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Effect of Bi addition on the physical and optical properties of $Ge_{20}Te_{74-x}Sb_6Bi_x$ ($x = 2, 4, 6, 8, 10$) thin films deposited via thermal evaporation

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ABSTRACT

Chalcogenide materials in different forms (bulk, thin film, nanocrystals etc.) are finding applications in various sectors *e.g.* in infrared optics for communication, imaging, limiting, remote sensing and laser power delivery etc. Here we report the synthesis of $Ge_{20}Te_{74-x}Sb_6Bi_x$ ($x = 2, 4, 6, 8, 10$) chalcogenide alloys and estimation of some physical properties *i.e.* average coordination number, lone pair electron, number of constraints, heat of atomization, compactness, glass transition temperature etc. The transmission spectra of thin films have been acquired using UV–Visible–NIR spectrophotometer in the wavelength range of 400 nm–2600 nm. Various optical properties like refractive index, extinction coefficient, optical band gap, real and imaginary parts of dielectric constants have been evaluated using the transmission spectrum. The optical band gap of the synthesized samples has shown similar trend with the band gap determined theoretically. The average coordination number has been found to increase whereas the number of lone pair electron is found to decrease. This shows that the system under investigation is moving towards more rigid region as per constraint theory. The heat of atomization energy and theoretical band gap has also shown variation with the addition of Bi content. The tailoring of band gap along with an increase in rigidity may lead to an increase in the domain of technological applications for these alloys.

1. Introduction

With an enhanced focus on development of research in multidisciplinary fields, chalcogenide materials research has attracted attention of researchers from materials, chemical, physical and biological sciences [1–6]. In chalcogenide glasses, the ternary Ge-Sb-Te glasses have found applications in infrared optics and non-volatile memories [7]. Among amorphous materials, chalcogenide glasses offer a wide transparency range in the total infrared region up to 20 μm [8]. The transparency region is governed by the phonon energy spectrum of the amorphous material and therefore is operated by the mass of the constituent elements. Hence, chalcogenide glasses having tellurium have wider transparency domain in comparison to selenium and sulphur based glasses. The addition of fourth element act as a glassy network changer by forming X–Te bonds (X is fourth element). Here, we have chosen Bi element as network modifier in Ge-Sb-Te system. This is assumed that the addition of Bi will create the configurational disorder in the glassy network which further may led to alter the structural, optical, electrical and thermal properties remarkably [9]. Moreover, multi-component chalcogenide glasses having heavy elements are enthralling because of their ample structural characteristics and distinctive physical properties which pave the way towards thermoelectric devices [10]. The structural, morphological and optical properties of multi-component chalcogenide glasses have shown photo-darkening with the visible light exposure [11]. Multi-component chalcogenide glasses have shown Kerr nonlinearity in slab waveguides at 1200 nm and 1550 nm in femtosecond regime [12]. Linear and nonlinear optical properties of multi component chalcogenide films have been reported by El Bana et al. and have observed a red shift in the absorbance edge *i.e.* a decrease in optical band gap with the addition of third element (Sn) [13]. A comparison of thermo- and photo-induced changes in the optical parameters of $Ge_{20}Sb_5S_{75}$ amorphous chalcogenide thin films deposited by spin-coating and vacuum thermal evaporation has been done by Slang et al. [14]. The optical band gap and refractive index of spin coated

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thin films have reported to be comparatively less than the thermally evaporated thin films under as prepared conditions, whereas optical bandgap and refractive index have shown a gradual increase with thermal treatment [14].

The nonlinear optical properties of multi-component Se–Sn (Bi, Te) chalcogenide thin films have been investigated by Yadav et al. using Z-scan technique utilizing 800 nm femtosecond laser source and reported a higher nonlinear refractive index in comparison to pure silica [15]. Considering an improvement in optical properties of multicomponent chalcogenide thin films and their dependence on light, temperature effects *etc*. have instigated the authors to develop multicomponent chalcogenide glasses and correlate their physical and optical properties for optoelectronic applications.

In the present work, we have synthesized $Ge_{20}Te_{74-x}Sb_6Bi_x$ ($x = 2, 4, 6, 8, 10$) alloys via melt quench technique and deposited thin films via thermal evaporation. Various physical parameters have been determined empirically and transmission spectra of thin films have been utilized to evaluate the optical properties. The investigated optical properties have shown dependence on the theoretically calculated physical properties. The obtained result will further help to understand the various electrical and thermal properties.

2. Experimental details

Conventional melt quench technique has been used for the synthesis of bulk alloys of $Ge_{20}Te_{74-x}Sb_6Bi_x$ ($x = 2, 4, 6, 8, 10$). Pure elements (5 N) of the constituent elements have been weighed as per their atomic percentage. The total weight of one batch has been taken as 3 g. Each batch has been put in cleaned quartz ampoules and then ampoules have been sealed under vacuum of ~10^{-4} Pa. The sealed ampoules have been then subjected to a muffle furnace for step heating at the heating rate of 3–4 °C/min. The ampoules have been kept at the highest temperature of 1000 °C for 12 h. The ampoules have been quenched in ice cooled water. The density of samples has been measured using Archimedes principle. The bulk alloys have been taken out by breaking the ampoules. The obtained samples have been used for structural characterization using X-ray diffraction (SHIMADZU Analytical: XRD 6000 with Cu-K_α (0.154056 *nm*)). The thin films of the bulk alloys have been evaporated on pre-cleaned glass substrates using HINDHIVAC (12A4D) thermal evaporator and kept inside the evaporation chamber for 24 h. The thickness of thin films has been monitored using DTM-101 thickness monitor attached to thermal evaporator. The thickness of thin films has been kept at 800 nm with an uncertainty of 30 nm. The thin films have been then used to acquire transmission spectra using Perkin Elmer lambda 750 UV–Visible–NIR spectrophotometer at room temperature.

3. Results and discussion

X-ray diffraction results clearly show that there is no sharp peak (Fig. 1). This indicates that the samples are amorphous in nature. To understand the physical behavior of samples, some of the physical parameters have been evaluated. The average coordination number (<r>) for chalcogenide glasses can be calculated from an empirical relation [16]; $<r> = (aA+bB+cC+dD)/(a+b+c+d)$, where *a,b,c,d* and $A(=4), B(=2), C(=3), D(=3)$ are the atomic percentage and coordination number of Ge, Te, Sb, Bi respectively. The calculated values of <r> have been listed in Table 1.

The total number of constraints for each atom has been calculated using the relation [17]; $N_t = N_\alpha + N_\beta$, where $N_\alpha (= <r>/2)$ and $N_\beta (= 2<r> - 3)$ represent the number of bond stretching and bond bending constraints. As chalcogenides can be categorized into three groups i.e. (i) spongy or under-coordinated glasses having average coordination number < 2.4 and $N_t < 3$; (ii) fully-coordinated or ideal glasses having average coordination number = 2.4 and $N_t = 3$; (iii) over-coordinated glasses having average coordination number > 2.4 and $N_t > 3$. The value of total number of constraints (Table 1) shows that the system is rigid or over coordinated. From literature it is clear that the rigid systems have high glass transition temperature and hence appears to be more thermally stable [17,18].

The glass formation of chalcogenides is majorly governed by the existence of lone-pair electron. The lone-pair electron induces the flexibility in system [19]. The values of <r> has been used to estimate the number of lone-pair electron using the relation; L = V - <r>, where V is the number of valance electrons. The values of L have been given in Table 1. It can be seen that the value of *L* decreases with increasing of Bi content (Fig. 2). It may be attributed to the enhanced interaction of Bi ions with the bridging Te atoms. The high values of *L* show that the system is a good glass former.

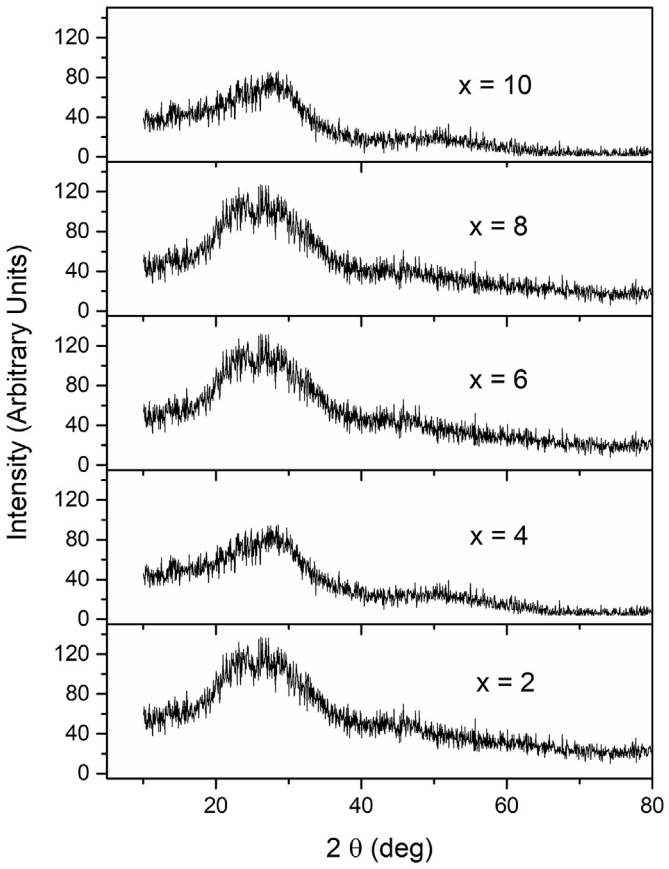

Fig. 1. X-Ray diffraction patterns for $Ge_{20}Te_{74-x}Sb_6Bi_x$ ($x = 2, 4, 6, 8, 10$) glassy alloys.

Table 1
Values of average coordination number (<r>), number of bond stretching constraints (N_α), number of bond bending constraints (N_β), total number of constraint (N_t), valance electrons (V), lone pair electron (L), heat of atomization (H_s), average single bond energy (H_s/<r>) and theoretical band gap (E_g) for $Ge_{20}Te_{74-x}Sb_6Bi_x$ ($x = 2, 4, 6, 8, 10$) glassy alloys.

x	<r>	N_α	N_β	N_t	V	L	H_s(kcal/g-atom)	H_s/<r>	E_g (eV)
2	2.48	1.24	1.96	3.20	5.52	3.04	55.82	22.51	0.647
4	2.50	1.25	2.00	3.25	5.50	3.00	55.88	22.35	0.633
6	2.52	1.26	2.04	3.30	5.48	2.96	55.95	22.20	0.618
8	2.54	1.27	2.08	3.35	5.46	2.92	56.01	22.05	0.604
10	2.56	1.28	2.12	3.40	5.44	2.88	56.07	21.90	0.589