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# Exciton Investigations and the Urbach Tails of Gd Doped and Undoped GaSe

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## Abstract

Absorption measurements were carried out in GaSe and GaSe:Gd samples in temperature range 10-320 K in steps 10 K. The first and the second ( $n=1$  and  $n=2$ ) excitonic levels were marked. The first exciton energies for  $n=1$  were calculated as 2.118, 2.008 eV in GaSe, and 2.125, 2.006 eV in GaSe:Gd at 10, 320 K and respectively. The second exciton energies for  $n=2$  were calculated as 2.140, 2.125 eV in GaSe at 10, 80 K and 2.141, 2.120 eV in GaSe:Gd at 10, 120 K and respectively. Binding energies of GaSe and GaSe:Gd were calculated as  $(29.46\pm 1$  and  $21.33\pm 1$  meV), respectively. The direct band gaps were estimated as 2.147, 2.037 eV in GaSe and 2.146, 2.027 eV in GaSe:Gd at 10, 320 K and respectively. There are abrupt changes in the Urbach energy for GaSe at 100 and 240 K, and GaSe:Gd at 90 and 220 K. However, there are abrupt change both in the steepness parameter for GaSe:Gd at 90, 240 K and in the  $\sigma_0$  values for GaSe:Gd at 70 and 240 K. These temperatures obtained from the changing of the steepness parameter,  $\sigma_0$  values and Urbach energy may be at phase transition temperatures.

**Key Words:** GaSe, GaSe:Gd, exciton, Urbach tails, binding energy, phase transition.

## 1. Introduction

Gallium selenide (GaSe) is a layered semiconductor which can be cleaved to yield highly perfect surfaces and has been shown to belong to a new class of materials with characteristics attractive to the application of solar energy conversion application [1 - 6]. Transport properties of GaSe along the layers have been widely investigated in the past twenty-five years [1 - 6]. The near band edge optical and electrical properties of strongly anisotropic crystals are subject of considerable technical interest. In the recent

years, among the III-VI layer crystals, GaSe has been the most investigated and the three-dimensional character of the charge carriers in this compound now appears to be well established [1 - 9]. The luminescent properties of semiconducting compounds doped with rare earth elements have been studied intensively with the aim of revealing their capability to provide effective generating both in the visible range of the optical spectrum and in the IR region [10]. However, it is not clear whether the small anisotropy reported in GaSe [10] is a specific feature of this crystal or a general property of all III-VI layer compounds.

A systematic investigations of the effects of thermal annealing on the optical absorption and structure of evaporated GaSe thin films is reported [11,12]. Optical gap was determined in films annealed at various temperatures and for different periods [11,12]. Impurity levels in the layered III-VI compounds GaSe have been investigated by doping with elements of I, II, and III groups [13]. To identify the manganese related defect levels in GaSe, GaSe:Mn single crystals were grown with various Mn dopant levels using the Bridgman technique and photoconductivity and photoluminescence properties were investigated in the resulting crystals [14]. Narrow-band luminescence of rare earth ions in  $A^{III}B^{VI}$  group materials associated with intra-centre transition was only seen in GaS and GaSe single crystals doped with ytterbium and neodymium [15]. Absorption spectra of the layer crystal GaSe doped with Ni of different concentrations (0.5, 0.1, 0.05, and 0.01 %) were investigated in the temperature range 4.2 to 300 K. In the region 1.5 to 2.0 eV an impurity absorption due to intra-centre transitions between the  $3f$  and  $3p$  states of the ion Ni was revealed [16].

Layered crystals of GaSe are grown by the Bridgman method [17 - 19]. Zinc (Zn) was doped into GaSe single crystals grown by the Bridgman technique in a wide range from 0.005 to 0.5 at % to the stoichiometric melt [20]. Melt growth of GaSe single crystals by Bridgman-Stockbarger method in ampules with differently shaped bottoms has been investigated [19]. Good quality single crystals have generally been obtained from non-stoichiometric melts using the Bridgman [21] and Crochralski [22] techniques. Recently, small samples have also been grown from the vapour phase by chemical transport process [23].

The behaviour of several dopants such, as Rare Earth Elements (REE) in p-GaSe and other III-VI compounds, is interesting because of their effect on crystal band structure and scattering anisotropy. This effect has been shown in n-InSe:Er [24] and p-GaSe:Gd [25] crystals by measuring the temperature dependencies of their magnetoresistance and Hall effect.

## 2. Basic Equations

The absorption coefficients were obtained from the transmission data using the relationship [26]

$$T = (1 - R_0)^2 \exp(-A) = (1 - R_0)^2 \exp(-\alpha d), \quad (1)$$

where  $R_0$  is the reflectivity ( $R_0$  is 0.2605 [27])  $A$  is the absorbance,  $\alpha$  is the optical

absorption coefficient ( $\text{cm}^{-1}$ ) and  $d$  is the sample thickness. The optical absorption coefficients determined for all temperatures using the values of  $R_0$  at room temperature by assuming that the temperature change from 10 to 320 K produce only small change in  $R_0$  [28].

The binding energies of GaSe and GaSe:Gd samples were calculated using following equation [7]:

$$R = \frac{4}{3}(E_{n=2} - E_{n=1}). \quad (2)$$

The direct band gap was calculated from following equation using direct exciton energy levels:

$$E_{exc}^d = E_g^d - R/n^2 \quad (3)$$

where  $n=1,2,3,\dots$

The following empirical expression is often used to describe the temperature dependence of the energy gap [29]:

$$E_g(T) = E_g(0) - \delta \frac{T^2}{T + \beta} \quad (4)$$

where  $E_g(T)$  is the energy gap,  $E_g(0)$  is the energy gap at 0 K and  $\delta$  and  $\beta$  are constants, depending on the material. The constant  $\beta$  is approximately equal to the Debye temperature  $\theta_D$ .

An exponentially increasing absorption edge in a number of insulators including ionic crystals, semiconductors and organic crystals follows the empirical expression [30]:

$$\alpha = \alpha_0 \exp \left[ \frac{\sigma(h\nu - E_0)}{kT} \right], \quad (5)$$

where  $\alpha_0$  and  $E_0$  are characteristic parameters of the material,  $\sigma$  is the steepness parameter,  $k$  is the Boltzmann constant and  $T$  is the temperature.

The steepness parameter which characterizes the steepness of the straight line near the absorption edge is expressed empirically as a function of temperature [31]:

$$\sigma = \sigma_0 \left( \frac{2kT}{\hbar w_p} \right) \tanh \left( \frac{\hbar w_p}{2kT} \right), \quad (6)$$

where  $\sigma_0$  is a temperature-independent but material dependent parameter. Some researches have stated that  $\hbar w_p$  corresponds to the energy of phonons associated with Urbach tail [31]. The absorption coefficients obtained for a 1 s-exciton considering only the quadratic term of the exciton-phonon interaction operator are very similar to those expressed by Eq. (3), and the parameter  $\sigma/kT$  for the interaction between exciton and longitudinal-optical (LO) phonons coincides with Eq. (4) with a constant factor [31].

### 3. Experimental Procedures

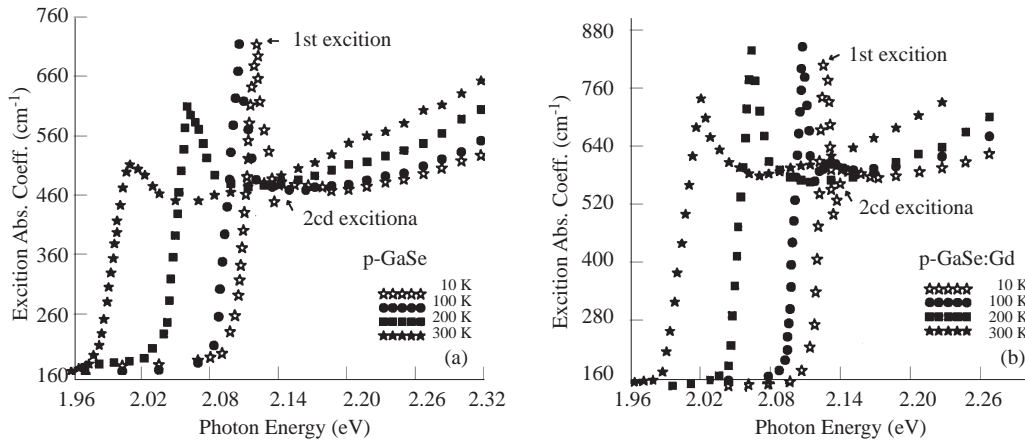
GaSe and GaSe:Gd (0.015 % Gd (Gadolinium)) single crystals were grown by the modified Bridgman-Stockbarger method. A sealed quartz ampule was annealed at 1000 ° C for 10 hours in an outgassing furnace. The temperature of the quartz ampule was decreased to room temperature over 7 hours. The stoichiometric mixture of Ga-Se-Gd put into the quartz ampule which subsequently was sealed under a vacuum of  $10^{-6}$  mbar. A quartz crucible (13 mm in diameter and about 200 mm in length) with carbon coating was used. The ampule was suspended in the middle of the vertical furnace with two zones. The temperature of the furnace was set 1000 ° C for 32 hours. The temperature of low temperature zone of the furnace was lowered to 580 ° C at a rate of 6 ° C /h. Both of the furnace zones cooled to 350 ° C in 62 hours. The solidified ingot was cooled to room temperature in 45 hours. GaSe and GaSe:Gd single crystal ingots were 12 mm in diameter and about 75 mm in length. They had no cracks and voids on the surface. The freshly cleaned crystals had a mirror-like surface and there was no need for mechanical polishing. The X-ray Laue back reflection method was used to test the crystallinity of prepared samples [33]. The grown crystal was cleaved into perpendicular planes of natural cleaved planes. Pure GaSe and GaSe:Gd samples were cleaved from the ingots with a razor blade and cut  $48 \pm 1 \mu\text{m}$  and  $46 \pm 1 \mu\text{m}$  in thick. The GaSe and GaSe:Gd surfaces used in this study were of dimensions  $1.5 \times 2 \text{ mm}^2$  and  $2 \times 2 \text{ mm}^2$ , respectively. The absorption measurements were carried out in GaSe and GaSe:Gd samples in temperature range 10-320 K.

Optical measurements as a function of temperature were made in a closed-cycle He cryostat. For optical measurements the Perkin Elmer UV/VS Lambda 2S double beam spectrometer was used and works in the range 190-1100 nm. The wavelength accuracy of the spectrometer is better than  $\pm 0.3$  nm. Therefore  $E_g$  can be calculated with accuracy better than  $\pm 0.7$  meV considering the wavelength accuracy of the spectrometer.

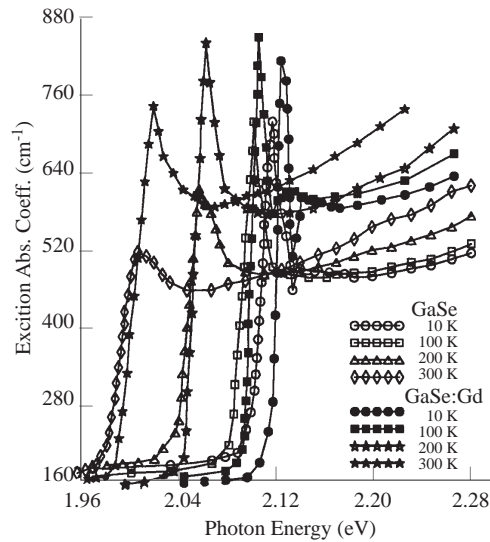
### 4. Results and Discussion

The undoped and Gd doped GaSe (0.015 at. % Gd) samples were found to be p-type by using Hall effect and hot probe techniques. The exciton absorption spectrums have been obtained from the experimental absorbance values at different sample temperatures using Eq. 1. Some typical exciton absorption spectra obtained at sample temperatures of 10, 100, 200 and 300 K are illustrated in undoped and Gd doped samples in Figure 1(a) and 1(b), respectively. The exciton absorption coefficients at the absorption peaks decrease with increasing temperature in the temperature range of 10-120 K (see Fig. 2). Decreasing of the exciton absorption coefficient in this temperature range, arises from the decreasing capability of the absorbing media. The exciton absorption coefficient of p-GaSe and p-GaSe:Gd samples for different temperatures (10-100-200-300 K) are shown in Figure 2. Analyzing the experimental data for p-GaSe and p-GaSe:Gd samples, we found that absorption coefficients of p-GaSe are between 166.7 and 714.30  $\text{cm}^{-1}$  and of p-GaSe:Gd are between 166.0 and 846.50  $\text{cm}^{-1}$  at 10 K. The absorption edges of all the investigated compounds shifted considerably when the temperature was changed from

10 to 320 K. As seen in Figure 2, the absorption coefficients of excitons in p-GaSe are smaller than those of p-GaSe:Gd.



**Figure 1.** Typical excitonic absorption spectrum obtained at 10, 100, 200 and 300 K for a) GaSe b) GaSe:Gd samples.



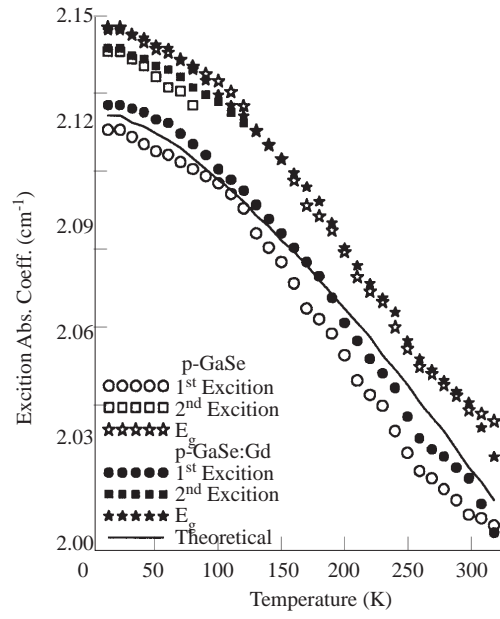
**Figure 2.** The exciton absorption spectra versus photon energy for GaSe and GaSe:Gd samples.

The experimental results for the temperature dependence of the first excitonic structure for undoped and Gd doped samples in the temperature range of 10-320 K are respectively shown in Figure 3. The first ( $n=1$ ) and second ( $n=2$ ) excitonic levels (see

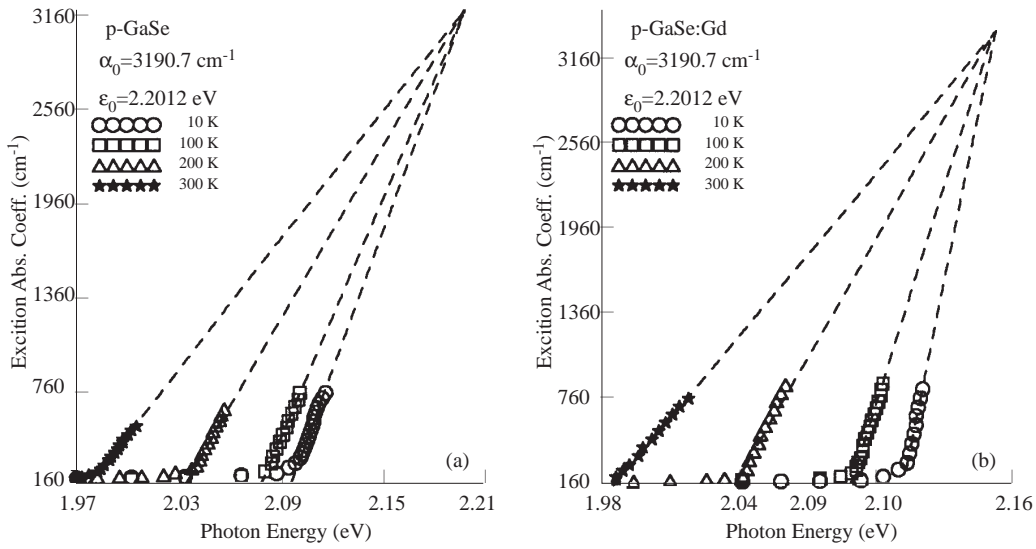
Figure 2) were marked. The energy of the 1<sup>st</sup> exciton level for p-GaSe and p-GaSe:Gd samples are given in the Table. The energy of the 1<sup>st</sup> exciton level (n=2) were found to be 2.140, 2.136, and 2.125 eV at 10, 40, 80 K, in p-GaSe and 2.141, 2.138, 2.130, 2.120 eV at 10, 40, 80, 120 K for in p-GaSe:Gd, respectively. The second exciton level which has not been observed in p-GaSe has been observed in p-GaSe:Gd at 120 K and this situation can be think thought of as a Gd effect. The binding energies calculated from Eq. 2 for p-GaSe and p-GaSe:Gd are  $29.46 \pm 1$  meV and  $21.33 \pm 1$  meV. Gd doping in the p-GaSe changes the first and the second exciton energies and the absorption coefficient peak in the lower energy region. This effect cause a change in the binding energy. The temperature dependence of the experimental (Eq. 3) and theoretical (Eq. 4) band gaps has been obtained from binding energies and have been shown in Figure 3. This curve represents the values of  $E_g(T)$  found by Eq. (4). The direct band gaps were obtained by adding binding energies onto the exciton energies. The direct and first exciton energy levels for p-GaSe and p-GaSe:Gd samples are given in the Table. The first exciton energies in p-GaSe:Gd are greater than those of p-GaSe. The effect of Gd increases first exciton energies of p-GaSe. The increase in the fist exciton energies may arise from light Gd concentration (%) and that the impurities decrease the trap level. It is evident that the first and second exciton energies decreased with increasing temperatures. The temperature coefficients  $\delta$  were calculated as  $5.363 \times 10^{-4} \pm 0.5$  eV/K for p-GaSe and  $5.2 \times 10^{-4} \pm 0.5$  eV/K for p-GaSe:Gd from a satisfactory fitting of the experimental curve using the Eq. (4). However,  $\beta$  was calculated as  $192 \pm 2$  K for p-GaSe and  $189 \pm 2$  K for p-GaSe:Gd. For p-GaSe and p-GaSe:Gd the direct energy gap decrease towards to lower values with increasing temperature and the temperature coefficient has a negative sign (see Figure 4). This change is typical for crystals having layered structures.

**Table 1.** The direct band gap, 1<sup>st</sup> level of exciton energy, steepness parameter,  $\sigma_0$  values and Urbach energy of GaSe and GaSe:Gd samples versus sample temperatures.

Samples	Sample Temp.	$E_{gd}$ (eV)	1 <sup>st</sup> exciton Energy (eV)	Steepness Param. ( $\sigma$ ) $\times 10^2$	$\sigma_0$ Values $\times 10^2$	Urbach Energy (meV)
	10 K	2.147	2.118	0.900	1.500	5.765
p-GaSe	120 K	2.125	2.096	6.723	7.023	179.630
	220 K	2.073	2.044	18.642	23.850	58.169
	320 K	2.037	2.008	39.775	44.131	85.962
	10 K	2.146	2.125	9.100	113.000	0.763
p-GaSe:Gd	120 K	2.122	2.101	7.280	137.810	10.845
	220 K	2.075	2.054	19.160	14.650	53.662
	320 K	2.027	2.006	118.31	132.480	4.836



**Figure 3.** The temperature dependence of the band gap energy and the first and second excitonic structures for GaSe and GaSe:Gd samples.

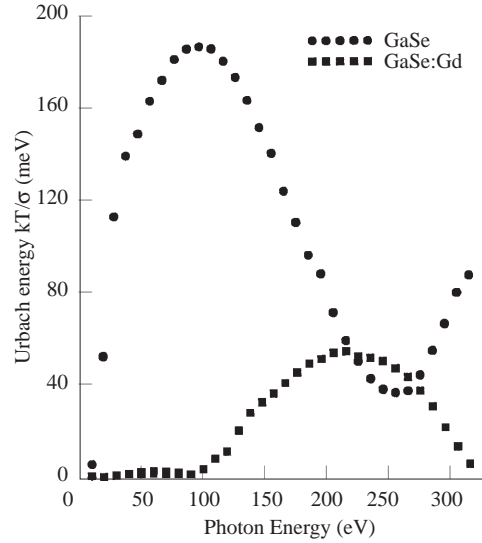


**Figure 4.** Typical absorption spectra obtained at 10, 100, 200 and 300 K for a) GaSe b) GaSe:Gd samples.



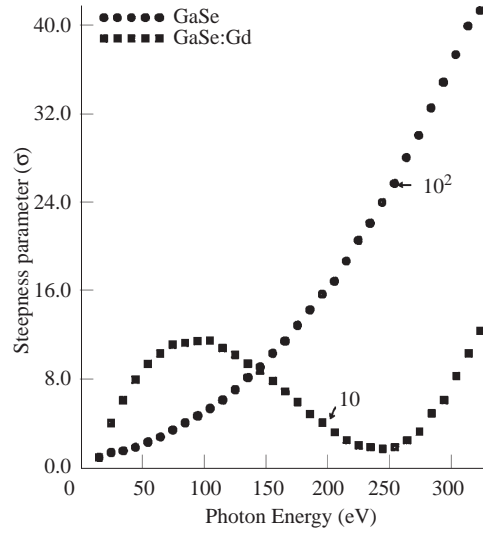
The Urbach tail was observed for all samples between 10-320 K. Typical Urbach tails for various temperature are shown in Figures 4(a) and (b). It is found that all extrapolations of the Urbach tails converge at  $(E_0, \alpha_0) = (2.201 \text{ eV}, 3190.7 \text{ cm}^{-1})$  and  $(2.154 \text{ eV}, 3327.5 \text{ cm}^{-1})$  as shown in Figures 4(a) and (b), respectively. These results show that absorption spectra of all samples obey Urbach rule. As seen Figures 4(a) and (b), all of the points intersect the same  $(E_0, \alpha_0)$  point at the temperature range 10-320 K.

Figure 5 shows the Urbach energy ( $kT/\sigma$ ), which corresponds to the inverse of a slope of the Urbach tails of the p-GaSe and p-GaSe:Gd samples as a function of temperature. The Urbach energy of p-GaSe increased with increasing sample temperature in the range 10-100 K and 260-320 K and decreased for  $110 \leq T \leq 250$  K. The Urbach energy of p-GaSe:Gd increased with increasing sample temperature in the range 10-220 K and decreased for  $230 \leq T \leq 320$  K.

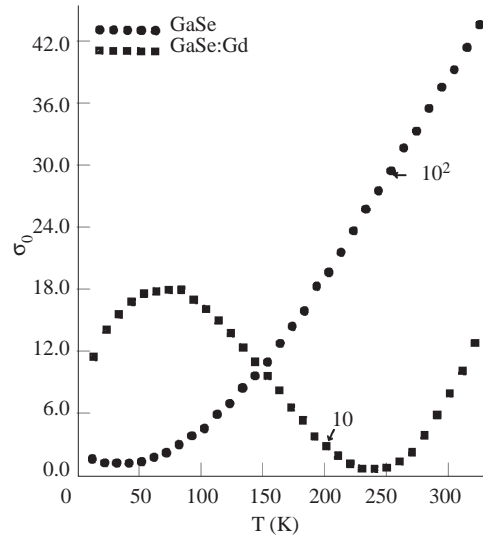


**Figure 5.** The Urbach energy as a function of the temperature for GaSe and GaSe:Gd samples.

The Figure 6 and Figure 7 shows steepness parameters ( $\sigma$ ) and  $\sigma_0$  values of the p-GaSe and p-GaSe:Gd samples as a function of temperature. The steepness parameters and  $\sigma_0$  values of the p-GaSe increased with increasing sample temperature in the range 10-320 K. The steepness parameter,  $\sigma_0$  values and Urbach energy for p-GaSe and p-GaSe:Gd samples are given in the Table (10, 120, 220 and 320 K). The steepness parameter and  $\sigma_0$  values increase with increasing temperature. The steepness parameters and  $\sigma_0$  values of the p-GaSe:Gd increased with increasing sample temperature in the range 10-70 K and 240-320 K and decreased for  $80 \leq T \leq 220$  K. However, these temperatures obtained from the changing of the steepness parameter,  $\sigma_0$  values and Urbach energy may be phase transition temperatures.



**Figure 6.** The temperature versus the steepness parameters ( $\sigma$ ) for GaSe and GaSe:Gd samples.



**Figure 7.** The  $\sigma_0$  values as a function of the temperature for GaSe and GaSe:Gd samples.

In conclusion, the results are in good agreement with the literature [16,34 - 38]. It is seen from the experimental absorption results that the first and second level of exciton energies of p-GaSe:Gd are greater than that of p-GaSe. The Gd doping cause a new appearance in terms of the first exciton energies and increases in the intensity of excitonic

absorption peak in p-GaSe:Gd. As seen in Figure 2, the slopes of the exciton peaks in Gd doped samples are greater than those of undoped samples. The increases arise as compensation to the impurities in the undoped sample (see Figure 2). These impurities, which are optically active in band gap of p-GaSe, may be made inactive by doping Gd to the sample. The peaks which gives the excitonic absorption intensity in p-GaSe:Gd is greater than those of p-GaSe. This result shows that there are many impurities in p-GaSe single crystal and these impurities in p-GaSe are compensated by doping Gd. These are expected results, because of the behaviour of the Gd atoms in the p-GaSe. REEs in GaSe both eliminate impurities between layers and bring into inactive impurities existing in the band gap by forming complex [25]. This result is in agreement with our previous investigation of n-InSe:Ho [39].

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