

A Study of Impurities (Ag, Bi & Ge) on the optical properties of Se-Te thin films

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Abstract

Thin films of chemical composition $\text{Se}_{80}\text{Te}_{20}$, $(\text{Se}_{80}\text{Te}_{20})_{98}\text{Ag}_2$, $(\text{Se}_{80}\text{Te}_{20})_{98}\text{Bi}_2$ and $(\text{Se}_{80}\text{Te}_{20})_{98}\text{Ge}_2$ are prepared by thermal evaporation technique. The optical properties of these thin films are determined by a method, based only on the transmission spectra at normal incidence, measured over the spectral range of 500-2500 nm. The dispersion of refractive index is discussed in terms of the single-oscillator Wemple and DiDomenico model. Optical energy gap (E_g) decreases while refractive index (n) increases on the incorporation of Bi addition in Se-Te system. On the other hand E_g increases while n and extinction coefficient (k) decreases on incorporation of Ag and Ge in Se-Te system. Results are interpreted in terms of cohesive energy (CE) and electronegativity (χ).

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1. Introduction

Amorphous chalcogenide thin films have received a great deal of attention due to a new advanced and replaceable technology material because of their interesting electrical, optical and thermal properties [1-3]. High refractive index ranging between 2.0 and 3.5 and low optical losses permits their development as infrared optical materials [4]. The absence of long-range order in these glasses allows the modification of their optical properties to a specific technological application by continuously changing their chemical composition. The study of optical constant of materials is interesting because of the use of these materials in optical fibers and the optical properties of all materials are related to their atomic structure, electronic and band structure. One of the chalcogenide glass fiber is the Se-Te-Ge glass fiber [5].

Among the amorphous chalcogenide alloys, mostly, selenium based materials are preferred because of its unique property of reversible transformation, which makes these alloys useful as optical memory devices. The choice of Se based alloys is due to its device application like rectifier, photocells, and switching and memory. But Se is not stable in standard operational conditions because its glass transition is close to room temperature. In order to stabilize these glasses it is common to add certain additive which act as a cross-linking agents and increase the dimensionality of structure and stability of the material. It has been found that substitution of Se by Te in Se-Te glasses breaks up the Se_8 ring structure and slightly increase the chain fraction but reduces the chain length [6]. Se and Te have the function of forming the network of the glass. Se-Te glassy alloy have gained much importance among chalcogenide glasses because of their high photosensitivity, greater hardness, high crystallization temperature and smaller ageing effect as compare to pure α -Se [7] and useful in practical application [8]. It was believed earlier that impurities have little effect on the properties of amorphous semiconductors as each impurity atom satisfies its requirement by adjusting its neighboring environment.

The role of various metals such as Ag, Cu, Sn etc. as “additives” in affecting the properties of chalcogenide glasses have been received much attention [9, 10]. It would be interesting to study the role of Ag, Bi metals in affecting the properties of the glasses of the Se-Te system. In this communication, we report the effect of Ag, Bi and Ge atom on the optical properties of Se-Te system. Addition of Bi reduces the stability [11] and changes the conductivity from p-type to n-type in certain glasses and was therefore surprising. Ag is chosen as an additive material because it alloys with most of the metals and modify their physical properties. In Se-Te-Ge system, Ge is known to contribute to long term room temperature stability. Ge also serves to increase the chemical and thermal durability of the glass. There are some studies on several glasses of the Se-Te-Ag, Se-Te-Bi and Se-Te-Ge system [12-15]. The knowledge of accurate values of wavelength dependent refractive index of thin films yields fundamental information on the optical energy gap (E_g), defect levels, phonon and plasma frequencies, etc. The optical behavior of material is utilized to determine its optical constant. Optical constants like refractive index (n) and extinction coefficient (k) are calculated by well known Swanepoel method [16],

using transmission spectrum in the UV-Vis-NIR region. Analysis of absorption coefficient was also carried out to determine the E_g and the nature of transitions.

2. Experimental details

Glassy alloys of $(\text{Se}_{80}\text{Te}_{20})_{98}\text{M}_2$ ($\text{M} = \text{Ag}, \text{Bi}, \text{Ge}$) were prepared by melt quenching technique. Sample under investigation were prepared from highly pure Se, Te, Ag, Bi and Ge (99.999%) elements. The constituents were weighed according to their atomic percentage and sealed in quartz ampoule in vacuum of $\sim 10^{-5}$ mbar. The ampoules containing the material are heated to 1000°C and held at highest temperature for 12 h. The ampoules were frequently rocked during heating to make the melt homogeneous. The quenching was done in ice-water. Quenched samples were obtained by breaking the quartz ampoules. The amorphous nature of these alloys was verified by X-ray diffraction (X-Pert PRO) as no prominent peak was observed in the spectra. Thin film samples were deposited by vacuum evaporation technique (HINDIVAC 12A4D Model) on to thoroughly cleaned microscope glass substrates. A vacuum of the order of 10^{-5} mbar was maintained during the evaporation process. The films were kept inside the deposition chamber for 24 h to achieve the metastable equilibrium. The compositions of evaporated samples have been measured by an electron microprobe analyzer (JEOL 8600 MX) on different spots (size $\sim 2 \mu\text{m}$). For the composition analysis, the constitutional elements (Se, Te, Ag, Bi and Ge) and the bulk original alloys are taken as reference samples. The composition of $2 \times 2 \text{ cm}^2$ sample is uniform within the measurement accuracy of about $\pm 0.5\%$. X-ray diffraction (XRD) study has been performed on the deposited thin films to check the nature of films using Philips PW1710 X-ray diffractometer (the radiation used was $\text{CuK}\alpha$). The normal incidence transmission spectra in the transmission range 500-2500 nm of $\text{Se}_{80}\text{Te}_{20}$ and $(\text{Se}_{80}\text{Te}_{20})_{98}\text{M}_2$ ($\text{M} = \text{Ag}, \text{Bi}, \text{Ge}$) thin films were obtained by UV-Vis-NIR spectrophotometer [Perkin Elmer Lambda-750]. All the measurements were performed at room temperature (300 K).

3. Results

3.1 Refractive index, film thickness and static refractive index

The spectral distribution function curve of transmittance for the composition $\text{Se}_{80}\text{Te}_{20}$, $(\text{Se}_{80}\text{Te}_{20})_{98}\text{Ag}_2$, $(\text{Se}_{80}\text{Te}_{20})_{98}\text{Bi}_2$ and $(\text{Se}_{80}\text{Te}_{20})_{98}\text{Ge}_2$ films have been used to compute refractive and absorption indices, using the Swanepoel method. Optical transmission spectra of these thin films are given in fig 1.

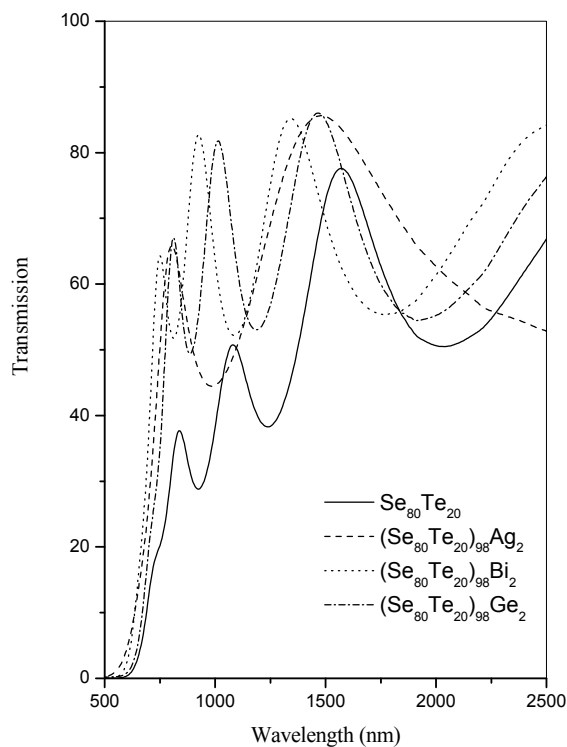


Fig. 1 Transmission spectra of $\text{Se}_{80}\text{Te}_{20}$, $(\text{Se}_{80}\text{Te}_{20})_{98}\text{M}_2$ ($\text{M} = \text{Ag}, \text{Bi}, \text{Ge}$) thin films.

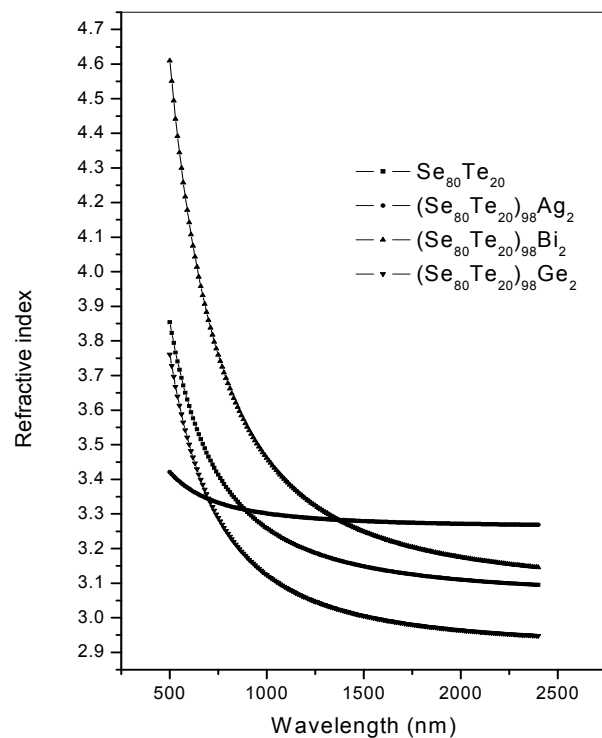


Fig. 2 Plot of refractive index versus wavelength for $\text{Se}_{80}\text{Te}_{20}$, $(\text{Se}_{80}\text{Te}_{20})_{98}\text{M}_2$ ($\text{M} = \text{Ag}, \text{Bi}, \text{Ge}$) thin film.

The film has a complex refractive index $n^* = n - ik$, where n is the refractive index and k is the extinction coefficient or absorption index, which indicate the amount of absorption loss when the electromagnetic wave propagate through the material. Both n and k are dependent on the frequency. The value of refractive index of film in the spectral region of medium and weak absorption, can be calculated by the expression

$$n = \left[N + (N^2 - s^2)^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad (1)$$

where

$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2} \quad (2)$$

where T_M and T_m are the transmission maximum and the corresponding minimum at a certain wavelength λ . Fig. 2 shows the spectral dependence of refractive index. If n_1 and n_2 are the refractive indices of two adjacent maxima and minima at wavelengths λ_1 and λ_2 Then according to the basic equation for interference fringes

$$2nd = m_o \lambda \quad (3)$$

where d is the film thickness and order number m_o is an integer for maxima and a half integer for minima. The thickness of the film is given by the expression

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (4)$$

By taking the exact integer or half integer values of m_o for each λ , accuracy of the film thickness can be increased significantly. By using the earlier calculated values of n (using equation 1), the new values of thickness have been calculated by equation (3). Using the values of m and the average of these new thickness values, the new values of n have been calculated for each λ as suggested by Swanepoel [16]. The final values on dispersion of refractive index $n(\lambda)$, have been calculated using the single-effective-oscillator model proposed by Wemple and DiDomenico (WDD) [17]. They found that all the data can be described to an excellent approximation by the following expression

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad (5)$$

where E_o is the energy of the effective dispersion oscillator, an average energy gap and E_d is the so-called dispersion energy and it measures the average strength of interband optical transitions.

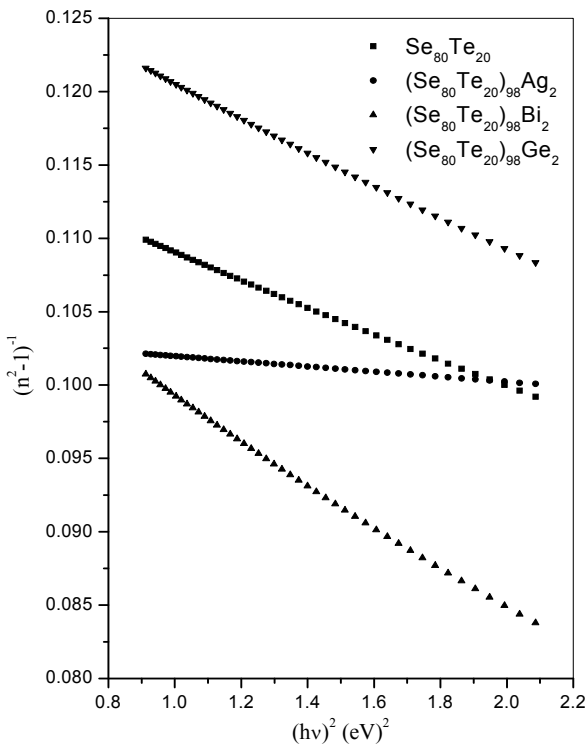


Fig. 3 Plot of refractive index factor $(n^2-1)^{-1}$ versus $(h\nu)^2$ for $Se_{80}Te_{20}$, $(Se_{80}Te_{20})_{98}M_2$ ($M = Ag, Bi, Ge$) thin films.

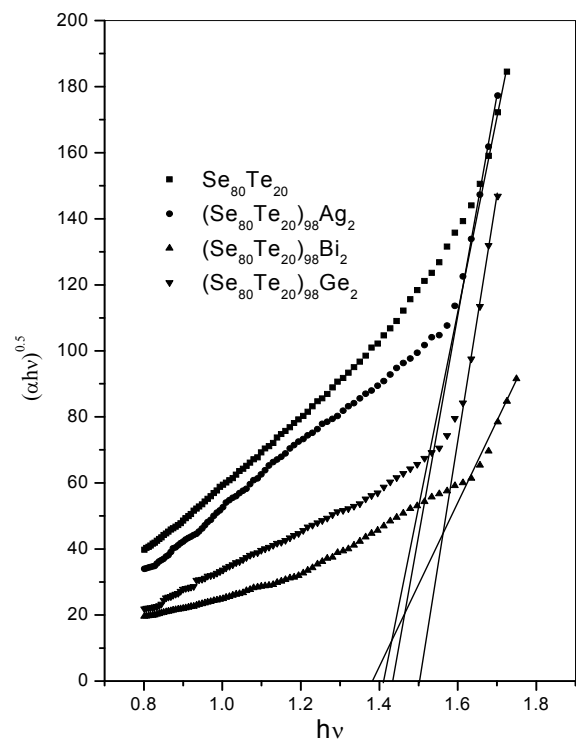


Fig. 4 Plot of $(\alpha h\nu)^{0.5}$ versus $h\nu$ for $Se_{80}Te_{20}$, $(Se_{80}Te_{20})_{98}M_2$ ($M = Ag, Bi, Ge$) thin films.

E_o and E_d values can be calculated from the slope and intercept on the vertical axis of plot of $1/(n^2-1)$ versus $(hv)^2$ (Fig. 3). Table 1 collect the values of dispersion parameters, static refractive index (n_o) and high frequency dielectric constant $\epsilon_\infty = (n_o)^2$. The static refractive index is calculated from the relation

$$n_o^2 = \left(1 + \frac{E_d}{E_o}\right) \quad (6)$$

The values of static refractive index are obtained by extrapolating equation (5) as $(hv) \rightarrow 0$. Furthermore, a simple empirical relationship by WDD which relate the dispersion energy E_d to the other physical parameters of the material, $E_d = \beta N_c Z_a N_e$, where N_c is the effective co-ordination number, Z_a is the formal chemical valency of the anion, N_e is the effective number of valence electron per anion and β is a constant ($\beta = 0.26 \pm 0.03$ eV for ionic material and $\beta = 0.37 \pm 0.04$ eV for covalent and amorphous material).

3.2 Absorption index and optical energy gap

Analysis of optical absorption spectra is one of the most productive tool for understanding and developing the band structure and energy gap of both crystalline and amorphous non-metallic material. The optical absorption edges are described using the non-direct transmission model proposed by Tauc and the optical energy gaps are calculated by Tauc's extrapolation. Optical energy gap is formally defined as the intercept of the plot of $(ahv)^{0.5}$ against (hv) . The high absorption region determines the optical energy gap. The strong absorption region, involves optical transition between valence and conduction band. The absorption coefficient of amorphous semiconductor in the high-absorption region ($\alpha = 10^4 \text{cm}^{-1}$) can be calculated by using the Tauc's relation [18].

$$ahv = B(hv - E_g)^m \quad (7)$$

B is a constant, E_g is the optical energy gap of the material and m determines the type of transition ($m = 1/2$ for the direct transition and $m = 2$ for indirect allowed transition). Fig. 4 shows a linear relation of $(ahv)^{0.5}$ versus (hv) , which indicates that the absorption mechanism in this system is non-transition. The values of optical energy gap (E_g) obtained for indirect allowed transition for investigated thin films by making $(ahv)^{0.5} \rightarrow 0$ are given in the table 1. The absorption index or extinction coefficient, which can be expressed in terms of absorption coefficient, is given by the equation $k = \alpha\lambda/4\pi$. Fig. 5 illustrates the dependence of k on the wavelength for different samples of thin films.

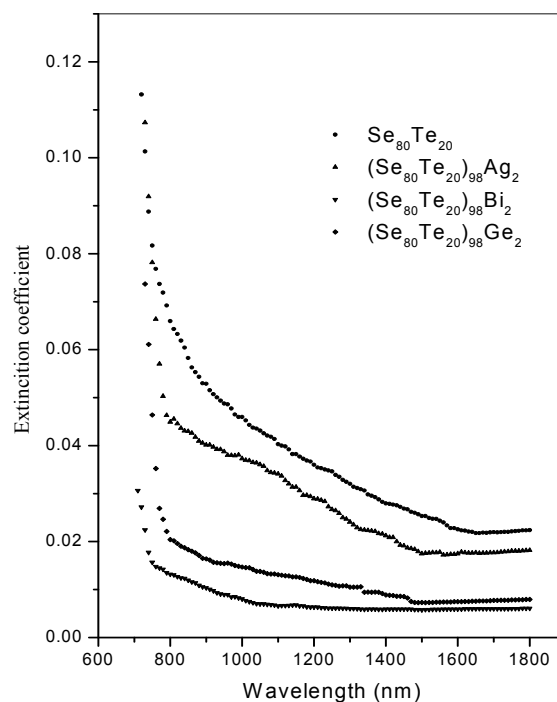


Fig. 5 Plot of extinction coefficient versus wavelength for $Se_{80}Te_{20}$, $(Se_{80}Te_{20})_{98}M_2$ ($M = Ag, Bi, Ge$) thin films.

Table 1 Values of refractive index (n), extinction coefficient (k), oscillator energy (E_o), dispersion energy (E_d), static refractive index (n_o), high frequency dielectric constant (ϵ_∞), optical energy gap (E_g), cohesive energy (CE) and electronegativity (χ) are given at 800 nm for $Se_{80}Te_{20}$, $(Se_{80}Te_{20})_{98}M_2$ ($M = Ag, Bi, Ge$) thin film are given at 800 nm.

Composition	n	k	E_o (eV)	E_d (eV)	E_g (eV)	CE kcal/mol	n_o	ϵ_∞
$Se_{80}Te_{20}$	3.370	0.0660	3.02	31.13	1.41	43.12	3.363	11.309
$(Se_{80}Te_{20})_{98}Ag_2$	3.323	0.0449	3.06	29.70	1.43	42.47	3.262	10.640
$(Se_{80}Te_{20})_{98}Bi_2$	3.677	0.0132	3.01	27.16	1.38	42.38	3.166	9.847
$(Se_{80}Te_{20})_{98}Ge_2$	3.243	0.0183	3.17	30.23	1.51	43.39	3.247	10543

4. Discussion

From the fig. 2 it is clear that the refractive index decreases with increase in the wavelength for Ag and Ge added Se-Te system. On the part of Bi addition to Se-Te thin films the refractive index is found to have higher value than Ag and Ge added system. As Bi is introduced to host Se-Te alloy the coordination number of the system increases (2-2.02) resulting in cross-linking of chains. The addition of Bi atoms is incorporated in cross-linking the Se chains by bonding with Se atoms. The decrease in the refractive index with the increase in wavelength for Ag and Ge added system may be correlated with the increase in the transmittance and decrease in the absorption coefficient and it also shows the normal dispersion behavior of the material. In case of Bi added system, the increase in the refractive index may be ascribed to increased polarizability of larger Bi-atoms (atomic radius = 1.50Å) in comparison with Se and Te atoms. The large Bi-atoms may cause more polarization and the increase of refractive index in relation with polarizability. Dispersion of the refractive index, in terms of WDD model throws valuable light on the structure of the material, through the value of E_d , dispersion energy. Single-oscillator energy, E_o is considered as average energy gap. E_o , is therefore related to the average molar bond energy of the different bonds present in the material. In table 1 a decrease is observed in E_o , for the amorphous Se-Te system with Bi content, while it increases in the case of the amorphous Se-Te system with Ge content. This decrease is observed for Bi in E_o for the film belonging to the $(Se_{80}Te_{20})_{98}Bi_2$ due to the smaller bond energy of Bi-Se bonds (1.75 eV) in comparison with that of Se-Te bonds (1.76 eV) and Se-Se bonds (1.91 eV) but on the other hand for Ge an increase is observed in E_o is due to larger bond energy of the Ge-Se bonds (2.12 eV). Fig. 5 Shows decrease of extinction coefficient with the increase in wavelength. The variation of extinction coefficient can be related with the variation of optical transmittance. The decrease in the extinction coefficient with an increase in the wavelength shows that the transmittance is increased. From the table 1 we revealed that the optical energy gap increases with Ag and Ge addition to Se-Te system, while a decrease is observed with Bi addition. It has been argued that Bi content changes the donor acceptor ratio of existing centers, decreases the optical energy gap. In Se-Te-Bi system chemical bond approach predicted only three types of bonds, viz. Bi-Te, Bi-Se and Se-Se are expected to form for the investigated composition. Addition of Bi leads to the formation of Bi-Se bonds at the expense of the Se-Se bonds and Bi is expected to combine preferably with the Se because the bond energy of Bi-Se is greater than that of Bi-Te (1.3 eV). This results in decreasing the Se-Se bonds and this also explains the increase in the glass transition temperature due to the formation of a large number of heteropolar bonds Bi-Se and decreasing in the homopolar Se-Se, Te-Te and Se-Te bonds. Value of E_g for $Se_{80}Te_{20}$ system is found to be 1.41 eV which is almost comparable with the values obtained by other researchers for same composition [19, 20]. The variation of E_g may be interpreted in terms of change in cohesive energy (CE) for Bi and Ge additive Se-Te system. The cohesive energies of the investigated compositions were calculated using the method suggested by the chemical bond approach [21]. Knowing the

bond energies, we can estimate the CE (stabilization energy of an infinitely large cluster of the material per atom) for investigated samples. The CE of the prepared samples can be evaluated from the following equation:

$$CE = \sum C_i D_i / 100 \quad (8)$$

where C_i and D_i are the numbers of expected chemical bonds and the energy of each corresponding bond. The results of CE are listed in table 1. From the table 1 we observed that CE decreases with Bi content, which means a decrease in the average stabilization energy. The decrease in the CE implies a lower bonding strength, leading to decrease in the optical energy gap while an increase is observed in CE for Ge added content, which means that average stabilization energy increases and hence the E_g increases for Ge. An increase in E_g for Ag based system is also observed which may be explained with electronegativity, χ between Se-Te and Se-Te-Ag alloy has been calculated using Sanderson's principle [22]. According to this principle electronegativity of the alloy is the geometric mean of electronegativity of the constituent elements. When the electronegativity difference is large, it is expected that the probability of defects formation will be more. According to Mulliken [23], the electronegativity is the average of the ionization potential and the electron affinity. It is difficult to assign an electron affinity value for a semiconducting alloy. Thus, it will be appropriate to correlate the electronegativity with optical energy gap. In the present system, electronegativity of Se-Te-Ag is 2.44 which is less than the electronegativity of Se-Te (2.46), so we found that optical energy gap increases with decreasing electronegativity. A similar increasing behavior for Ag based system [11, 24] and decreasing behavior in Bi based system has been obtained by [8].

5. Conclusion

Effect of impurity addition of Ag, Bi and Ge on the optical properties of vacuum evaporated thin films of $Se_{80}Te_{20}$, $(Se_{80}Te_{20})_{98}M_2$ have been studied using transmission spectra. The optical absorption measurements on these films indicate that the absorption mechanism is due to indirect transition. The refractive index has been found to decrease while optical energy gap have been observed to increase with Ag and Ge. On the other hand refractive index increases and optical energy gap decreases on incorporation of Bi. The change in the optical energy gap has been explained on the basis of cohesive energy and electronegativity.

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