

Optical Characterization of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ ($x=7, 9, 11, 12, 13$) Semiconducting Glasses

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ABSTRACT

Chalcogenide glasses are recognized inorganic glassy materials. The VI group elements are lone pair semiconductors (i.e. S, Se and Te). These usually occur in ores found in nature as many metal ores are oxides or sulphides. When one or more chalcogenide elements S, Se or Te are mixed with elements such as As, Ge, Si, Ti, Pb, P, Sb and Bi within certain range of composition, the glass so formed is known as chalcogenide glass. Chalcogenide glasses form an important class of the materials which are used in various solid state devices, photonic applications and in infrared optics. The present reported work is concerned with the structural and optical characterization of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ ($x=7, 9, 11, 12, 13$). Chalcogenide materials are prepared by rapid cooling from the melt. Thermal Evaporation Technique is used to prepare the thin film. To study the optical properties of the material, UV/VIS /IR spectroscopy has been carried at room temperature in wavelength range 200-3500 nm.

Introduction

Chalcogenide glass is a glass containing one or more chalcogenide elements. The chalcogenide glasses are semiconducting non crystalline material with covalent bonding which contains one or more chalcogen elements (S, Se, Te) in combination with one or more elements of III, V subgroups of periodic system (Ga, Si, Ge, P, As, Sb, Bi). They are generally p-type semiconductors with positive Seeback Coefficient describing the thermoelectric power, such as Ge-Te, Ge-Se systems exhibit the p-type conduction. However, in some system such as Bi-Ge-Se and Pb-In-Se the thermoelectrtic power indicates n-type conduction. The

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addition of certain metallic elemental impurities like Bi and Pb to these bulk chalcogenide glasses causes the p-n transition. The added impurities disturb the equilibrium between the charged defect states present in the band gap and unpin the fermi level. B. T. Kolomites and N. A. Goryunova initiated a systematic study of chalcogenide glasses with their co-workers who discovered semiconducting properties. Glass formation of chalcogenide material is relatively easy and many kinds of glasses have been prepared by means of melt quenching, vacuum deposition and other less common methods such as spin coating and mechanical amorphization. Among these glasses, only selenium vitrifies as an elemental glass, which is fairly stable at room temperature. Most of the stable binary glasses are compounds of a chalcogens atom and a group IV or V atom, such as Ge-Se and As-S, where atomic ratios can be varied widely. In fact the field of chalcogenide glasses is a hot bed of electronic processes that are governed by the species of chalcogens atoms. For many applications they are more suitable than crystalline materials commonly used.

The applications of the amorphous material have got a wide range. They are used in electronic, electrochemical, magnetic and optical areas of modern technology. Many amorphous semiconductors are used as passive and active element in electronic devices. However the recent discovery shows that many other types of the materials can be produced in the amorphous form either as bulk glasses or as thin films which led to a rapid expansion in the use of materials. One of the main advantages of amorphous materials over crystalline materials is that, they are relatively easy to prepare, in large scale. Homogenous amorphous thin films can be prepared for solar cell applications. Bulk glasses can often be prepared easily by melt quenching technique. The applications of such material are in the fabrication of the solar cells, thin film transistor and in electrophotography. The ability of certain ions to diffuse readily in oxides or chalcogenide glasses in the presence of a concentration gradient or electric fields opens up a range of electrochemical applications such as solid state batteries, electrochemical sensors and electronic optical devices. Chalcogenide glass materials find their applications in infrared optical communication system due to their long range IR transparency. They are extensively used for the fabrication of optical fibers, prisms and optical windows. Near the glass transition temperature, the material remains workable over a range of temperature and can be easily fashioned into fibers as these materials have ultra low optical loss characteristics in the infrared region. They are extensively used for optical communication applications. They have also been reported in active optical devices like light emitting diodes.

The phenomenon of electrical switching exhibited by certain tellurium rich glass finds application in switching devices. Amorphous semiconducting thin films are used as storage target in electron beam memory devices. Chalcogenide glasses are also used as infrared filters and in other optical elements.



Chalcogenide glasses have found several applications relating to their photoconducting properties. Two major applications are in xerography and photodetection. The present paper deals with the study of optical properties of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ system. The pure selenium has short life time and low sensitivity. This problem can be overcome by alloying selenium with some of the impurities such as Ge, Sn, As, Pb, Sb and Bi etc., which in turn gives high sensitivity, greater hardness, higher crystallization temperature and small aging effect as compared to pure selenium.

MATERIAL SYNTHESIS

Bulk Sample Preparation:

Bulk sample of chalcogenide glasses $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ (where $x = 7, 9, 11, 12, 13$) were prepared by melt quenching technique. Se and Pb in powder form with 99.999% purity (Alpha Aesar) and Ge with 99.999% purity (Across organics) were weighted according to their atomic weight percentage. These materials were put in quartz tube cleaned with chromic acid, distilled water and then with acetone. Quartz ampoules have length about 10 cm and diameter of 0.8 cm. The ampoules were sealed at very high vacuum of 10^{-5} Torr in order to avoid the oxygen contamination and counter balance the high vapour pressure in the ampoule created at higher temperature. The sealed ampoule were heated in a furnace at a heating rate of $3^\circ\text{C} - 4^\circ\text{C}/\text{minute}$ and temperature was raised to 1000°C . The ampoules were kept at highest temperature for 15 hours and continuously rocked at an interval of 1 hour to ensure the homogenous mixture. The quenching was done in ice-cold water immediately after taking out the ampoules from the furnace. The glass samples prepared were extracted by breaking the quartz ampoules.

Thin Film Preparation:

Thin film can be prepared from a variety of the materials such as metals, semiconductors, insulators or dielectric etc. There are various techniques for thin film preparation such as vacuum thermal deposition by resistive heating, electron gun or laser gun deposition, sputtering, chemical vapor deposition, chemical deposition.

Our present work dealt with thermal vacuum deposition by resistive heating. This is the most commonly method and the main requirement for this method is high vacuum deposition system at a pressure of about 10^{-4} Pa or even less. Fine powder of the material to be deposited to be put into the flash cleaned boat. Flash cleaning was done by passing a heavy current through the boat so as to make it pressure of 10^{-4} Pa. A shutter was incorporated in between the source and the substrate so that no vapor stream of the material can reach the substrate directly prior to attaining the required deposition conditions. After establishing required source

temperature, substrate temperature and vacuum in the chamber, the Sutter is opened to start the deposition of the film on the clean substrate. When the required thickness of the film is obtained the shutter is moved back to original position.

For removal of inorganic impurities methanol was used. After all cleaning the substrate is dried and put into the deposition chamber. Thin film was kept in the deposition chamber in the dark for 24 hour to attain the thermodynamic equilibrium. The vacuum evaporation process is carried out in a coating system (HINDHIVAC MODEL 12A4D INDIA).

X-ray diffraction

The vitreous nature of samples is confirmed by using X'Pert Pro X-ray diffractometer. Data were collected using Ni filtered Cu-K α (1.54 Å) radiation in the $10^\circ < 2\theta < 70^\circ$ range. The XRD spectra do not contain any sharp prominent peak and it confirms that samples have amorphous nature. **Fig.1.1** shows the X-ray diffraction pattern of Se₈₂Ge₁₁Pb₇. Other samples (x=9, 11, 12, 13) have the same diffraction patterns.

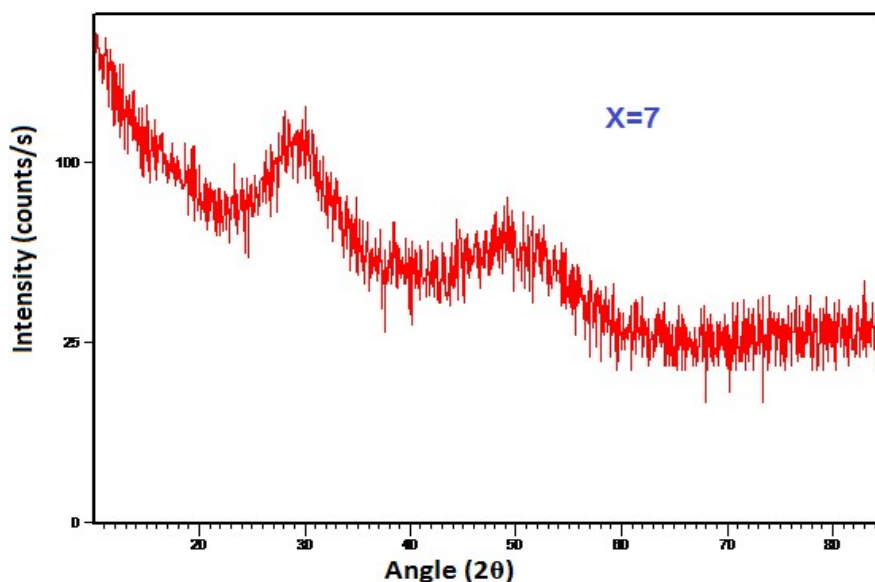


Fig.1.1 X-ray diffraction pattern for Se₈₂Ge₁₁Pb₇

Optical and Dielectric parameters

To know the material's optical behaviour, it becomes essential to know the optical band gap and refractive index (n) of material. The optical constant, refractive index can be calculated using Swanepoel's method.

According to Swanepoel's method [19, 20], the values of the refractive index of film in the spectral region of medium and weak absorption can be calculated by expression.

$$n = [N + (N^2 - S^2)^{1/2}]^{1/2} \quad (1)$$

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

Here T_M and T_m are the transmission maxima corresponding minima at a certain wavelength λ , s is the refractive index (1.5) of the substrate. The transmission spectrum of glass films having different thickness are shown in **Fig.1.2**.

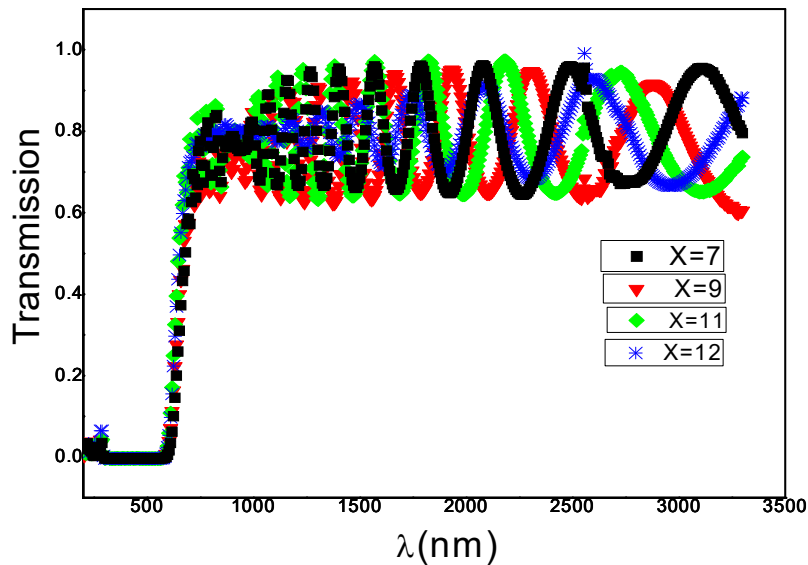


Fig.1.2 Transmission spectrum of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ ($x=7, 9, 11, 12$) glass thin film of different thickness.

The value of extinction coefficient (k) has been calculated using the relation

$$k = \frac{\alpha \lambda}{4\pi} \quad (3)$$

where α is the absorption coefficient [19] and is given by

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{x} \right) \quad (4)$$

where x is the absorbance. The variation of extinction coefficient with the wavelength is shown **Fig.1.4** (different thickness).

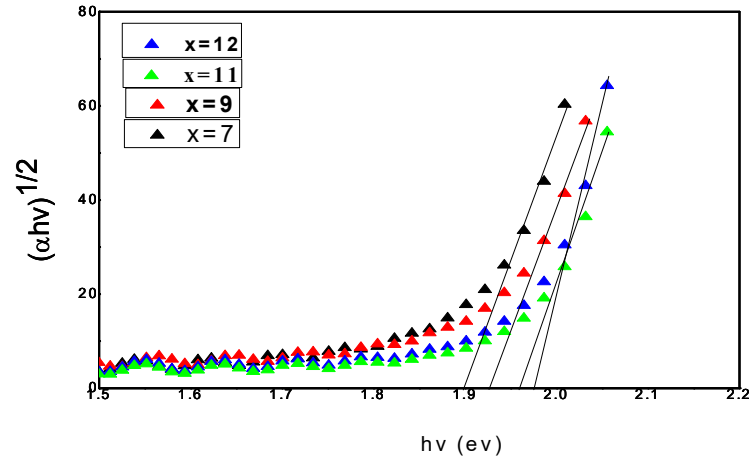


Fig.1.3 Plot of $(\alpha hv)^{1/2}$ versus (hv) for thin films (different thickness) of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ ($x=7, 9, 11, 12$).

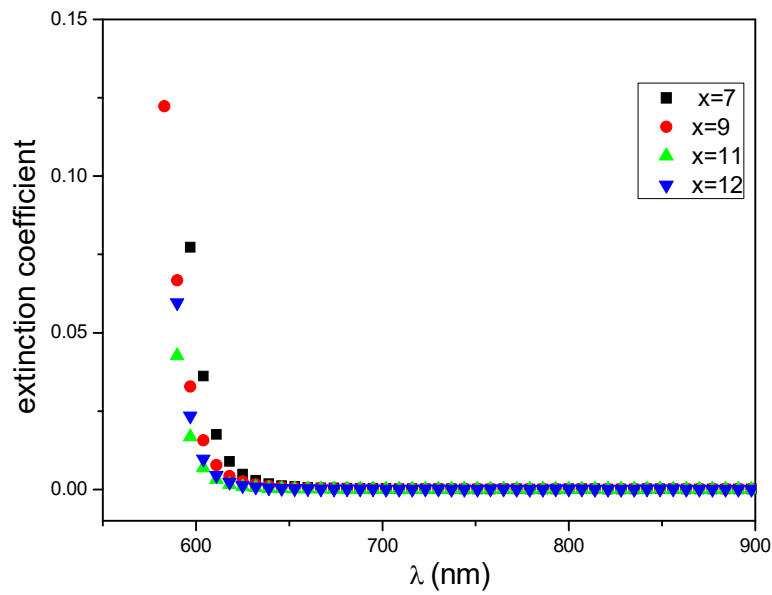


Fig.1.4 Variation of extinction coefficient with wavelength for thin films of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ ($x=7, 9, 11, 12$).

The thickness of the films are calculated by using the relation

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_2 n_1 - \lambda_1 n_2)} \quad (5)$$

Here λ_1, λ_2 are the wavelengths of two consecutive maxima or minima and n_1, n_2 are their corresponding refractive indices.

The optical absorption spectrum is the important tool for studying the band gap of material. The absorption coefficient of chalcogenide glass changes rapidly for photon energies near to their band gap.

The absorption coefficient of an amorphous semiconductor in the high absorption region can be calculated by using Tauc's relation.

For high absorption coefficient ($\alpha \geq 10^4 \text{ cm}^{-1}$), Tauc's power law [21] states that

$$\alpha h\nu = B(h\nu - E_g^{\text{opt}})^m \quad (6)$$

where B is the constant, E_g^{opt} is the optical band gap of the material and m determines the type of transition ($m=1/2$ for direct transition and $m=2$ for indirect allowed transition).

The value of the optical energy gap (E_g^{opt}) obtained for indirect allowed transition for thin film of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ by making $(\alpha h\nu)^{1/2} \rightarrow 0$ are given in the Table 4.4 and shown in **Fig.1.3**.

Table 1.1 Values of thin film thickness (d), refractive index (n), extinction coefficient (k), optical energy gap (E_g^{opt}) and real part (ϵ_r), imaginary part (ϵ_i) of dielectric constant for $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ glass thin films.

X	d (nm)	N	k	ϵ_i	ϵ_r	E_g^{opt} (ev)
7	978	2.52	0.000129	0.00065	6.3504	1.90
9	944	2.35	0.000166	0.000166	5.5225	1.93
11	1399	2.19	0.000136	0.000136	4.77961	1.96
12	1003	2.18	0.000488	0.000112	4.7524	1.97

Optical band gap of the material is around the 2ev and refractive index of the material is about 2.4. Refractive index decreases as Pb content added in the material. The variation of optical band gap E_g^{opt} and refractive index (n) has both composition and thickness dependence. If the thickness variation is dominant then compositional variation effect is difficult to observe. With increase in the thickness there might be increase in grain size, density of state and disorder in matrix which consequence in band tailing in gap and reduce the optical absorption edge. Material also exhibits the high value of dielectric constant.

Conclusion

Chalcogenide glasses form an important class of the materials which are used in various solid state devices, photonic applications and in infrared optics. The present reported work is concerned with the structural and optical characterization of $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ ($x=7, 9, 11, 12, 13$).

The ternary composition $\text{Se}_{82}\text{Ge}_{18-x}\text{Pb}_x$ ($x= 7, 9, 11, 12, 13$) bulk alloys have been prepared by melt quenching technique and thin films by thermal vacuum deposition technique. The amorphous nature has been confirmed through the x-ray diffraction. The absence of sharp peaks confirms the amorphous nature of material.

To study the optical properties of the material, UV/VIS /IR spectroscopy has been carried at room temperature in wavelength range 200-3500 nm. The material possesses the band gap around 2ev and high value of refractive index around 2.4.

The dc conductivity of the samples has also been calculated, which shows its temperature dependence due to hopping conduction in localized state across the fermi level.

Chalcogenide glass has high refractive index (n) and compositionally tunable optical energy gap (E_g^{opt}). Thus it has applicability in photonic applications, hollow core photonic crystal fibres, fiber communication, infrared optics and pollutant detector.

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