
First Investigation of Optical Properties and Local Structure of Gd³⁺ Doped Nano-Crystalline GeSe₂

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Abstract: Pure and Gd-doped nano-crystalline GeSe₂ were prepared by the melt-quenching technique. The crystal structure, local structure and emission properties are investigated. Structure analysis using Rietveld program suggests monoclinic structure for both virgin and doped samples with nano-particle size 41nm for GeSe₂ and 48nm for Gd-doped sample. A wide optical band gap as estimated from absorbance measurements is 4.1eV and 4.8eV for pure and doped samples in accordance with the confinement effects. Raman spectra show two unresolved components at ~ 202 cm⁻¹ with broad line width. Also, well identified low intensity ($\nu < 145$ cm⁻¹) and high intensity ($\nu > 250$ cm⁻¹) bands are detected. For Gd-doped sample, the main band is shifted to lower energies and its FWHM is reduced by ~ 50% accompanied by an intensity increase of about ~ 17 fold times. The photoluminescence analysis of the pure sample shows a main emission band at ~ 604 nm. This band is splitted into two separated bands with higher intensity. The detected emission bands at wavelength > 650 nm are assigned to transition from ⁶G_J to the different ⁶P_J terms.

Keywords: Nano-Crystalline GeSe₂ Doped with Gd³⁺, Microstructure, Optical, Raman and Photoluminescence Characteristics

1. Introduction

Chalcogenides based Ge-Selenides have significant infrared (IR) transparency in the wavelength region between ~1 and 12 μ m which makes them suitable for passive IR optics, for example as optical fibers, wave guides, sensors, nano-lens and photo-resist materials for the micro and nano fabrication [1-6]. Various works have been reported on the Ge-Se system chemically modified by addition of I-VII group elements of the periodic table [7-9].

Rare-earth doped chalcogenides have been studied in recent years for active applications in the near- and mid- IR [10, 11]. The primary advantage for choosing a chalcogenide host is the smaller phonon energy (~ 350 cm⁻¹ for selenides) as compared to fluoride (~ 550 cm⁻¹) and silicate (~ 1100 cm⁻¹) hosts. This smaller phonon energy results in a smaller multiphonon transition probability thereby allowing mid-IR transitions normally quenched in the larger phonon energy hosts to become active [12, 13].

Raman spectroscopy has been an important tool for investigating the properties of chalcogenide materials. A

large number of strong, narrow Raman lines are observed in the crystal and the glass [14-16]. Raman-scattering spectra of amorphous and single-crystal germanium di-chalcogenides at high pressures have been reported [17, 18]. K. Murase et al. [17] found that there is no change in the frequencies of the A₁ and A_{1c} modes in a-GeSe₂ up to 2GPa. In the case of GeSe₂ single crystal, as the pressure increases to 5GPa, a splitting appears of the highest intensity mode at 211cm⁻¹.

Chalcogenide semiconductors usually show photoluminescence (PL) spectra with large Stokes shift. In the case of a typical chalcogenide semiconductor GeSe₂ the excitation by near or above band gap light (~ 2eV) causes a Gaussian shaped photoluminescence spectrum with ~ 0.3eV full width at half maximum (FWHM) amplitude at around 1eV for both crystalline and glassy forms [19-21].

It is very important for luminescence research to find systems in which the emitted light lies in the visible region. The emitted luminescence spectra favor some rare earth compounds to be used as laser materials, lamp phosphors or

as x-ray phosphors [22-24]. In particular Gd³⁺ compounds are interesting from a fundamental and a practical point of view [25]. Gd³⁺ activated phosphors have attracted much attention for their well defined emission in the ultraviolet region [14, 26, 27].

Recently, Pr³⁺- or Dy³⁺- doped selenide glasses with much lower phonon energy have also been investigated and favorable 1.3 μ m emissions have been observed [28]. Yet now, all Raman and PL investigations have been performed for Ge-Se system in the glassy and crystalline states. No previous research were applied to Ge-Se in the nano-crystal scale which due to confinement affects open the door to more available and interesting characteristics. Moreover, doping with rare earth elements has been rarely studied. In this work we present new diagnostic Raman and PL data on nano-crystalline GeSe₂ and GeSe₂:Gd. From absorbance measurements a wide optical band gap of 4.8 for the doped sample is reported. New Raman activities and PL emission bands were recorded for virgin and Gd-doped samples over the visible range. The main objective for the present work is the development of visible source based on the radiative transition of Gd³⁺ in nano-crystalline GeSe₂.

2. Experimental Work

GeSe₂ and Ge_{0.7}Se₂Gd_{0.3} were prepared by direct fusion of highly pure elements: Geshot (99.999%), Se shot (99.999%), and Gdpowder (99.999%) produced by Aldrich Chem. Co. Inc. The necessary quantities of the elements required for the preparation of an ingot of 7 gm were weighed according to their atomic weights using an electrical sensitive microbalance of accuracy 10⁻⁴ gm. The weighed elements were transferred to pre-cleaned quartz tubes (diameter = 2 cm and length= 20 cm). The tubes were then sealed under vacuum of 10⁻⁴Torr. Heating up to 1000°C was carried out. The furnace temperature was maintained at 1000°C for 72 h. During the synthesis process, the molten tubes were occasionally shaken to ensure homogeneous mixing of the constituents. The molten tubes were allowed to cool inside the oven down to room temperature. X-ray diffraction using Philips diffractometer (X'pert MPD) goniometer type PW3050/10 with Cu-K α radiation was elaborated. The crystal structure (lattice parameters, atomic coordinates, occupancy factors, displacement factors) and microstructure (crystallite sizes (D_F)) and r.m.microstrain(e_g) were refined applying Rietveld profile method using MAUD and WinFit programs[29]. Absorbance measurement was carried out by using Perkin-Elmer Spectrophotometer, model lambda 35 in the UV/Visible spectral range. Raman spectrometer (Bruker) was used for Raman investigation. Calibration is done automatically by the instrument with Neon lamp. This instrument is characterized by the removal of fluorescence background and high wave number accuracy. The laser wavelength 532-785nm, laser characteristics (lasing medium) AlGaAs (laser type) semiconductor and the spot size of laser is 20xobjective 4x10⁻¹²(4 μ m²). All spectra were recorded at room temperature under similar spectral parameters. The

Perkin Elmer Ls55 fluorescence spectrometer used to measure Photoluminescence intensity of the samples has holographic gratings to reduce stray light, as well as automated polarizers. Ls55 uses a high energy pulsed Xenon source for excitation and has a wide wavelength rang 200-900nm. The advantages of this source are the minimal photo bleaching of samples and the improved low light detection capability relative to other light sources.

3. Results and Discussion

3.1. Structure and Microstructure

The X-ray diffraction patterns of GeSe₂ and Ge_{0.7}Se₂Gd_{0.3} are shown in Fig. 1. The search-match program showed no diffraction lines related to the elements or their oxides; only one phase of GeSe₂ was present according to the ICDD card number (71-0117)with the monoclinic space group P2₁/c. During Rietveld analysis, a preferred orientation along the [0 0 ℓ] direction was detected. The latter could not be avoided during measurements in spite of back-loading and fine grinding of samples. This preferred orientation is mainly due to the presence of the stacking layers aligned on the top of each other along the [0 0 ℓ] direction [30]. Fig. 2(a, b) shows the profile fitting resulting from the structure refinement of the two compounds under study. The structural parameters obtained from Rietveld refinement are shown in Table 1.

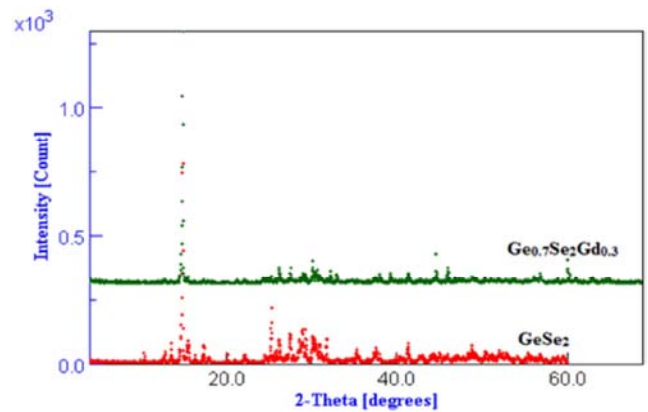
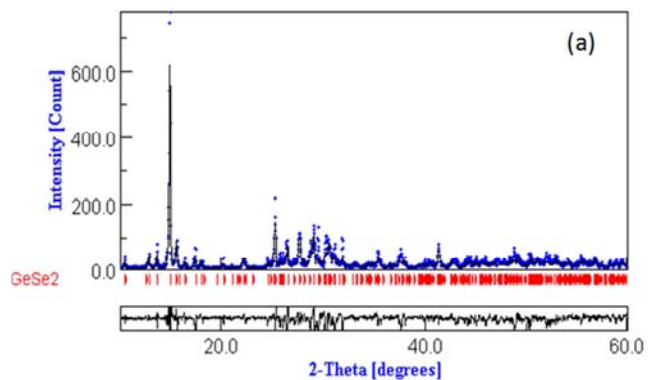


Fig. 1. X-ray diffraction patterns of GeSe₂ and Ge_{0.7}Se₂Gd_{0.3}.



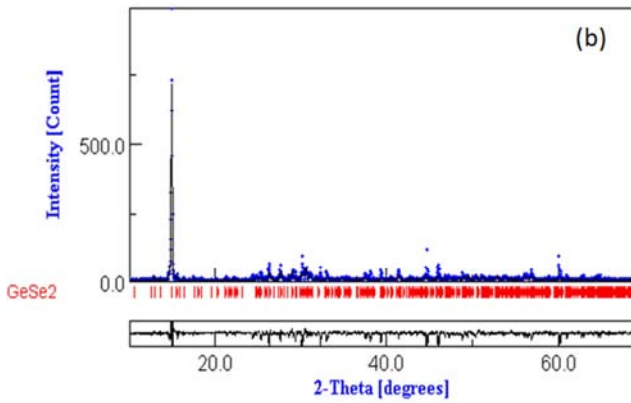


Fig. 2. The profile fitting of (a) GeSe_2 and (b) $\text{Ge}_{0.7}\text{Se}_2\text{Gd}_{0.3}$.

The results of WinFit Single Line Analysis (S.L.A) and Multiple Line Analysis (M.L.A) of the prepared compounds are given table 1. The prepared samples exhibit monoclinic nano-crystalline structure. Doping with Gd causes an increase of crystallite size (D_F) by 16.5% with respect to GeSe_2 due to the big atomic radius of Gd. It is to be noted also that the value of $\langle e_g \rangle$ is approximately doubled.

Table 1. The structural parameters of the systems.

| parameter | GeSe_2 | $\text{Ge}_{0.7}\text{Se}_2\text{Gd}_{0.3}$ |
|------------------------------------|-----------------|---|
| a ($^\circ$) | 7.0809 | 7.0736 |
| b ($^\circ$) | 16.8458 | 16.7568 |
| c ($^\circ$) | 11.8494 | 11.8806 |
| R_w (%) | 11.2 | 10.8 |
| R_p (%) | 10.7 | 9.3 |
| (S.L.A) D_β (nm) | 40.7 | 43.3 |
| D_F (nm) | 44.9 | 46.5 |
| (M.L.A) D_β (nm) | 40.2 | 46.7 |
| D_F (nm) | 41.1 | 47.9 |
| $\langle e_g \rangle$ of 00 ℓ | 0.019% | 0.0415% |

3.2. Absorbance Measurements

To investigate the optical properties of nano-crystalline $\text{GeSe}_2:\text{Gd}$, the UV-Vis. absorption spectra were followed for the samples in the form of grinded powder dispersed in distilled water. The obtained data of GeSe_2 and $\text{Ge}_{0.7}\text{Se}_2\text{Gd}_{0.3}$ are given in Fig. 3. The optical absorption edge was determined by drawing straight line through the sharp edge. The intersection with the abscissas taken as the value of the optical gap (E_g), so E_g could be estimated to be about 4.1eV for GeSe_2 and 4.8eV for $\text{Ge}_{0.7}\text{Se}_2\text{Gd}_{0.3}$. These large values of E_g with respect to bulk amorphous GeSe_2 (2.14eV) [31] are due to the quantum confinement effect because of the nano-nature of the crystallite size. It is evident that doping with Gd increases the width of the forbidden band gap. This is probably due to the strong cohesive energy of Ge-Gd and Se-Gd bonds with respect to Ge-Se bond.

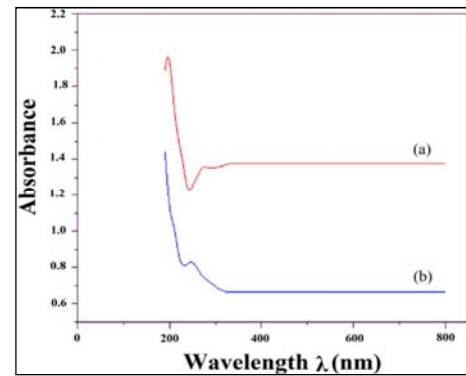


Fig. 3. Wavelength versus absorbance for (a) GeSe_2 and (b) $\text{Ge}_{0.7}\text{Se}_2\text{Gd}_{0.3}$.

3.3. Raman Investigation

Fig. 4(a,b) shows the Raman spectra for the virgin and Gd-doped nano-crystalline samples. We have performed curve fitting procedure on the experimental high resolution Raman spectra using independent Gaussian function. The deconvoluted spectra are also illustrated. The Raman activities, peak position, full width at half maximum (FWHM) and their relative intensities are listed in table 2. As clearly seen, for nano crystalline GeSe_2 , the main vibrational mode is centered at 202.08cm^{-1} (Peak 5) in addition to four lower intensity bands at the left and the right sides of the main band.

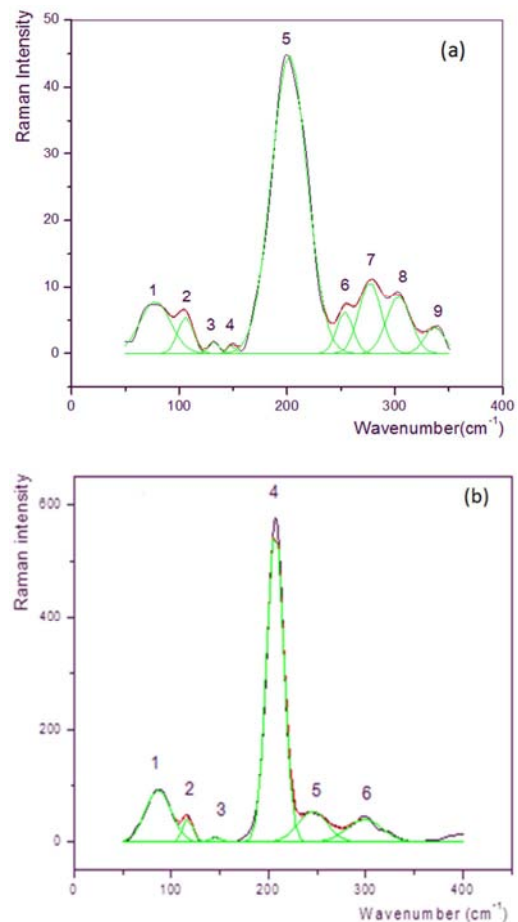


Fig. 4. Raman spectra of (a) GeSe_2 and (b) $\text{Ge}_{0.7}\text{Se}_2\text{Gd}_{0.3}$.

Table 2. The Raman activities, peak position, FWHM and relative intensities for GeSe₂ and Ge_{0.7}Se₂Gd_{0.3}.

| Peak | GeSe ₂ | | | Ge _{0.7} Se ₂ Gd _{0.3} | | |
|------|-------------------|--------|-----------|---|--------|-----------|
| | Position | FWHM | Intensity | Position | FWHM | Intensity |
| 1 | 77.774 | 28.531 | 7.7083 | 86.599 | 26.176 | 93.490 |
| 2 | 105.87 | 14.238 | 5.4150 | 116.93 | 10.232 | 43.541 |
| 3 | 132.19 | 8.5222 | 1.8569 | 145.65 | 11.453 | 8.5930 |
| 4 | 148.51 | 6.0726 | 1.3667 | 206.87 | 17.216 | 566.25 |
| 5 | 202.08 | 32.874 | 44.810 | 245.27 | 30.454 | 54.497 |
| 6 | 253.67 | 14.971 | 6.2837 | 298.7 | 36.195 | 40.405 |
| 7 | 277.01 | 20.195 | 10.739 | - | - | - |
| 8 | 303.64 | 22.069 | 8.6006 | - | - | - |
| 9 | 336.91 | 18.181 | 3.9459 | - | - | - |

Earlier reports for crystalline GeSe₂ shows two strong Raman bands at $\nu_1=210.3\text{cm}^{-1}$ with $\text{FWHM} = 3.0\pm 0.2\text{cm}^{-1}$ and at $\nu_2=215.4\pm 0.5\text{cm}^{-1}$ with $\text{FWHM} = 3.2\pm 0.4\text{cm}^{-1}$ [32]. The authors reported that these FWHM are considerably narrower than the corresponding Raman bands of the glassy format $\nu_1=198\text{cm}^{-1}$ and $\nu_2=212\text{cm}^{-1}$ [33]. Similar bands in crystalline GeSe₂ at 210.4cm^{-1} and 216cm^{-1} were also reported by T. Nakaoka et al. [34]. In our case, the Raman analysis of the nano-crystalline GeSe₂ shows only one strong mode at 202.08cm^{-1} . The splitting of the A₁ (symmetric tetrahedral breathing) Raman mode reported for both crystalline and glassy GeSe₂ is completely absent as shown in Fig. 4. The absence of the splitting of the main mode in the present study could be a result of a superposition of the A₁ vibration of corner sharing GeSe₄ tetrahedra and the A_{1C} vibration of edge sharing GeSe₄ tetrahedra that appear at very close frequency and has intensity lower than the first one.

The result of curve fitting of Raman spectra at 202cm^{-1} of Ge-Se cluster model of R. Holomb et al. [35] indicates that, the peak located at $\sim 204.1\text{cm}^{-1}$ is in very good accordance with the Raman mode at $204/205\text{cm}^{-1}$ calculated for six-membered rings and larger ring like Ge_nSe_m cluster topologically similar with the high temperature (HT) GeSe₂.

An anomalous feature characterizes the nano-crystalline GeSe₂ under study with respect to glassy GeSe₂ is the existence of well identified low intensity Raman modes at low frequencies $\nu < 145\text{cm}^{-1}$. The spectral ranges from $30\text{-}150\text{cm}^{-1}$ are attributed to the bond-bending vibrations in layered structure materials [18]. On the other hand the clearly observable four high frequency modes shown in Fig. 4(a) at $\nu > 250\text{cm}^{-1}$ were also reported by Z. V. Popovic et al. [36], while studying the Raman scattering spectra of the β -modification of GeSe₂ under hydrostatic pressure. The authors observed that as the pressure increases, the high temperature (HT) layered structure of GeSe₂ undergoes a transformation to low temperature (LT) modification with preserving the modes at 275cm^{-1} and 304cm^{-1} .

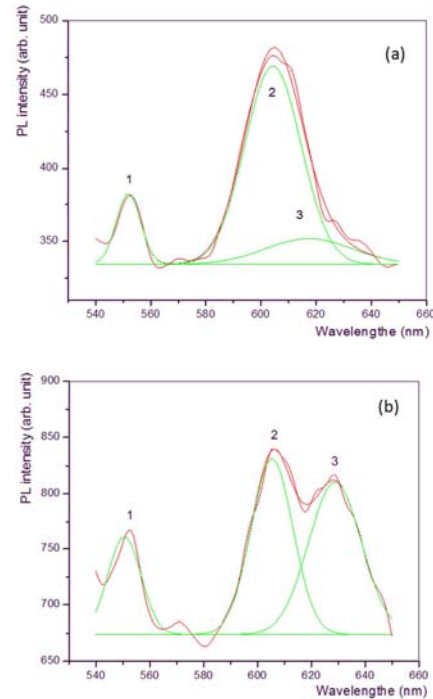
In Fig. 4(a), the existence of the modes at 277.01cm^{-1} and 303.64cm^{-1} gives evidence that, the nano-crystalline GeSe₂ under study exhibits the LT structure in which the GeSe₄ tetrahedra are connected via common corners.

Raman spectra are also manipulated to determine the local

environment of Gd³⁺ in the GeSe₂ host lattice. As given in Fig. 4(b) and table 2, doping the nano-crystalline GeSe₂ with Gd, considerably affect the Raman vibration spectrum of the virgin sample and hence the local environment of the existing atoms as the nine lines recorded for GeSe₂ (table 2) are reduced to six lines only. The principle band at 202.08cm^{-1} is shifted to higher energies (206.87cm^{-1}), its FWHM is decreased by $\sim 50\%$ and its intensity increased by ~ 17.2 fold times with respect to that of the pure sample. The stronger band near 206cm^{-1} in nano-crystalline Ge_{0.7}Gd_{0.3}Se₂ can be attributed to the overlap of ν_1 (A₁) symmetric stretching modes of corner-sharing GeSe₄ and GdSe₄ tetrahedral, the increased intensity detected for Gd-doped sample can be assigned to more formation of such structure building unit. Further theoretical calculations are needed for the assignment of Raman modes of this nano-chalcogenide material to determine the local environment of Gd³⁺ in the GeSe₂ host lattice.

3.4. Photoluminescence (PL) Investigation

The observed PL spectra for nano-crystalline GeSe₂ and Ge_{0.7}Se₂Gd_{0.3} are shown in Fig. 5 (a,b). These spectra were obtained using excitation energy of 2.69eV . Curvefitting procedure was applied to the experimental spectra using independent Gaussian function. The recorded emission bands are given in table 3. As shown, over the visible region, the major emission is located at 604.33nm (2.05eV) accompanied by a shoulder at 617.37nm (2.01eV) in addition to less intensity line at 551.9nm (2.25eV).

**Fig. 5.** PL spectra for nano-crystalline (a) GeSe₂ and (b) Ge_{0.7}Se₂Gd_{0.3}.**Table 3.** The recorded emission bands for nano-crystalline GeSe₂ and Ge_{0.7}Se₂Gd_{0.3}.

| Peak | GeSe ₂ | | | Ge _{0.7} Se ₂ Gd _{0.3} | | |
|------|-------------------|--------|-----------|---|--------|-----------|
| | Position | FWHM | Intensity | Position | FWHM | Intensity |
| 1 | 551.90 | 8.7547 | 48.567 | 550.63 | 12.248 | 87.101 |
| 2 | 604.33 | 20.402 | 135.26 | 605.44 | 15.504 | 157.68 |
| 3 | 617.37 | 31.504 | 17.493 | 628.83 | 19.500 | 136.56 |

Photoluminescence studies on melt-quenched $\text{Ge}_x\text{Se}_{1-x}$ ($0.2 < x < 4.3$) glasses revealed the presences of a broad peak with a maximum located at about half the band-gap energy ($\sim 1.1\text{eV}$) for GeSe_2 when the excitation is 2.335eV [37]. Also, M. Koos et al. [38] predicted a peak at 1.17eV for glassy GeSe_2 . Annealing at 573°K shifts the peak towards higher energies by about 0.1eV thus corresponds roughly to the value recorded for crystalline GeSe_2 .

In our case for nano-crystalline GeSe_2 , the measured optical band gap (Fig. 3) is $\sim 4.1\text{eV}$, so the PL emission band recorded at $\sim 2.05\text{eV}$ (604.33nm) can be attributed to band-band transition. The other higher energy (2.25eV) emission is probably created through transition between valance-band states up to states into the conduction-band caused by free electrons.

Fig. 5(b) gives the emission spectrum for nano-crystalline $\text{Ge}_{0.7}\text{Se}_2\text{Gd}_{0.3}$ sample. As shown in the figure, the major band with its shoulder detected for virgin sample is splitted into two intense bands by introducing Gd as a rare earth atom. The position, the intensity and FWHM of the emission bands are given in table 3. It is to be noted that, the intensities of all emission bands are nearly doubled by Gd incorporation.

The results reported by Kastner and Hudgens [39] have been interpreted as showing that the radiative centers in chalcogenides are neutral dipole centers (i.e. closely situated charge pairs) rather than randomly distributed charge ones. According to Kastner and Fritzsche [40], the density of intimate pairs is independent of doping up to concentrations characteristic of alloying i.e. PL would be insensitive to doping. If doping were to substantially alter the concentration of singly coordinated centers (D^-) or three-fold coordinated (D^+) centers (the famous defects in disordered chalcogenide semiconductors) or their relative density then a change in PL bands could be expected, provided that one or both these defects acted as radiative centers [38].

According to the emission spectra of Gd^{3+} (Fig.6), one can assign the bands at wave number $> 550\text{ cm}^{-1}$ to transitions from ${}^6\text{G}_J$ to the different ${}^6\text{P}_J$ terms.

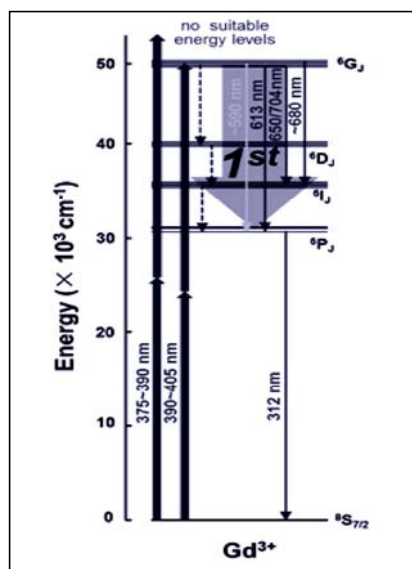


Fig. 6. Energy spectra of Gd^{3+} .

No previous investigation using PL have been carried out in Gd doped GeSe_2 so it was difficult to compare the recorded emission bands with other works to determine precisely the corresponding energy levels of Gd. R. T. Wegh et al. [41] reported first results on Gd^{3+} to study the luminescence of rare earth ions under vacuum ultraviolet (UVU) excitation. The author reported that the detected emissions at 577.6 nm , 606.7 nm and 631.2 nm are assigned to ${}^6\text{G}_J \rightarrow {}^6\text{P}_J$ transitions of Gd^{3+} . Brixner and Blasse [42] were the first to observe ${}^6\text{G} \rightarrow {}^8\text{S}$ emission of Gd^{3+} in several host lattices at higher energies at about 205 nm and 186 nm . Other experimental and theoretical works are necessary to confirm the possibility of using nano-crystalline GeSe_2 doped with Gd as a radiative visible source.

4. Conclusion

First optical properties through Raman and photoluminescence studies are performed for nano-crystalline pure and Gd-doped GeSe_2 . New results, with comparison to glassy and crystalline GeSe_2 , are given. Doping with Gd is found to alter the local environment of the existing atoms as predicted by Raman and PL analysis. The assignment of Raman emission lines and energy level transitions of Gd^{3+} in the host GeSe_2 are suggested.

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