all the annealed samples have rhombohedral unit cell form with hexagonal lattice constants. The lattice parameters a and c increase as the Te content increase.

3- The activation energy of conduction in the crystalline state decreases with increasing Te content.

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