Insight into the Growth and Optical Characterization of Layered $GeSePb_x$ (x = 0, 0.1, 0.2, 0.3, 0.4) Single Crystals Using Direct Vapour Transport technique

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Abstract: This research investigates germanium monochalcogenide (GeSe) and lead-doped GeSe, whose optical properties are important for various applications. Direct Vapor Transport (DVT) grown platelet-like shaped single crystals of $GeSePb_x$ (x = 0,0.1,0.2,0.3,0.4). UV-VIS-NIR spectrophotometry reveals interesting spectra of absorption with regard to inter-band transitions involving phonons. Energy band gap values for GeSe exceed those for $GeSePb_x$(x = 0,0.1,0.2,0.3,0.4) thus stressing the importance of compositional purity. On account of its layer structure, GeSe has highly anisotropic absorption spectra which are suitable for manipulation of light-matter interaction. In order to develop electronics and optoelectronics devices, a thorough analysis of optical parameters in $GeSePb_x$(x = 0,0.1,0.2,0.3,0.4)single crystals will be necessary.

***IndexTerms*–Crystal Growth, Metal Chalcogenide, Optical Band Gap.**

I. INTRODUCTION

Today's sophistication in science and technology owes much to the availability of high-quality materials, particularly semiconductors, which serve as the foundation for a wide array of electronic devices and industrial applications. Layered chalcogenides have gained significant attention in materials science due to their diverse properties, including electronic and optical characteristics [1-3]. These semiconductors, characterized by strong bonding within layers and weak van der Waals bonds between them, have been utilized in various applications such as solid-state lubricants, photovoltaics, and solar energy conversion devices. Since 1950, advancements in science and technology, largely driven by materials science, have been instrumental, particularly in the development of semiconductor materials like silicon (Si) and germanium (Ge), which have revolutionized automation and electronics through integrated circuits [4-8].

However, due to inherent limitations such as the indirect bandgap and its value, there has been a continuous quest for alternative materials to silicon (Si) and germanium (Ge). Between 1970 and 2000, numerous semiconductor groups emerged, offering potential applications both on Earth and beyond. These include group III-V, group II-VI, and group I-II-VI2 semiconductors, alongside a specific category known as Transition Metal Dichalcogenides (TMDCs), belonging to group VI. TMDCs, particularly group VI compounds, are notable for their exceptional stability, attributed to electron transitions between d-d orbitals of constituent elements without disrupting covalent bonding. Commercially used as lubricants, group VI TMDCs have also shown promise in solar cell applications, particularly between 1977 and 1990, where the solid-liquid interface serves as a primary charge transfer interface. This class of compounds, with around 60 variants of the general formula MX2 (where X is a chalcogen such as S, Se, Te, and M is Re, Pt, Sn, Pb, or a transition metal from groups IVb, Vb, VIb), forms a well-defined family both structurally and chemically. Among these metal chalcogenides, binary IV-VI layered compounds—consisting of Ge, Sn, or Pb cations and S, Se, or Te anions—are particularly intriguing semiconductors, categorized into three groups based on crystal structure [9].

II. EXPERIMENTAL

In the present investigation the single crystals of GeSePbx (x = 0, 0.1, 0.2, 0.3, 0.4) are grown using Direct Vapour Transport (DVT) Technique. The main requirement of this technique is precise setting of the temperature gradients between two zones

(growth and source zone) to enhance the transport of material in vapour form. For this purpose, a two zone furnace having required dimensions has been used shown Figure.1. The schematic diagram of the furnace with the controlling system is shown in Figure 2. The furnace was constructed by us in our University Science and Instrumentation Centre (USIC). The high quality quartz ampoules were used for growth experiment having dimensions of 24 cm length, 2.4 outer diameter and 2.2 cm inner diameter. The ampoule was first washed with laboratory wash and boiled water and washed with hot mixture of concentrated HNO_3 and concentrated H_2SO_4 taken in equal proportion, followed by washing of ampoule with distilled water. After this the ampoule was filled with concentrated HF and heated, to make the inner surfaces of the ampoule become rough which enhances the nucleation process during the growth. Later on, the ampoule was washed 8 to 10 times by distilled water to remove any residue of these chemicals in ampoule. Such a cleaned ampoule was kept in furnace at constant temperature 100 ºC for nearly 24 hour to make it moisture free.

For charge preparation this cleaned ampoule was then filled with stoichiometric proportion of Ge (99.999%) pure, Se (99.99%) and Pb (99.99%) pure of about 10 gram for growth, after that the ampoule was sealed under pressure of 10^{-5} Torr. The sealed ampoule was loaded in two-zone horizontal furnace. The temperatures of both the zones were raised up to desired temperature and maintained that temperature for 3 days, then after furnace was cooled off at the room temperature. The ampoule was broken and we find a shiny charge again this charge is filled in so cleaned the ampoule. Then it is heated slowly at the rate of 40 ºK/h up to the growth temperature to obtain the single crystals of $GeSePb_x$ (x= 0,0.1,0.2,0.3,0.4). The ampoule was kept at that temperature for 7 days. After the growth period the furnace was cooled at the rate of 20 ºK/h to room temperature. The ampoule was taken out of the furnace and broken to remove crystals from it. We obtained black opaque shiny crystals in this process. The appropriate growth condition for all the samples is reported in Table 1. The maximum size of the crystals grown in this process is also mentioned in the Table 1.

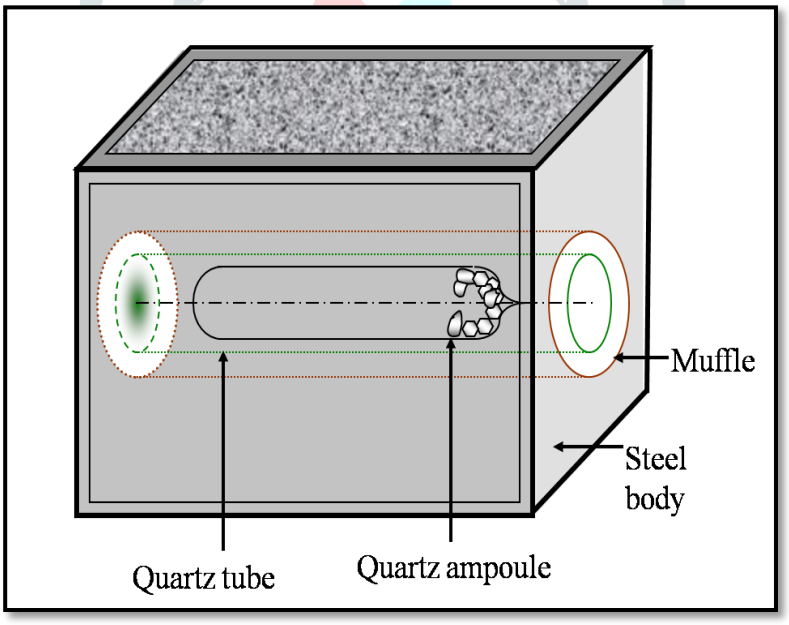

Figure 1: The dual zone horizontal furnace with axially loaded ampoule

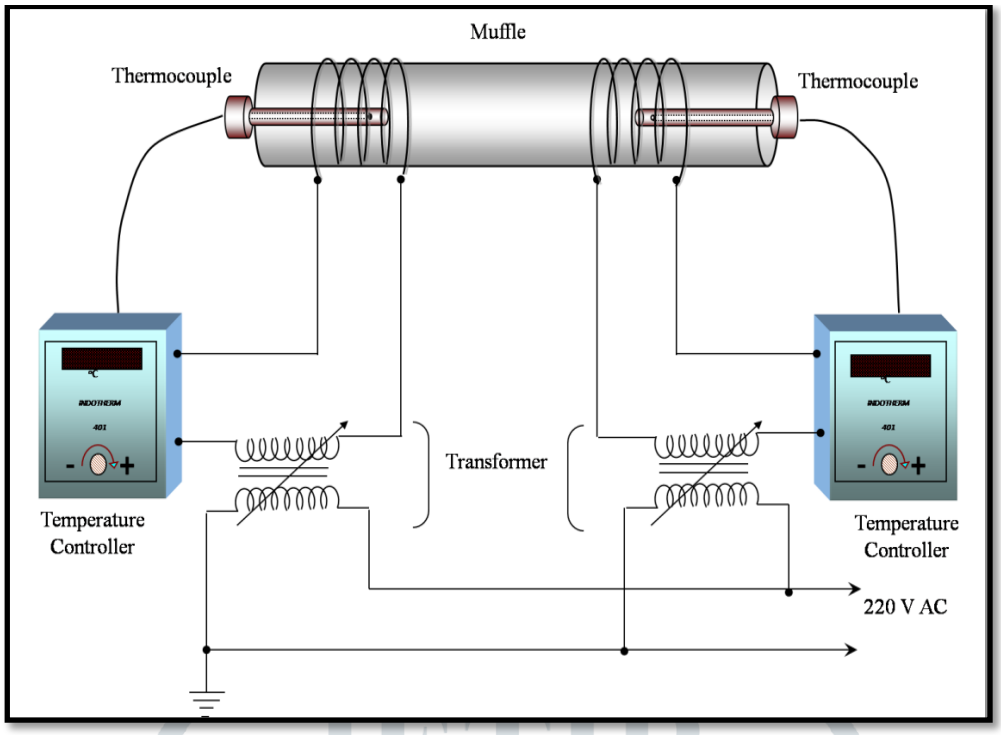

Figure 2: Schematic diagram of complete furnace structure with temperature controlling system.

The growth parameters of grown crystals such as temperature distribution, growths period etc. used for the growth of different materials have been given in Table 1.The growth of any compound in crystal form depends upon various parameters such as the length of the ampoule, purity of the source materials used, quality of the quartz tube, level of vacuum, amount and type of transporting agent, temperature distribution of the furnace, appropriate proportion of constituent element, time duration for growth cycle, the rate of increase and decrease of temperature etc.

The optical absorption measurements were conducted using a Perkin Elmer Model Lambda-19 Spectrophotometer. The surfaces of the grown crystals exhibited a mirror-like finish, with confirmed alignment of the crystal axes along the basal plane. Measurements were carried out at room temperature, with incident light directed perpendicular to the basal plane, i.e., along the c-axis of the crystal flakes. Due to the crystal structure's limitations, measurements along the c-axis were not feasible. Crystal flakes were affixed to thick black paper with an aperture exposing them to incident light, while a replica of the black paper served as the reference, ensuring consistent positioning. $GeSePb_x$ (x = 0,0.1,0.2,0.3,0.4) thin platelets were utilized directly for absorption spectra [10]

III. RESULTS AND DISCUSSION

Crystal Growth:

The crystals of $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) compound have been successfully grown using direct vapour transport technique. The photographs of the ‘as grown’ crystals of $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) are shown in Figure 3. The dimensions of grown crystals have been shown in Table 1. The grown crystals have been found enough large in dimensions. It is found that $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) compounds grow in the form of thin platelets.

Table 1: Growth parameters for grown crystals.

Crystal	Temperature Distribution(^{0}K)		Growth Period (Days)	Dimensions of Grown Crystals (cm ×cm)
	Reaction Zone	Growth Zone		
GeSe	903	853	7	0.8 × 0.7
$GeSePb_{0.1}$	875	845	7	0.8 × 0.9
$GeSePb_{0.2}$	885	835	7	0.9 × 0.6
$GeSePb_{0.3}$	890	825	7	0.9 × 0.7
$GeSePb_{0.4}$	895	805	7	0.7× 0.5

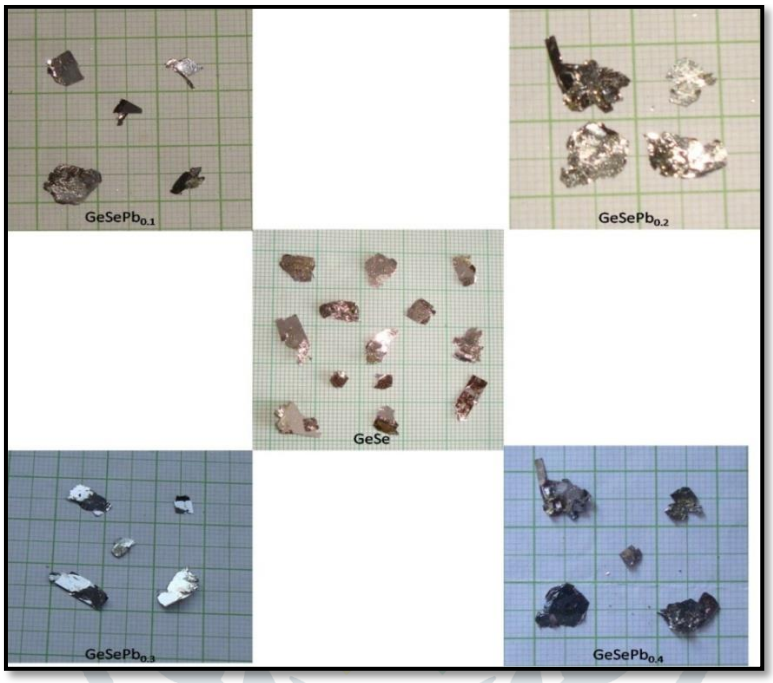

Figure 3: As grown single crystals of GeSePbx (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4).

UV-VIS-NIR Spectrophotometer:

An important technique for measuring the band gap of a semiconductor is the absorption of incident photons by the material. The absorption spectrum was taken for all samples in the wavelength range 700–1450 nm and the values of the absorption coefficient α were determined at every step of 5 nm as shown in Figure 4. It is well known [11] that α obeys the relation

$$(\alpha h\nu) = A(h\nu - E_g)^r (1)$$

For direct transition and

$$(\alpha h\nu) = \sum_j B_j (h\nu - E'_g \pm E_j^p)^r \qquad (2)$$

For Indirect transitions

where α is the absorption coefficient, hν is the energy of the incident photon, Eg is the energy for the direct transition, E'g is the energy for the indirect transition and E_{pj} is the energy of phonon assisted transitions. A and B are parameters depending in a more complicated way on temperature, phonon energy and photon energies Ep. By plotting graphs of $(\alpha h\nu)^{1/r}$ against hν for various values of r as shown in table 2, it is possible to determine which of the condition given in the table dominates. Extrapolation of these graphs to zero absorption will provide appropriate values of the energy gaps of $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) the compounds. Since all the curves indicate some discontinuity straight lines, it is quite possible that they may represent inter-band

transitions involving the emission or absorption of phonons as shown in Figure 5. In order to make an accurate determination of the points of discontinuities, we have followed the method earlier successfully used for layer compounds [12-15].

Table 2: Various exponents 'r' for different types of band gap transitions.

Types of Transition	Direct		Indirect	
	2D	3D	2D	3D
Allowed (Step Function)	0	½	1	2
Forbidden	1	3/2	2	3

Table 3: The direct band gap values in eV for $GeSePb_x$ (DVT) (x= 0, 0.1, 0.2, 0.3, 0.4)

Sample	Band Gap
	3D Allowed
GeSe (DVT)	1.440
GeSePb0.1 (DVT)	1.420
GeSePb0.2 (DVT)	1.310
GeSePb0.3 (DVT)	1.240
GeSePb0.4 (DVT)	1.180

Table 3 shows the calculated values of 2D allowed direct band gap for $GeSePb_x$ (DVT) (x= 0, 0.1, 0.2, 0.3, 0.4) single crystals which reveals that as the concentration of Pb increases the direct band gap decreases as shown in figure 6. Similarly, other values of direct allowed and forbidden band gap for 2D and 3D model can be calculated.

Using absorption spectra, transmission (T) and reflection (R) coefficients have been computed by equations 3 and 4 [16,17] .

$$A = - \log T \qquad (3)$$

$$R = 1 - (T+A) \qquad (4)$$

where symbols have their usual meanings. The relation between T and R in graphical form is shown in Figure 7.The reflectance R, of the same crystal exhibits two shallow depressions. This behavior indicates the existence of two strong absorptions bands in both IR and UV ends of spectrum. Crystal shows abrupt depression in the both the near IR and the UV sides of the spectrum. At the same region of the spectrum, R, of the same crystal steadily increases while it exhibits a few narrow ripples indicating the existence of a couple of sharp absorption bands overlapping broad conduction band characteristics for semiconducting material [18].From Figure 6 it implies that reflectance and absorbance possess the same trend but the value of reflectance is high so the surface of the grown crystal is shiny.

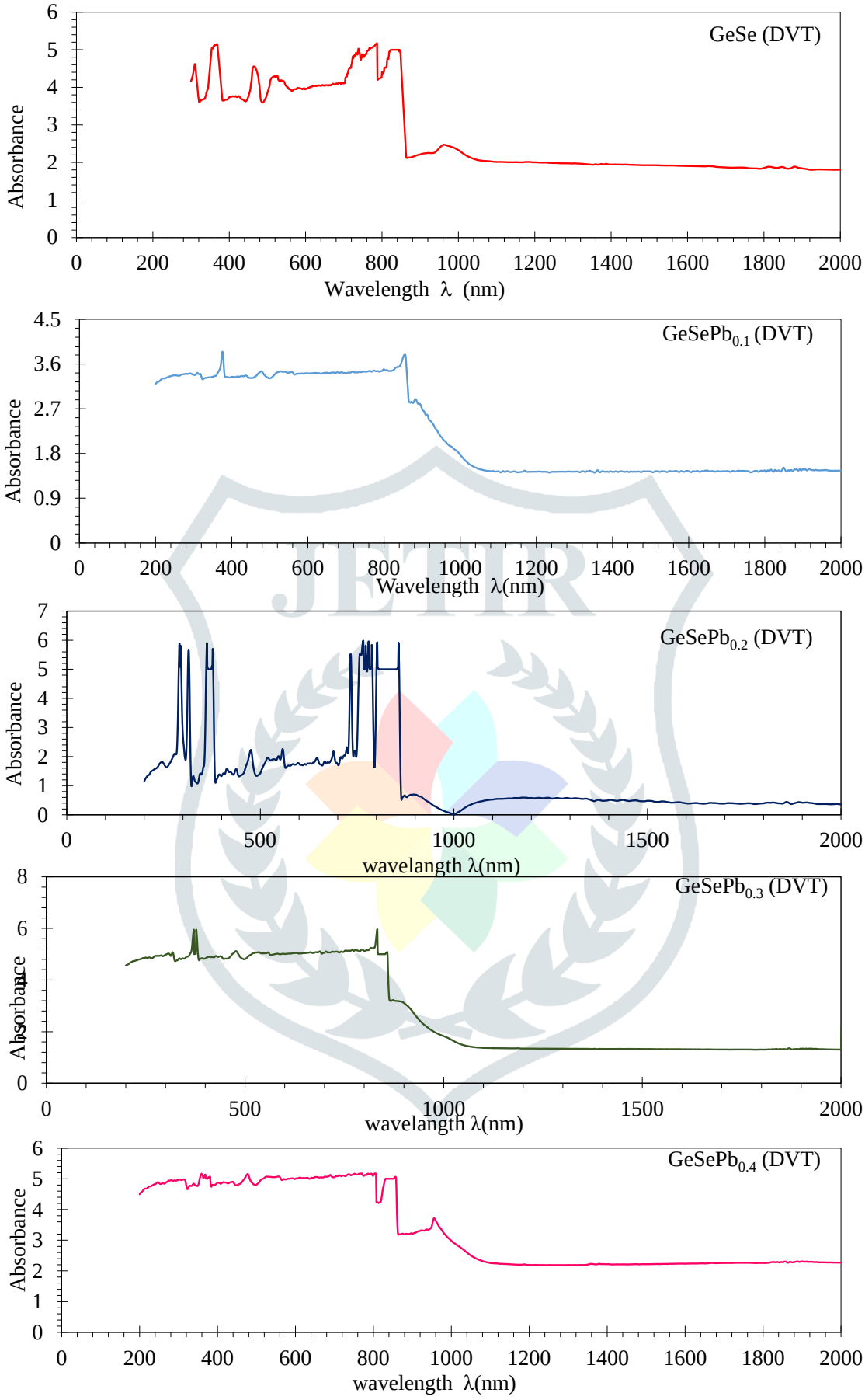

Figure 4: Absorption spectra for as grown $GeSePb_x$ (DVT) (x= 0, 0.1, 0.2, 0.3, 0.4) single crystals.

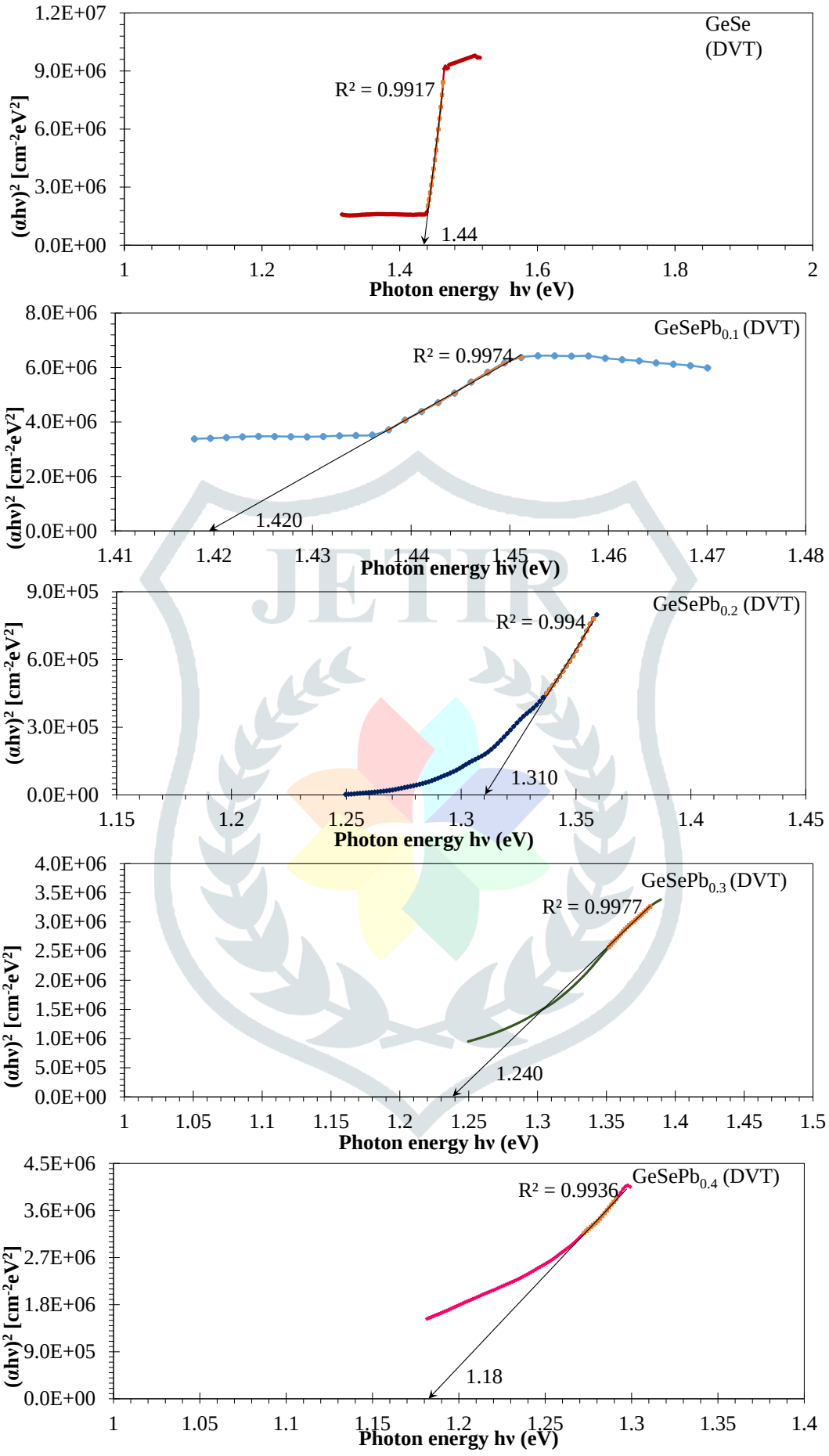

Figure 5: Spectral Variation of $(\alpha h\nu)^2$ vs. Photon Energy of $GeSePb_x$ (DVT)(x =0, 0.1, 0.2, 0.3, 0.4) single crystal.

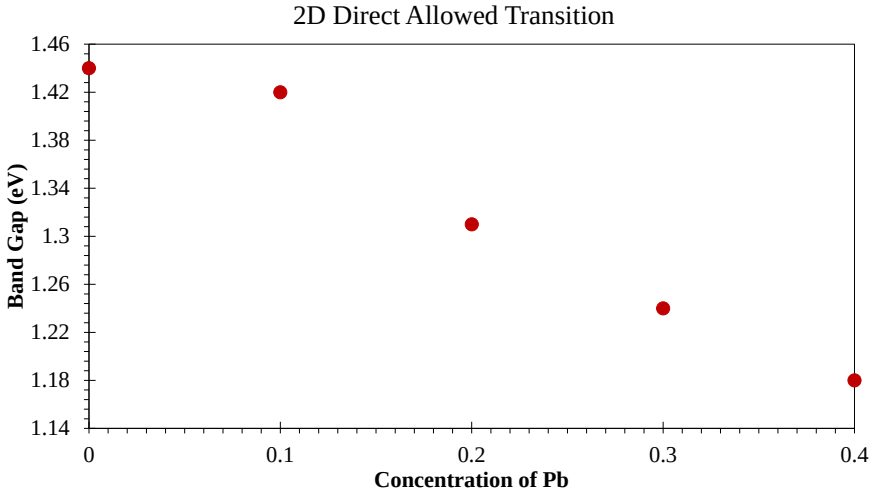

Figure 6: Variation of band gap with increasing concentration of Pb.

IV. CONCLUSION

In the present work It is concluded that it is possible to grow single crystals of $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) by direct vapour transport technique.Single crystals of $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) were found to grow in the form of thin platelets showing a mirror like metallic luster.Growth conditions and growth mechanism for the growth of large size $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4)single crystals have been determined by trial and error method. The absorption spectrum of $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) single crystal studied in the wavelength range of 200nm to 2000nm for determining the bang gap values and calculating other optical parameters. Following conclusions are drawn from the careful study of the obtained data.It has found that from an accurate analysis of the absorption spectra for $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) single crystals, both direct as well as indirect transitions are simultaneously present, what support the views expressed by *Willet et. al.* [19, 20].From the study of two dimensional has been found that in both allowed and forbidden transitions take place.Several optical parameters such as transmittance and reflectance are determined and their nature is shown for the samples of $GeSePb_x$ (DVT) (x = 0, 0.1, 0.2, 0.3, 0.4) as grown crystals are shown.

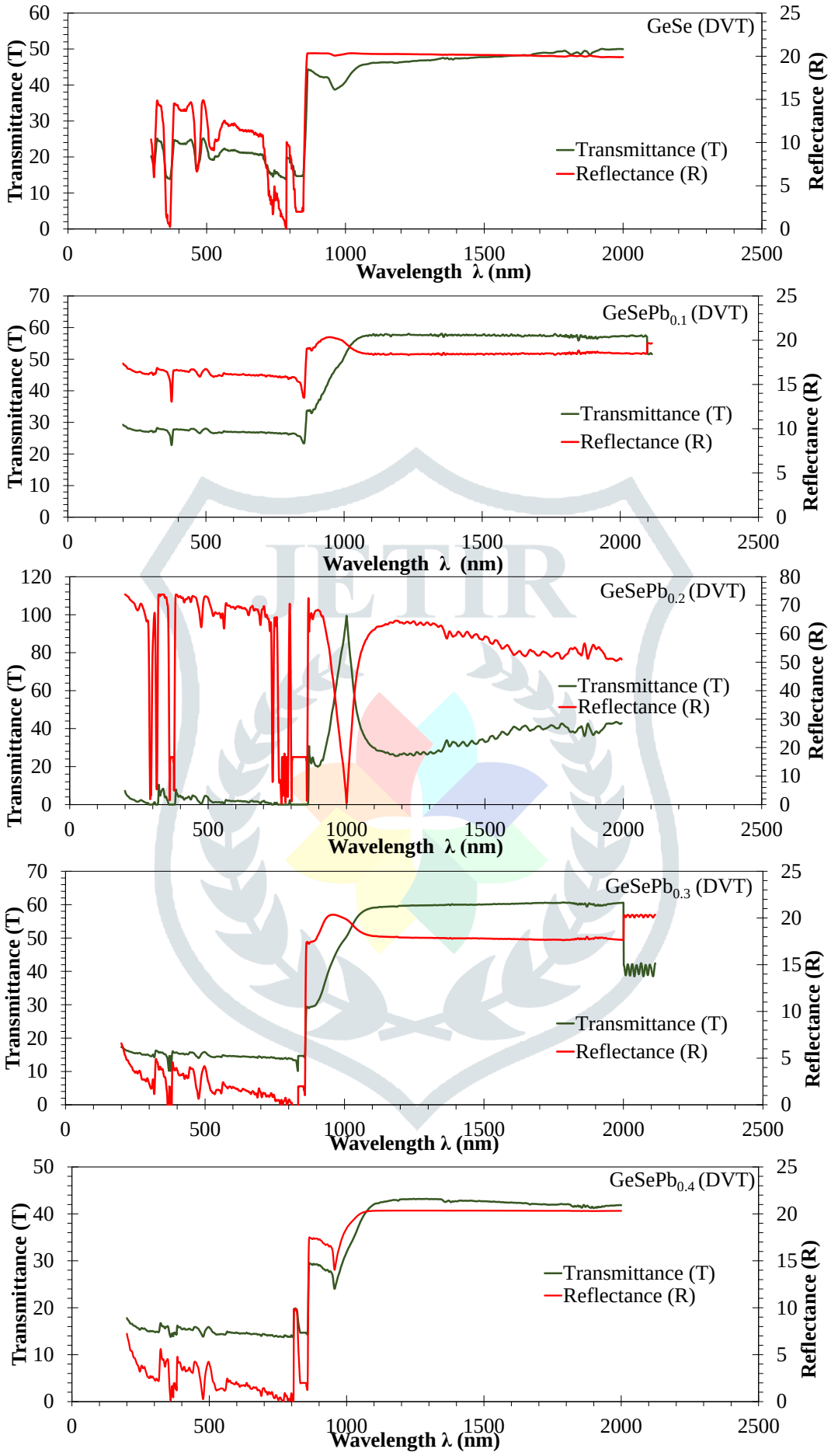

Figure 7:The Transmittance and Reflectance spectra of $GeSePb_x$ (DVT) (x=0, 0.1, 0.2, 0.3, 0.4)single crystal

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