Investigation on synthesis, growth and physical characterization of $CdGa_2Se_4$ single crystal by modified vertical Bridgman method

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$CdGa_2Se_4$polycrystalline material was synthesized by meltoscillation method. Good quality$CdGa_2Se_4$ single crystal was grown by modified vertical Bridgman method. The crystalline phase and growth orientation wereconfirmed by powder X-ray diffraction pattern and unit cell parameters were confirmed by single crystal X-ray diffraction analysis.The stoichiometric compositions of $CdGa_2Se_4$ were measured using energy dispersive spectrometry (EDS). The structural uniformity of $CdGa_2Se_4$ was studied using Raman scattering spectroscopy at room temperature. The transmission spectrum of $CdGa_2Se_4$single crystal was achieved in the near IR region andthe absorption edge of the material is near 680 nm.The calculated optical band gap is 1.8 eV. Thermal property of $CdGa_2Se_4$ has been studied using differential thermal analysis (DTA).Thermal diffusivity, specific heat capacity and thermal conductivity were measured. Electrical property was measured using Hall Effect measurement and it confirms the n-type semiconducting nature.Photoconductivity measurements with different temperatures have confirmed the positive photoconducting behavior.

Keywords: A1. Characterization,A2. Growth from melt,B1. Inorganic compounds, B2. Nonlinear optic materials, B2.Semiconducting indiumcompounds;

1. Introduction

A wide range of ternary chalcopyrite semiconducting compounds has been studied in recent decades, with emphasis on the I-III-VI_2 and II-IV-V_2 compounds which have an adamantine structure. Third family of ternary compounds which have received considerable attention are the II-III_2-VI_4 compounds, which also have an adamantine structure but are defect structures with only three of every four cation sites occupied. This family of semiconductors shows a great interest of technological applications such as possible infrared-transmitting windows materials. Cadmium digallium tetraselenide ($CdGa_2Se_4$) is one of the ternary defect chalcopyrite -type well known semiconductors[**1**]. It has a direct and wide energy gap,generally used in NLO applications which have high photosensitivity and strong luminescence in the visible range. Electro-photographic layer based on it shows good photographic contrast and high resolution [**2**]. $CdGa_2Se_4$ is actually a promising material used in various nonlinear optical devices such as gyrotropic media, narrow-band optical filter [**3**], solar cells, detectors and temperature sensors [**4**]. For these reasons, $CdGa_2Se_4$ may have interesting applications as a blue-emitting diode. A.H. Reshak et.alhad calculated the second order hyperpolarizability and microscopic first hyperpolarizability using DFT. They concluded that the $CdGa_2Se_4$ has higher nonlinear optical susceptibilities compared to $CdGa_2S_4$ [**5**]. In most of the previous studies of photoconductivity, absorption and photoluminescence, the iodine vapour transport method has been employed to prepare crystals of $CdGa_2Se_4$ [**6-7**]. Iodine vapour transport method grown single crystals are generally too thin to be used for the measurement of physical properties, and they have the possibility of contamination with iodine impurity [**8**]. The Bridgman method is appropriate to obtain large crystals of $CdGa_2Se_4$ because this compound has been reported to melt congruently at977 °C[**9**]. Feigelson and Route [**10**] succeeded in growing optical quality crystals of $CdGa_2S_4$ by the Bridgman method through the devised pre-synthesis process. H. Horinaka, et al [**11**] succeeded in growing $CdGa_2Se_4$ single crystal of dimension of 7 mm ×7 mm by Bridgman method using binary compounds. As for $CdGa_2Se_4$, efforts have been directed towardsthe growth of large crystals from the melt because of thepotential application to nonlinear optics.

In this manuscript, we report the synthesis, growth of $CdGa_2Se_4$single crystalsby the vertical Bridgman method and their characterizations such as single crystal x-ray diffraction (SXRD), powder x-ray diffraction (PXRD), thermogravimetric-differential thermal analysis (TG-DTA), specific heat capacity (Cp), thermal diffusivity, thermal conductivity, Raman spectroscopy,ultra violet- visible- near infrared (UV-vis-NIR) spectroscopy, Fourier transform infrared spectroscopy (FTIR),energy dispersive spectroscopy(EDS),Hall effect and photoconductivitymeasurements.

2. Experimental Section

2.1. Synthesis

5Npurity of Cadmium (Cd), Selenium (Se) and 6Npurity Gallium (Ga) elements were weighed in accordance with the stoichiometric composition of 1:2:4 and an excess of 2 wt% Se was taken for the compensation of the evaporation loss of Se. The synthesis process was performed in a quartz ampoule with an inside diameter 19 mm and length 240 mm. The starting material was loaded into a quartz ampouleand sealed under vacuum at 2×10^{-6} milli-bar. During synthesis, ampoule

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was rotated continuously in clockwise direction with 3 rpm speed. The temperature was raised from room temperature to 680ºC at a rate of 50ºC/hour and maintained for 12 hours. The maximum temperature of 1100ºC was reached at a rate of 12ºC/hour and maintained for 24 hour.Then temperaturewas reduced to 1000ºC at a rate of 13ºC/hour and then slowly cooled at a rate of 9ºC/hour to 680ºC, finally to room temperature at a rate of 60ºC/hour. The synthesized $CdGa_2Se_4$polycrystalline material was harvested and no reaction between polycrystalline material and quartzampoule was observed.

2.2. Crystal Growth

For the crystal growth process, the pre-synthesized $CdGa_2Se_4$ polycrystalline material was loaded into a conically tapered quartz ampoule of 2mm wall thickness and8 mm inner diameter. The ampoule was sealed at 2×10^{-6} milli-bar background pressure. $CdGa_2Se_4$ single crystal was grown by modified vertical Bridgman method in a two-zone tubular resistive heated furnace. The temperature profile of the growth furnace is shown in Fig.1 (a). The maximum temperature of the furnace was slowly raised from room temperature to 980ºC at a rate of 40ºC/h, and then maintained for complete growth run. The ampoule was rotating at a steady rate of 5 rpm and the ampoule was translated at a rate of 6mm/day. After the $CdGa_2Se_4$ melt solidified, the furnace temperature was slowly cooled at a rate of 20ºC/h to room temperature. A single crystal with 8 mm diameter and 60 mm length was grown using a quartz ampoule with spontaneous nucleation. The grown $CdGa_2Se_4$ single crystal was cut and polished with a 1 µm particle size alumina powder. Fig. 1 (b)shows the cut & polished wafers of $CdGa_2Se_4$ single crystal.

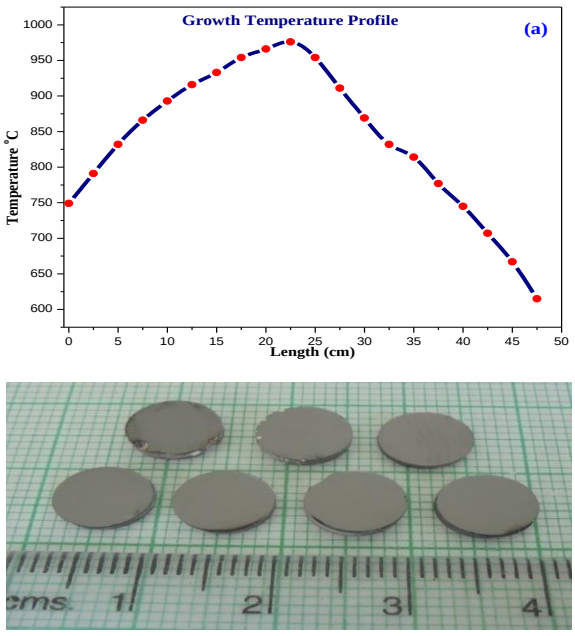


Fig. 1 (a) Temperature profile for growth furnace and (b) Cut and polished $CdGa_2Se_4$ single crystal wafers

2.3. Instrumentation for characterization

The $CdGa_2Se_4$ material phase confirmation and orientation of the grown crystal were identified by X-ray diffraction pattern using a XPERT- PRO diffractometer system. The single crystal XRD data of the grown $CdGa_2Se_4$ crystal was obtained using **SHELXTL software** by Bruker Kappa APEXII single crystal X-ray diffractometer instrument. Thermal analysis was carried out using a Perkin-Elmer Diamond TG-DTA instrument between the temperature range of 30-970ºC at a heating rate of 10ºC/min in nitrogen atmosphere. Samples were weighed in Al_2O_3 crucible. The specific heat was measured by using a differential scanning calorimetry using a NETZSCH DSC 200F3 at a heating rate of 10 °C/min. A 12.6 mg of the $CdGa_2Se_4$crystal was used as the sample and aluminum crucible was used. It was heated from RT to 300 °C at a constant rate of 10 K/min. The thermal diffusion coefficient of the $CdGa_2Se_4$ crystal was measured along the growth direction by the NETZSCH LFA 447 Nano flash apparatus. $CdGa_2Se_4$single crystal wafer of dimension $10\times10\times2$ mm^3 is prepared for thermal diffusion coefficient measurements. Prior to measurement, both the front and back faces of the specimen were coated with graphite to prevent the direct transmission of the laser beam through the translucent specimens. During this experiment, a short light pulse is used to heat the front surface of the wafer and IR detector (InSb sensor) is used to measure the temperature rise versus time on the opposite surface over the temperature range from 30 to 300 °C.The composition of $CdGa_2Se_4$ was determined using EDS analysis.The optical transmittance and absorbance studies were measured by JASCO spectrophotometer for the wavelength range 200–2500 nm with slit width 1 nm which covers near UV, visible and higher energy part of near IR region. The low energy part of near IR, mid-IR and far-IR region was covered by ALPHA-BRUKER spectrophotometer for the wavenumber range 500–5500 cm^{-1} with wavenumber accuracy of 0.01 cm^{-1}. Raman scattering experiment was performed using a Renishaw invia confocal Raman microscope, working in a backscattering configuration, equipped with high power NIR diode (λ = 785 nm, P = 300 mW) laser. The electrical properties of the $CdGa_2Se_4$ crystal were examined by ECOPIA-HMS 3000 type Hall measurement apparatus in the Van der Pauw configuration at room temperature and 1mm thick wafer was used for this measurement at room temperature.The cut and polished $CdGa_2Se_4$ was used for photoconductivity, both photo and dark current measurements. The aluminum contacts were deposited on the crystal surface by Hind high vacuum thermal evaporating system. The distance between the aluminumcontactsis about 1 mm. The Cryostat-25 instrument is coupled with Keithley Picoammeter and turbo pump. The $CdGa_2Se_4$ sample was mounted on the sample holder. The two electrical contacts were taken from the top of crystal surface.

3. Result and Discussion

3.1. Powder XRD pattern

The powder XRD pattern of the polycrystalline material is shownin Fig. 2 (a).The peak positions of PXRD pattern are in good agreement with the JCPDS file (75-1419) and it confirms the single phase of $CdGa_2Se_4$material. The single crystal ingot of $CdGa_2Se_4$ cut along the growth direction is shown in Fig. 2 (b) and it confirms the growth orientation to be <112>. The Full width at half maximum of (112) peak is about 0.138º.From the single crystal X-ray diffraction studies, it is observed that $CdGa_2Se_4$ single crystal belongs to the tetragonal crystal system.The unit cell parameters are (a = b = 5.431 (19) Å, c = 10.86 (4) Å and volume V = 320 (2) $Å^3$) in close agreement with the previously reported values [**11-12**].

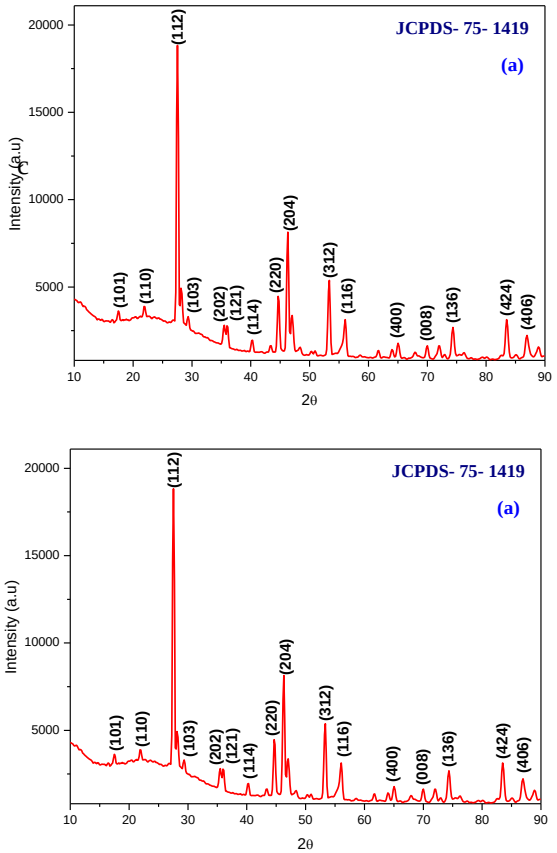


Fig. 2 (a) Powder X-ray diffraction pattern of the $CdGa_2Se_4$ polycrystalline material and (b). Powder X-ray diffraction pattern of the grown single crystal wafer cut along the growth direction

3.2. Thermal analysis

The thermal properties of a NLO material are crucial in assessing its potential in real nonlinear conversion devices pumped by high-power CW or pulsed lasers. The mid-IR chalcogenides based device performance is often limited by deleterious thermal effects. Thermal behavior of the grown $CdGa_2Se_4$ single crystal has been identified from TG-DTA analysis as shown in Fig. 3 (a) and 3 (b). In DTA, during heatingan endothermic peak at948ºC which corresponds to the melting point of $CdGa_2Se_4$ and during cooling an exothermic peak at 924ºC which corresponds to solidification of the $CdGa_2Se_4$are obtained.From the DTA analysis the enthalpy and area of the peaks for the melting and freezing respectively are calculated. The melting and solidifying peak area is 622.02and -616.239 mJ and enthalpy (ΔH) is19.28and -11.104 J/g, respectively.

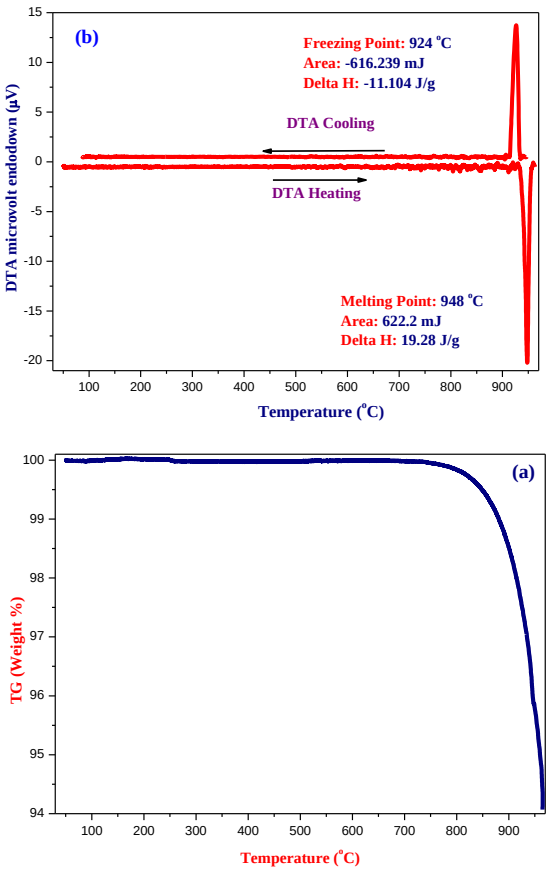


Fig.3 (a) TG and (b) DTA analysis of $CdGa_2Se_4$ single crystal

In addition to thermal stabilities, the thermal properties of solid-state materials exert important influence on their preparation and application. In laser science (high-power laser system), thermal properties of NLO crystals are basic and essential parameters. For laser crystals, the damage threshold and therefore possible laser applications can be influenced by the magnitude of the specific heat (Cp) [**13**]. Specific heat is one of the important factors that influence the crystal thermal properties. The specific heat Cp of $CdGa_2Se_4$ with temperature is shown in Fig. 3 (c). From the graph, we can see that the Cp increases almost linearly with temperature and the values

range from 0.31 to 0.58 J/g. K over the temperature range of 30-300 °C.

The thermal diffusioncoefficient of $CdGa_2Se_4$ along the growth axis in the temperature range from 30 to 300 °C was measured and the thermal conductivities were calculated.The thermal diffusion coefficient and thermal conductivitiesare shown in the Fig. 3 (d). From thermal diffusion coefficient, it can be seen that the thermal diffusion coefficients decreases with increasing temperature. The thermal diffusion coefficients along the growth axis are 1.127, 0.972, 0.842 and 0.667 mm^2/s at 30, 100, 200 and 300 °C respectively.

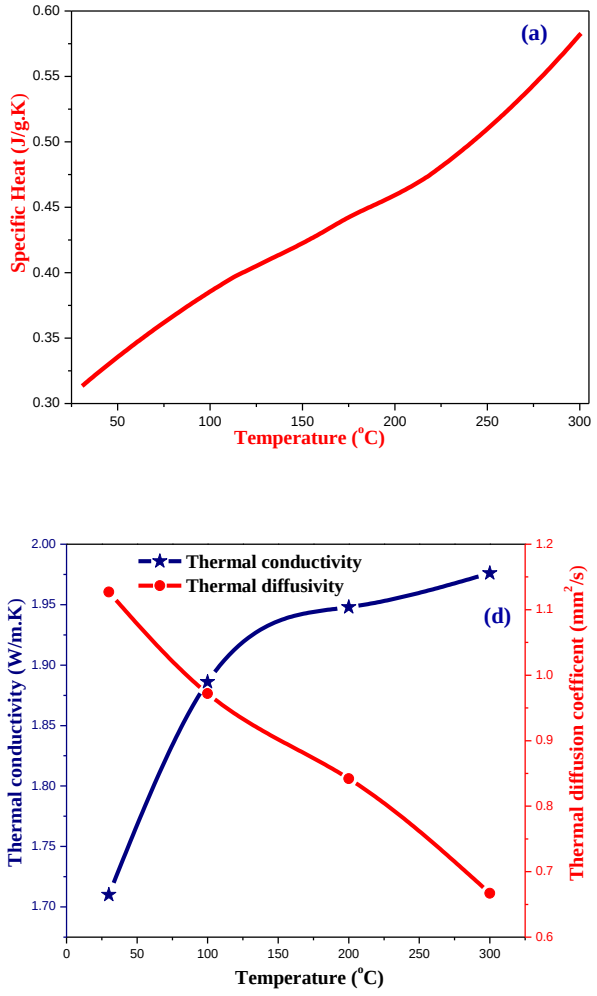


Fig. 3 (c) specific heat and (d) thermal diffusion coefficient and thermal conductivity of $CdGa_2Se_4$.

The thermal conductivity of a crystal is important from both fundamental and applied perspectives. The thermal conductivity was calculated using the equation

$$k = \lambda.\rho.Cp \quad (1)$$

where k, λ, ρ and Cp denote the principal thermal conductivity, thermal diffusion coefficient, density and specific heat of the crystal, respectively. The thermal conductivities along the growth axis (112) increase with increasing temperature and the values are 1.71, 1.886, 1.948 and 1.976 W/m.K at 30, 100, 200 and 300 °C respectively.

3.3. Raman spectroscopicanalysis

Raman spectra are used to determine the relationship between the lattice vibrational modes and the resonant patterns. The mode assignments have been performed by taking into account appropriate Raman tensors and the angular dependence of the mode intensities in (112) planes. In the Raman spectra there are 13 active modes (3A + 5B + 5E) [**14-15**]. The recorded Raman spectra are presented in Fig. 4. In the Raman spectra the peaks were observed at 65, 103, 122, 139, 152, 185, 225, 2240 and 277 $cm^{-1}$for $CdGa_2Se_4$ samples. The 139 and 185 cm^{-1} A modes of $CdGa_2Se_4$ comprise motions of only the selenium atoms. MacKinnon [**16**] points out that the 277cm^{-1} peak is due to scattering from two "breathing" phonons, since strong multiphonon effects are expected because of the large asymmetry in the Coulomb forces with respect to the breathing mode. $CdGa_2Se_4$ shows a very strong and sharp peak at 139 cm^{-1} which has been attributed to a breathing motion of A symmetry of the anions against the vacancy. $CdGa_2Se_4$ single crystal FWHM of the maximum intensity peak at bottom, middle and top portions are 8.04, 8.06 and 8.03 cm^{-1} respectively. It confirmed that with increasing the crystal length from bottom to top, the FWHM is nearly same for all the crystalline samples. This confirms that the composition is nearly same throughout the length of single crystal.G. Attoloni et al reported that the Group II (Zn, Cd) cations are less important than the Group III (Ga, In) ones as regards the high frequency part of the spectrum [**17**]. Concerning the array of ordered vacancies and its influence on the electronic and optical properties, Raman scattering providesthe interesting information that a breathing lattice mode should have a strong effect on the energies of the electrons in top valence bands.

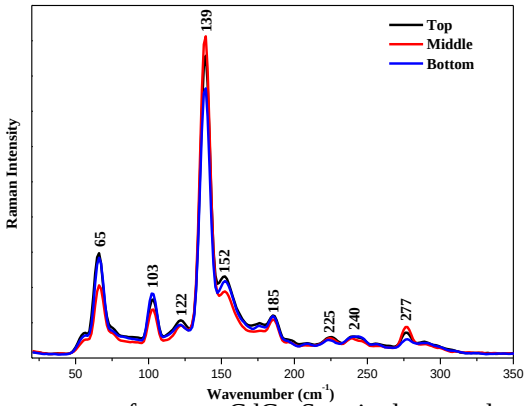


Fig. 4. Raman spectra of grown $CdGa_2Se_4$ single crystal at different parts

3.4. EDS Analysis

The EDS analyses were obtained from bottom, middle and top part of the grown $CdGa_2Se_4$single crystal.The compositional variations of $CdGa_2Se_4$ at different regions of the ingot are listed in Table 1. The average composition in atom percentage is Cd- 14.01%, Ga- 28.81% and Se- 57.23%. It is seen from EDSanalysis that the crystal is cadmium deficient, selenium and indium rich. EDS analysis gives the average composition of grown crystal as $Cd_{0.98}Ga_{2.01}Se_{4.01}$.Cadmiumatthe top portion indicates anexcessof ~2.71 at%, whereas bottom portion indicatesdeficiency of ~1.96at%.At the top and bottom portions indicating an excess of gallium~0.32 at% and ~0.42 at% respectively, whereas in the middle portion deficiencyis ~0.25 at%. Selenium at the middle and bottom portions indicate an excess of ~0.3 at% and ~2.24 at% respectively, whereas top portion Ga deficiency is ~2.33 at%.The size of the divalent cation is cadmium (0.78Å), trivalent cation is gallium (0.47Å), and divalent anion is selenium (1.98Å) ions respectively. In bottom portion, Gallium atoms may occupy in cadmium sites, it forms antisite (Ga_{Cd})defects and excess cadmium leads to vacancy defect. The excess of selenium leads to interstitial defects (Se_i).The elemental analysis of the middle part of $CdGa_2Se_4$ crystal leads to the chemical formula $Cd_{0.99}Ga_{1.98}Se_{4.03}$ revealing a nearly stoichiometric composition compared to bottom and middle part of the grown crystal.In top portion, cadmium and gallium atoms are present in excess amount. The excess of cadmium and gallium atoms produce an interstitial type of defects (Se_i). The average composition of the crystal has nearly stoichiometric composition of cadmium, indium and selenium ($Cd_{0.98}Ga_{2.01}Se_{4.01}$). In the grown crystal, cadmium has segregated at the top portion of the grown crystal and gallium is nearly uniform throughout the length of the crystal. The deficiency of selenium has increased as its crystal length increases.

3.5. UV-Vis-NIR and FTIR spectroscopy

The transmission spectrum plays acrucial role in identifying the potential of nonlinear optical (NLO) materials, because a specific nonlinear optical material can be of utility only if it has a wide transparency window with no absorption at the fundamental and the second harmonic wavelengths. The 1.8 mm thick cut and polished $CdGa_2Se_4$ single crystal wafers were used for UV-Vis-NIR and FTIR transmission and absorption studies.The $CdGa_2Se_4$ single crystal has 18% transparency in NIR region andthe cut off wavelength is about 680nm. Fig. 5 (a) shows the UV-Vis-NIR transmission and (inset) absorption spectra of $CdGa_2Se_4$ single crystal. The optical band gap of 1.8 eV is determined by applying the Tauc model. The optical band gap energy of $CdGa_2Se_4$ depends on the composition of the cation and anionpresent in the crystals. The obtained optical band gap is in good agreement with the previous report [**5**].

Thetransparency limit in the mid-IR to far-IR wavelength range of a crystal is defined by lattice absorption. It is caused by the interactive coupling between the incident radiation and the motions of thermally induced atomic vibrations. Fig. 5 (b) shows the FTIR transmission spectra of $CdGa_2Se_4$ single crystal. The FTIR spectrum shows that the grown $CdGa_2Se_4$ single crystal has IR transmission of ~40% in themid IR region. These spectra show that the crystal transmission is from 0.68 µm to19 µm. The slight increase of transparency with wavelength from visible to IR region may be due to the crystal surface defects, scratches on the surface and scattering centers present in the grown crystal.

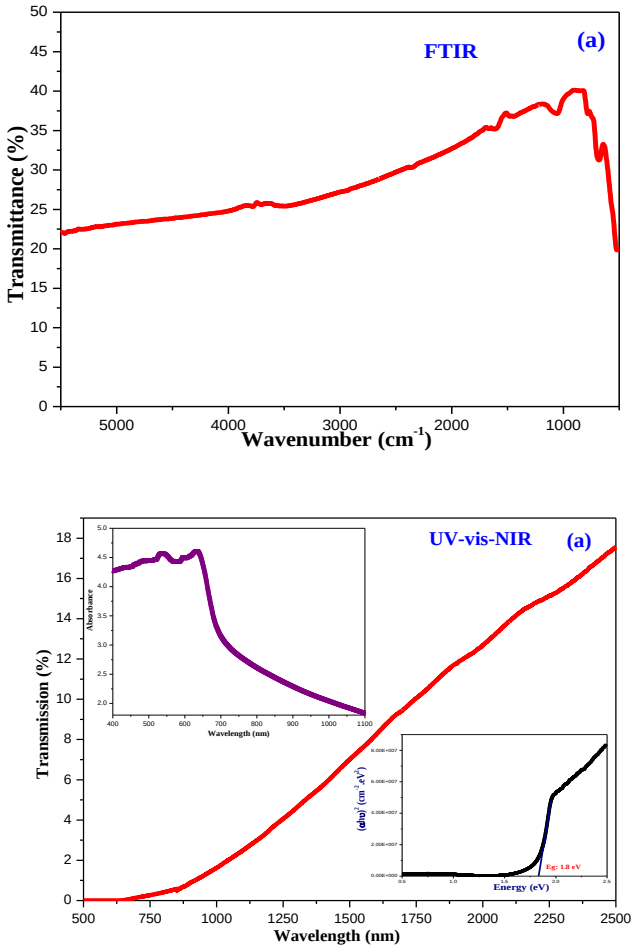


Fig. 5 (a). UV-vis-NIR transmittance, upper inset absorption spectra and bottom inset Tauc plot and (b) FTIR transmittance spectra of $CdGa_2Se_4$ crystal.

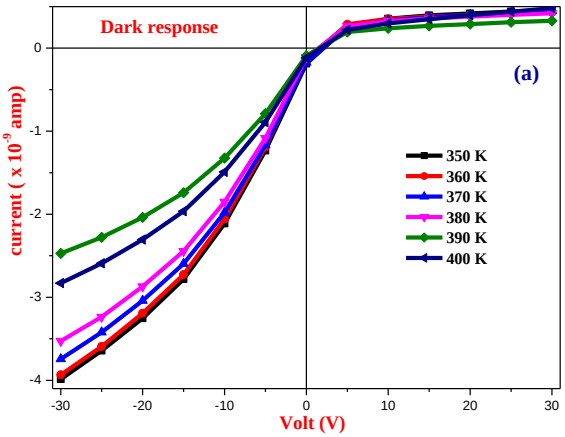
3.6. Electrical Measurements

The electrical properties of the as-grown $CdGa_2Se_4$ single crystal were examined by Hall Effect measurements. The negative sign of the Hall coefficient confirmed $CdGa_2Se_4$ crystal to be n-type semiconductor. The n-type semiconducting nature of$CdGa_2Se_4$ crystal was confirmed

from photoconduction measurements [**18**]. The measured electrical properties of the grown single crystalline wafers are Hall coefficient (-5.31×10^{10} cm^3/C), resistivity ($1.289\times10^8\Omega.cm$), mobility (4.87×10^2 $cm^2/V.s$), magneto resistance (3.37×10^9 Ω), bulk concentration (-5.23×10^8 $/cm^3$), sheet concentration (-6.59×10^7 $/cm^2$) and conductivity (1.27×10^{-8} /Ω. cm) respectively.

3.7. Photoconductivity Measurements

Photoconductivity is determinedfrom the photogenerated free charge carriers that are created by the interaction of photons with solids and annihilated through recombination process. Photoconductivity is the process by which the electrical conductivity of a solid material is changed by incident electromagnetic radiation. Absorption of some of the incident energy causes generation of the charge carriers, over and above the thermal equilibrium level. Due to these generated carriers, the phenomenon of photoconductivity occurs. Dark conductivity was the direct current conductivity (I_d) on $CdGa_2Se_4$single crystal without illumination. Photoconductivity (I_{Ph}) was the additional photoconductivity of an excess number of photogenerated chargecarriers under the illumination, which was gained by subtracting dark conductivity from the conductivity of the illumination (I_P), that's $I_{Ph} = I_P - I_d$. The dark conductivity and photoconductivity of as grown $CdGa_2Se_4$single crystal was measured as a function of temperature and voltage. The sample was illuminated by 12 Volt and 50 watts halogen lamp. The field dependent photoconductivity of the crystal is shown in Fig.6 (a) and Fig.6 (b). It is observed that the dark current (I_d) and the photocurrent (I_P) for all ranges of applied field shows linear response with respect to the voltage and at any instant, the photoconductivity is found to be greater than the dark conductivity. Hence, the $CdGa_2Se_4$ singlecrystal exhibits positive photoconductivity. The positive photoconductivity in this case may be due to the enhancement in the number of charge carriers or their lifetime in the presence of radiation or the temperature dependence of mobility of charge carriers. Fig.6(b) shows that the photocurrent increased with increasing temperature at particular applied voltage. This may be due to the temperature dependence of the mobility of the charge carriers.



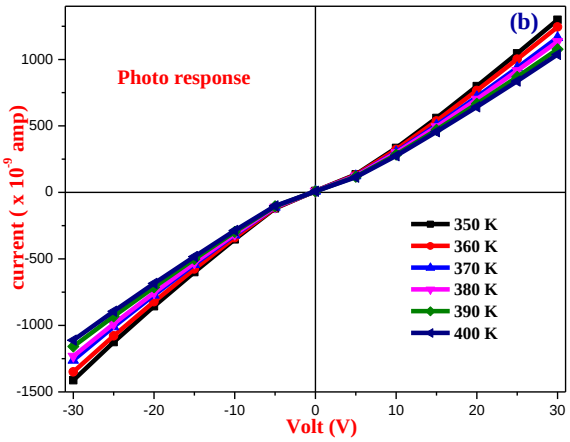


Fig. 6 (a) Variation of dark current versus applied voltage with temperature and 6(b) Variation of photocurrent versus applied voltage with temperature under illumination.

4. Conclusion

Melt oscillation method was used to synthesize$CdGa_2Se_4$ polycrystalline material. Crack free $CdGa_2Se_4$ single crystal with dimension of 8 mm diameter and 60 mm length has been grown using a steady ampoule rotation by modified vertical Bridgman method. The $CdGa_2Se_4$ crystal is grown along the <112> direction. From SXRD measurements the tetragonal crystal system with a = b = 5.431 (19) Å, c = 10.86 (4) Å and volume V = 320 (2) $Å^3$ was confirmed. TG-DTA analysis confirms that the melting point of the grown crystal is 948ºC. EDS analysis confirms the grown crystal'saverage composition as $Cd_{0.98}Ga_{2.01}Se_{4.01}$. Optical studies confirm that the transmission is from 0.68 µm to 19 µm. The Raman peak positions are same at different parts of the grown crystal and there is no remarkable change in three parts of growncrystal. The grown crystal's Raman intensity at 138 cm^{-1} peak confirms the structural uniformity of the grown crystal along the length of the crystal. The measured electrical properties at room temperature are Hall coefficient (-5.31×10^{10} cm^3/C), resistivity (1.289×10^8 Ω.cm) and conductivity (1.27×10^{-8} /Ω. cm) respectively.The average dark and photo resistivity value at different regions are measured using photoconductivity measurement.

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