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$Ge_{28}Se_{60}Sb_{12}$/PVA COMPOSITE FILMS FOR PHOTONIC APPLICATIONS

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New chalcogenide based composite films were prepared and characterized. The optical characterization has been done by analysing the transmittance (T) and reflectance (R) spectra in the spectral region 200–2000 nm. It was found that the optical energy gap increases (2.51eV to 3.56 eV) with decreasing $Ge_{28}Se_{60}Sb_{12}$ content. The results are interpreted in terms of cluster size of the colloid solution which depends on concentration of $Ge_{28}Se_{60}Sb_{12}$. Dispersion of refractive index has been analysed using the Wemple–DiDomenico single oscillator model. The refractive index (n), extinction coefficient (k), dispersion parameters, (E_o, E_d), static refractive index(n_o), static dielectric constant have been calculated for the investigated films. Generalized Miller's rule and linear refractive index are used to find the nonlinear susceptibility and non linear refractive index of thin films.

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1. Introduction

Inorganic/polymeric composites represent an important and growing class of materials with promising physical and optical characteristics. Recently new nano composites based on chalcogenide glasses and polymer for electroluminescence and different diffractive elements were investigated [1,2]. Photosensitivity of these amorphous composites is the key issue that can be exploited to alter properties such as mechanical, optical (linear and nonlinear), thermal etc [3].During '70 the research in this class of materials were based on the characterization of the bulk chalcogenide glasses of different compositions, where as in recent times the attention is paid to the study of chalcogenide colloidal solutions and their composite thin films. The realisation of thin films using less conventional techniques such as spin-coating or drop casting from solution is advantages for realizing large area, thick film, or localized material deposition with less cost. Chern and Lauks [4, 5] first found that amorphous chalcogenide films can be deposited from their solutions and retain many of the solute properties. For useful optical device manufacturing, it is important to retain the bulk glass stoichiometry in deposited thin films, since glass properties critically depend on material compositions. Even though attempts to understand the mechanism of dissolution of chalcogenides in amines and the existence of the presence of chalcogenide clusters with dimensions of several nanometres was reported earlier [6], factors such as the use of suitable solvent for bulk glass solubility, solution viscosity etc have only been studied recently by Shanshan Song et al[7]. Considering both the ease of dissolving and composition consistency, amine based solvents has been found to be the most appropriate solvent for chalcogenide glasses[7].Studies by T. Kohoutek et al.[8]show that the grain size of the thin films fabricated from the solutions are in good correlation with the cluster size of the solution used.

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In the present paper we report the preparation and optical characterization of $Ge_{28}Se_{60}$ Sb_{12} /PVA films from solutions of different concentration. We have chosen germanium based glass since the physical properties of germanium chalcogenide glasses have attracted much interest due to physical and technical reasons. For example Ge−Sb−Se glasses are attractive candidates for applications requiring low transmission losses, as they are transparent to IR radiation from 2 to 16 μm [9,10]and hence these glasses can be used to make IR optical fibers [11]. Polymers are highly photosensitive which have application in optical information recording while chalcogenide glasses are significant for their photosensitivity and are more stable compared to polymers. At the same time polymers and chalcogenide glasses have very different physio-chemical and optical properties with transparent and photosensitivity in different spectral range.Thus it is reasonable to combine the properties of these two groups of materials by getting nano-composites from polymers and chalcogenide glass for optimization of the sensitive parameters, simplification of the technology of fabrication, improving the stability of the registration media, solving problems related to ecological outputs etc. Most of the applications of chalcogenide glasses depend on our ability to engineer their compositions to meet the specific requirements. With this aim new composite films from $Ge_{28}Se_{60}$ Sb_{12} chalcogenide glasses and polyvinyl alcohol were fabricated from different concentrations and were characterized.

2. Experimental

The chalcogenide glass used in this study was prepared by conventional melt-quenching method[12]. $Ge_{28}Se_{60}$ Sb_{12} glasses were synthesized by melting the mixture of Ge, Sb, and Se elements (5N purity, Sigma Aldrich) in an evacuated fused-quartz ampoule. The ampoule was placed in a rotating and rocking furnace at 1050 ^{0}C for 24 h for thorough mixing and homogenization of the melt and then rapidly quenched to ice cold water. Using X-ray diffraction (XRD) technique (Bruker AXS D8 Advance X-ray Diffractometer) and energy-dispersive X-ray spectroscopy (EDS), the amorphous nature and the composition of the resultant bulk glass was found respectively. From the composition analysis it was found that the composition of the prepared glass was identical to the initial concentrations introduced in the batch.

Chalcogenide glass solutions of different concentrations of $Ge_{28}Se_{60}Sb_{12}$ were prepared by dissolution of bulk glass in n- butylamine solvent (Sigma-Aldrich, 99.9%).The dissolution was carried out inside a sealed glass container to prevent solvent evaporation. A magnetic stirrer was used to expedite the dissolution process. The composite films were obtained from the solution of $Ge_{28}Se_{60}$ Sb_{12} glasses and polyvinyl alcohol (PVA) $[-CH_2CH(OH)-]_n$ in different proportions. The concentrations of the ChG in the colloid solutions are as follows 1.2 mg/ml 0.9mg/ml and 0.24mg/ml for S_1,S_2 and S_3 respectively.The films were prepared from the homogeneous solutions of different concentrations by drop casting method. The composite films were made from these nano colloid solution and PVA in the ratio 1:1. The thickness of the films were measured using Metutoyo, Micrometer(series 193). The Atomic Force Microscope(AFM) images of $Ge_{28}Se_{60}$ Sb_{12} /PVA composite films surfaces were recorded using an Atomic Force Microscope(Veeco ,Nanoscope III, made by Digital Instruments Inc., USA) .In order to characterize the prepared thin film composites; the optical absorption for different film composition of the chalcogenide glass /polymer was investigated. The optical transmission spectra and reflection spectra have been recorded by using a spectrophotometer (JascoV-570 UV/VIS/IR). Transmission and reflection spectra have been used for the study of optical properties. The dispersion of refractive index has been studied using the Wemple–DiDomenico (WDD) single oscillator model. Some important parameters (dielectric constant, dielectric loss, optical conductivity etc.) have also been determined using n, k and absorption coefficient (α). Generalized Miller's rule and linear refractive index were used to find the nonlinear susceptibility and non linear refractive index of thin films.

3. Results and discussion

The transmission spectra of the chalcogenide glass/composite films with different concentrations are presented in Fig. 1. The composite films are transparent in the visible range compared to thermally evaporated thin film. It is clear from Fig 1 that as the concentration of the $Ge_{28}Se_{60}$ Sb_{12} component in the polymer composition decreases the absorption edge gets shifted towards the short wavelength side. The importance of this feature is related to the possibility to move the spectral range of photosensitivity of amorphous composites from ultraviolet to infrared. Similar results have been obtained on the films made of nano-composites polymer-sulphur [3,13]. AFM image of the composite films for $S_1$and S_2 is presented in figure2.

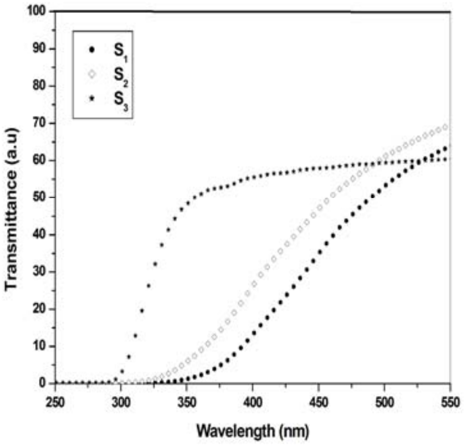

Fig 1: Transmission curves of $Ge_{28}Se_{60}$ Sb_{12} */PVA composite films with different concentrations.*

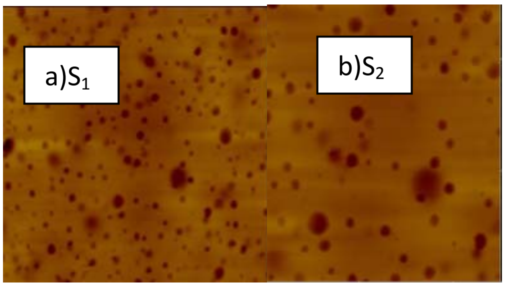

Fig. 2: AFM images showing the distribution of nano clusters in the composite films (a) S_1 *(b)* S_2.

3.1 Absorption coefficient and optical band gap

The absorption coefficient (α) of these materials strongly depends on optical transmission (T), reflection (R) and thickness of film (d) which is evaluated using the relation [14],

$$\alpha = [\ln(1 - R)/T]^2 / d \tag{1}$$

The optical energy gap (E_g) of the thin films has been determined from absorption coefficient data as a function of photon energy. According to the generally accepted "non-direct transition model" for amorphous semiconductors proposed by Tauc [15], for higher values of absorption coefficient where the absorption is associated with interband transitions, it yields the power part which obeys the Tauc et al [15] and Davis and Mott [16] relation:

$$\alpha h\upsilon = B(h\upsilon - E_g)^2 \tag{2}$$

where B is the slope of the Tauc edge called the band tail parameter. From the linear plots of $(\alpha h \nu)^{1/2}$ against (h ν) for these samples as shown in figure3, the optical energy gap has been determined from the intercepts of extrapolations to zero with the photon energy axis $(\alpha h\nu)^{1/2} \rightarrow 0$

(i.e. Tauc extrapolation). From the results obtained it is seen that an increase of concentration of $Ge_{28}Se_{60}$ Sb_{12} in the system leads to an decrease in the optical band gap.

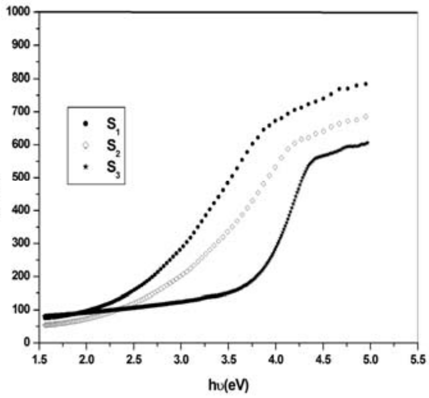

Fig 3: Plot of $(\alpha\ h\ v)^{1/2}$ *against* $(h\ v)$ *for* $Ge_{28}Se_{60}$ Sb_{12}*/PVA composite films with three different concentrations. The bandgap is found to be 2.51eV ,2.74eV and 3.56eV for* S_1*,* S_2 *and* S_3 *respectively.*

The dissolution mechanism of bulk $Ge_{28}Se_{60}$ Sb_{12} glass in butylamine is reported by Chern and Lauks [4,5].They proposed that the continuous network of the bulk glass solute is fragmented along the weakly bonded interlayer planes .The surface of the resulting macroscopic clusters react with the solvent. These clusters will be in nano meter range which depends on the concentration of the glass. The dependence of the bandgap with cluster size and grain size of the thin films was reported earlier [8,12]. The grainy surface pattern was found to be related to the cluster size of the dissolved chalcogenide material in the parent solution and as the grain size increases the band gap decreases. The increase in band gap with decrease in concentration can be due to the decrease in cluster size of the parent solution. It is found that as the concentration of the chalcogenide decreases there is a red shift in band edge and a change in the slope of absorption spectra.

The slope of the absorption edge characterizes the width of the localized states which in turn indicates the ordering of the structure. In the low absorption region the absorption coefficient α shows an exponential dependence on phonon energy hν and obeys the Urbach relation [14]

$$\alpha = \alpha_0 \exp(h\nu / E_e) \tag{3}$$

where α_0 is a constant and E_e is the Urbach energy, interpreted as the width of the tails of localized states in the band gap. The dependence of ln (α) versus hν, is a straight line, from which the inverse of the slope, gives the width of the tails of the localized states at the band gap. The values of E_e obtained for the different compositions are listed in Table 1. The width of the localized states for $Ge_{28}Se_{60}$ Sb_{12} /PVA composite films is found to decrease with decrease in concentration which shows the ordering of the structure.

3.2 Refractive index and extinction coefficient

The extinction coefficient (k) and refractive index (n) are important parameters characterising photonic materials .Values of n and k can be calculated from transmission and reflection spectra using the relation

$$k = {}^{\alpha\lambda}\!/_{4\pi} \tag{4}$$

where λ is the wavelength and α the absorption coefficient. The decrease in the extinction coefficient with an increase in wavelength shows that the fraction of light lost due to scattering .The refractive index (n) has been calculated using the relation [14]

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{5}$$

The extinction coefficient (k) and refractive index (n) at a particular wavelength is tabulated in Table 1. The high refractive index values of these glasses are advantageous for strong optical confinement and enhance the optical intensities for nonlinear interactions.

3.3 Dielectric properties and optical conductivity.

The knowledge of real part and imaginary part of the dielectric constant provide information about the loss factor. The real part of the dielectric constant is associated with the term that shows how much it will slow down the speed of light in the material and the imaginary part shows how a dielectric absorbs energy from an electric field due to dipole motion. The dielectric constant (ε_r) and dielectric loss (ε_i) have been determined from [14]

$$\varepsilon_r = n^2 - k^2 \tag{6}$$

$$\varepsilon_i = 2nk \tag{7}$$

The calculated values of ε_r, ε_i and n are given in Table 1.

Table 1. Values of concentration, optical energy gap (E_g), width of the tails of localized states in the band gap (E_e),refractiveindex (n) (at 1000nm), dielectric constant (εr) (at 1000nm) and dielectric loss (ε_i) (at 1000nm)of $Ge_{28}Se_{60}Sb_{12}$/ PVA composite films.

Sample	E_g (eV)	E_e (meV)	n	ε_r	ε_i $*10^{-5}$
S_1	2.51	543	1.74	3.00	42
S_2	2.74	477	1.72	2.97	33
S_3	3.56	200	1.66	2.80	16

The optical response of a material is studied in terms of the optical conductivity. It has dimensions of frequency which are valid only in a Gaussian system of units. The optical conductivity (σ) has been determined from the relation [14]

$$\sigma = \alpha nc / 4\pi \tag{8}$$

where c is the velocity of light, α is the absorption coefficient and n is the refractive index.

The optical conductivity is found to follow the same trend as that of the absorption coefficient and the refractive index with increasing wavelength. The optical conductivity was found to increase with increase in energy.

3.4 Dispersion analysis of the refractive index.

The dispersion parameters are significant factors in optical communication and in designing devices for special applications. The spectral dependence of the refractive index, in the visible and near infrared regions, has been analyzed in terms of the Wemple–DiDomenico (WDD) single effective oscillator model [17,18]. According to this model the relation between the refractive index and the single oscillator strength can be described using the relation.

$$\left(n^2-1\right)=\left[{E_dE_o}\Big/{E_o^2-\left(h\nu\right)^2}\right] \tag{9}$$

The dispersion energy(E_d) measures the average strength of interband optical transitions and is associated with the changes in the structural order of the material ie, it is related to the ionicity, anion valency and co ordination number of the material and E_0 is the effective oscillator energy. The increase in the dispersion energy value is usually associated with decrease in the band gap. The oscillator energy, E_o, is an 'average' energy gap, as it scales with the Tauc gap, E_g, i.e. $E_o \approx 2 \times E_g$, as was verified by several chalcogenide films [19-21]. The static refractive index (n_0) has been calculated from WDD dispersion parameters E_0 and E_d using the formula,

$$n_o = \left(1+{E_d}\big/{E_0}\right)^{1/2} \tag{10}$$

The calculated values of effective oscillator energy (E_0), dispersion energy(E_d),static refractive index (n_0) , oscillator strength, f ($f = E_oE_d$) and the static dielectric constant, ε_s ($\varepsilon_s = n_0^2$) are listed in table 2.

Table 2.The effective oscillator energy (E_0), dispersion energy(E_d),static refractive index (n_0) , oscillator strength(f)and the static dielectric constant(ε_s) non linear susceptibility ($\chi^{(3)}$)and non linear refractive index (n_2) for $Ge_{28}Se_{60}Sb_{12}$/ PVA films.

Sample	E_0 (eV)	E_d (eV)	n_o	f	ε_s	$\chi^{(3)}$ $*10^{-13}$ (esu)	n_2 $*10^{-12}$ (esu)
S_1	3.81	7.94	1.76	30.30	3.08	1.29	2.76
S_2	4.67	9.31	1.72	43.43	2.99	1.07	2.35
S_3	6.57	12.48	1.70	81.97	2.90	0.89	1.97

Simple empirical relation based on generalized Miller's rule can be used for the estimation of the non linear refractive index (n_2) and susceptibility ($\chi^{(3)}$). The non linear refractive index (n_2) and susceptibility ($\chi^{(3)}$) can be calculated by combining Miller's generalized rule [22-24] and low-frequency linear refractive index estimated from Wemple-DiDomenico single effective oscillator model. The linear optical susceptibility in the case of chalcogenide glasses is given by relation: $\chi^{(1)} = (n_2-1)/4\pi$. Using generalized Miller's rule we obtain

$$\chi^{(3)} = A(\chi^{(1)})^4 \tag{11}$$

Estimated A value is $1.7*10^{-10}$ (for $\chi^{(3)}$ in (esu) [23].The n_2 can be calculated from the relation,

$$n_2 = {12\pi\chi^{(3)}}\big/{n_0} \tag{12}$$

The calculated values of non linear refractive index (n_2) and susceptibility ($\chi^{(3)}$) are tabulated in table 2.It is found that depending on the band gap the nonlinear refractive index of the investigated films also changes.The high refractive index values of these glasses are advantageous for strong optical confinement and for nonlinear interactions[25].

4. Conclusions

Optical properties of thin films of $Ge_{28}Se_{60}$ Sb_{12}/PVA composite films were studied using their reflection and transmission spectra in the spectral region 200–2000 nm. The interband transitions were found to be indirect type and the optical energy gap has been estimated using the Tauc method. The optical energy gap has been found to increase depending up on the concentration of $Ge_{28}Se_{60}$ Sb_{12}. The increase in the optical energy gap is explained mainly on the basis of cluster size of the solution which in turn is related to the grain size of the films. This concentration dependence on the bandgap allows us use the new composite films for many optoelectronic devices.

The refractive index has been found to decrease with the decrease in concentration of the chalcogenide glass content. Dispersion of refractive index was studied using the WDD single oscillator model. The static refractive index has been found to increase with decrease in $Ge_{28}Se_{60}$ Sb_{12} concentration in PVA. The oscillator energy (E_0), was found to follows the empirical relation with the optical energy gap.The non linear susceptibility ($\chi^{(3)}$), non-linear refractive index (n_2), the dispersion energy and the energy of effective oscillator based on Wemple-Di Domenico model have been calculated for the composite films.

It was shown from the studies that the addition of inorganic semiconductor into the polymer results in fabrication of new composite films with low cost. The investigated new composites are prospective for different photonic devices and for nonlinear optical applications.

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