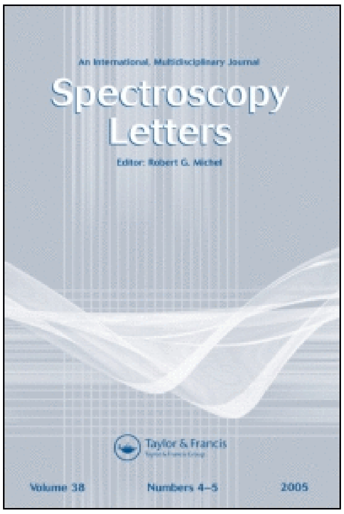

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

SPECTROSCOPIC INVESTIGATIONS AND IDENTIFICATION OF THE OCCURRENCE OF MULTIPHOTON ABSORPTION PROCESSES IN CADMIUM IODIDE

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Online publication date: 31 December 2001

To cite this Article Miah, M. Idrish(2001) 'SPECTROSCOPIC INVESTIGATIONS AND IDENTIFICATION OF THE OCCURRENCE OF MULTIPHOTON ABSORPTION PROCESSES IN CADMIUM IODIDE', Spectroscopy Letters, 34: 6, 803 — 811

To link to this Article: DOI: 10.1081/SL-100107902
URL: http://dx.doi.org/10.1081/SL-100107902

SPECTROSCOPY LETTERS, 34(6), 803–811 (2001)

SPECTROSCOPIC INVESTIGATIONS AND IDENTIFICATION OF THE OCCURRENCE OF MULTIPHOTON ABSORPTION PROCESSES IN CADMIUM IODIDE

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ABSTRACT

Spectroscopic investigations for cadmium iodide (CdI_2) crystal have been carried out at 80 K under laser excitation. Due to the self-trapped excitons of CdI_2, a broad-band stimulated emission spectrum with its peak emission around 520 nm was achieved from the crystal under two-photon pumping by means of ruby laser. The photoluminescence (PL) studies in the crystal show overall nonlinear dependence of the PL peak intensity on input laser energy. The occurrence of slopes about 2 and 3 obtained in the desired energy range of interest for ruby and neodymium laser excitations, respectively, indicate corresponding photon absorption process. The photon absorption coefficients for the processes were calculated.

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Key Words: Spectroscopy; Photon absorption process; Nonlinear transmittance; Laser; Cadmium iodide

INTRODUCTION

The identification of photon absorption processes in a material is essential for its application to optical electronic devices. Materials that possess optical nonlinearities have been studied extensively for their possible application in electronics. To assess a material for the above application, two important parameters one must characterize are its index of nonlinear refraction and two-photon absorption (2PA) coefficient[1]. Recently, multiphoton spectroscopy has become a powerful tool to investigate electronic and excitonic properties in insolators and semiconductors. Spectroscopic technique has been successfully used for the determination of nonlinear processes such as two-photon absorption (2PA) and three-photon absorption (3PA) in a dye medium[2–6]. The transition mechanism related to multiphoton absorption (MPA) processes depends on frequency and material parameters. Since cadmium iodide (CdI_2) has crystal structure with 4H polytypism, it is a better system for ascertaining the predictions of multiphoton processes[7]. Moreover, the band gap energy (E_g) of CdI_2 (3.5 eV) at the liquid nitrogen temperature (80 K) is approximately in resonance with the two-photon and three-photon of ruby and neodymium laser, respectively. Nonlinear luminescence for CdI_2 has also been published by Kumar and co-workers[8], where N_2 laser under one-photon absorption (1PA) was used in their experiments. The two-photon process in layered semiconductors has been studied by nonlinear transmittance (NLT) technique[9–10]. In this work nonlinear luminescence in CdI_2 at 80 K has been studied for the identification of different photon absorption processes in CdI_2 and the photon absorption coefficients for the processes have been estimated.

MATERIALS AND METHODS

Crystal samples used in the experiments were taken from high quality single crystals of CdI_2, grown from the melt by the refining method. The detail procedures for sample preparation are described elsewhere[11]. The grown crystal was found to be predominantly of the 4H type. Samples of dimensions of $3 \times 6 \times 7$ mm^3 were selected to get the maximum available power from the laser excitation. The maximum value which was allowed without crystal damage was about 95 MW cm^{-2} with 7 ns pulse duration for both ruby and neodymium lasers. The 2PA coefficient was measured by nonlinear trasmittance method. The 2PA and 3PA comparative luminescence measurements were monitored to estimate the 3PA coefficient. The ruby and neodymium lasers were used for two-photon and three-photon excitations, respectively. The nonlinear transmittance and luminescence measurements were carried out at liquid nitrogen temperature (80 K). For the measurements of stimulated luminescence, 2PA and 3PA coefficients the experimental arrangements reported elsewhere[12,10,13] were employed.

RESULTS AND DISCUSSION

A broad-band stimulated emission was achieved from CdI_2 crystal at 80 K by the two-photon pumping with radiation from a ruby laser, as shown in Fig. 1. This is the emission from self-trapped excitons of CdI_2.

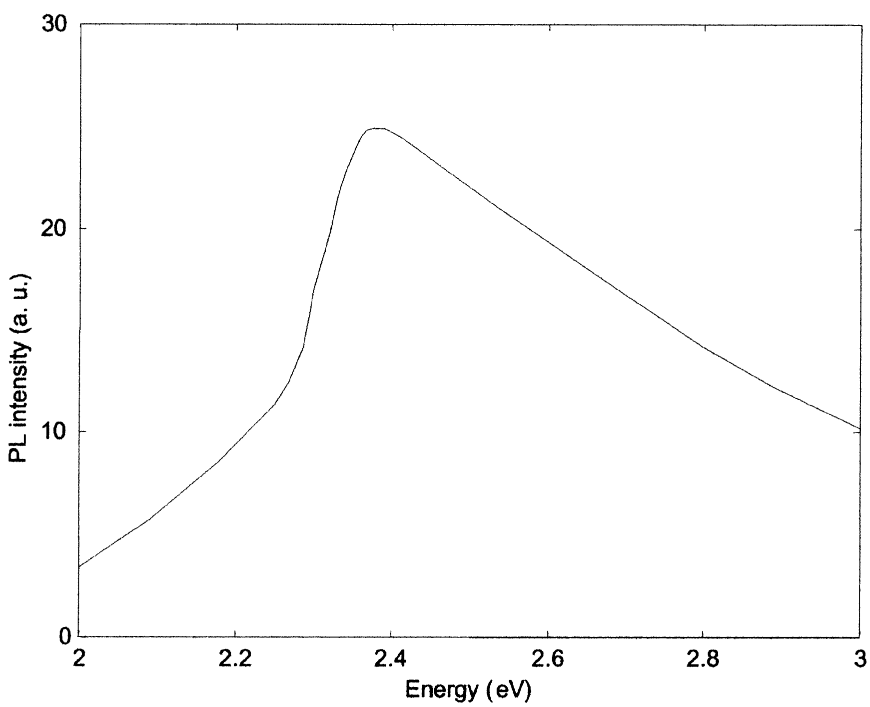

Figure 1. Stimulated emission spectrum of cadmium iodide at 80 K under ruby laser excitation. An orthogonal collection geometry was adopted for the measurement of luminescence.

A characteristic maximum emission in the green spectral region around 2.38 eV (522 nm) was observed. Shown in Fig. 2 is a dependence of the PL peak intensity at 522 nm on the excitation power of ruby laser. Above the threshold of about 6 MW cm^{-2} the dependence becomes super quadratic and the emission shows lasing character up to the saturation at about 27 MW cm^{-2}. The PL peak intensity varied quadratically with laser energy indicates the presence of sequential two-photon absorption[14]. The visible PL emission caused by band-gap exciton in CdI_2 has been assigned to the radiative recombination of self-trapped excitons, characteristic of the broad and structureless band. The self-trapped exciton emission is due to strong lattice relaxation and small exciton band width in CdI_2.

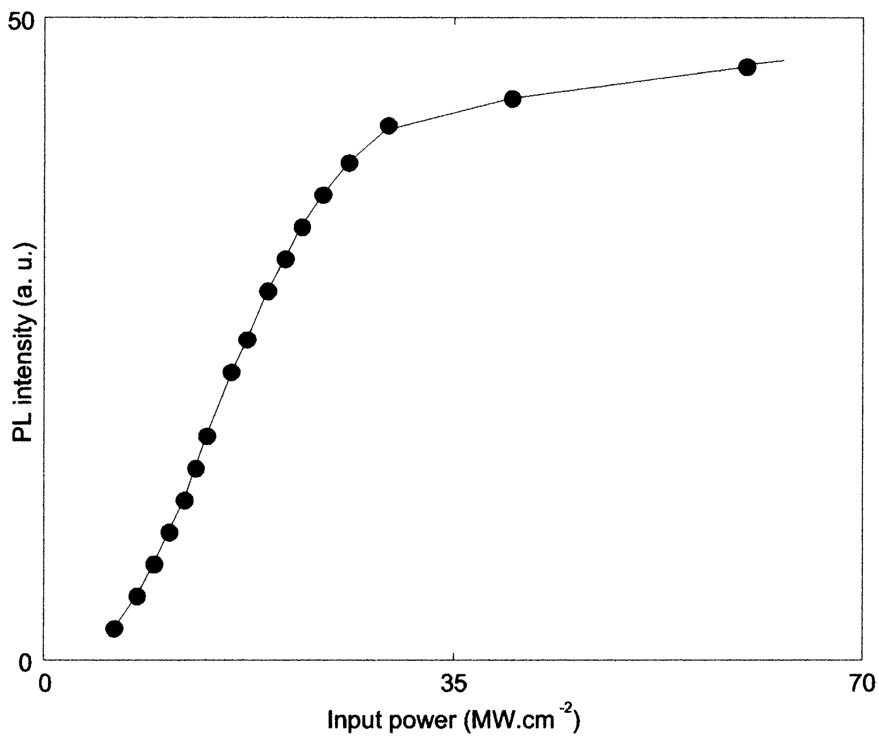

Figure 2. PL peak intensity as a function of the excitation intensity of ruby laser. Above the threshold of about 6 MW cm^{-2} the slope becomes super quadratic and the emission shows lasing features up to the saturation threshold of about 27 MW cm^{-2}.

The data for the PL peak intensity on input power of ruby laser are shown in Fig. 3. A straight line with a slope (m) of 1.9 ± 0.1 was fitted to the data by using a least-squares linear regression analysis. The occurrence of slope 1.9 ± 0.1 indicates that the nonlinearity is a second-order process, i.e., two-photon absorption process. The nonlinear transmittance method allows us to calculate directly the 2PA coefficient by measuring reciprocal transmittance (I_o/I). The incident laser power I_o and the transmitted laser power I obey the relation[9]

$$I_o/I = 2\beta/\alpha(e^{\alpha x} - 1)I_o + e^{\alpha x} \quad (1)$$

where there is also a one-photon contribution to the absorption characterised by an absorption coefficient α, and β is the 2PA coefficient.

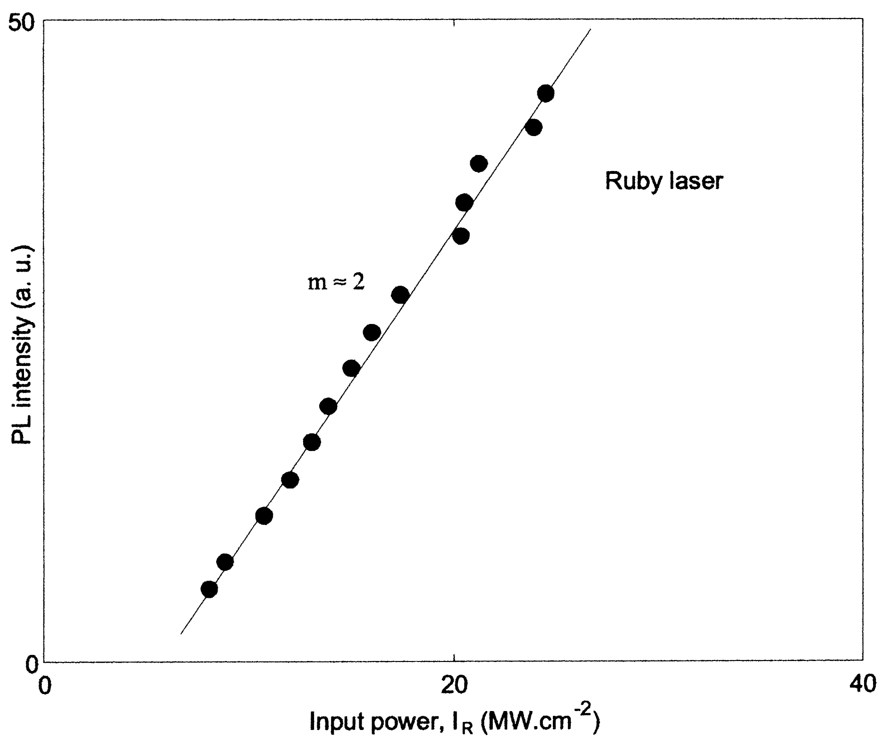

Figure 3. PL peak intensity as a function of the incident laser (ruby) intensity in the desired energy range of interest. The slope of the straight line is 1.9 ± 0.1, indicating that the nonlinearity is a second-order process, i.e., two-photon absorption process.

The above equation says that the plot of I_o/I versus I_o should be a straight line with slope $2\beta/\alpha(e^{\alpha x}-1)$ and the intercept $e^{\alpha x}$. Figure 4 shows such a plot for CdI_2. The plot of I_o/I versus I_o looks linear in the desired energy ranges of interest. By knowing the values of slope and the intercept of the plot, the α was calculated from $e^{\alpha x}$ and using the value of α, the 2PA coefficient β was calculated from $2\beta/\alpha(e^{\alpha x}-1)$. The values of α and β were found to be 5.5 cm^{-1} and 3.9×10^{-2} cm MW^{-1}, respectively. The results are in good agreement with those ($\alpha = 5.5$ cm^{-1} and $\beta = 4\times10^{-2}$ cm MW^{-1}) obtained by earlier workers[10].

Figure 5 shows the data for the dependence of PL peak intensity on the excitation power of neodymium laser. A straight line with a slope of 2.8 ± 0.1 was fitted to the data. The occurrence of slope 2.8 ± 0.1 is an indication of three-photon absorption process or third-order nonlinearity. A combination of nonlinear transmittance and nonlinear luminescence technique gives the

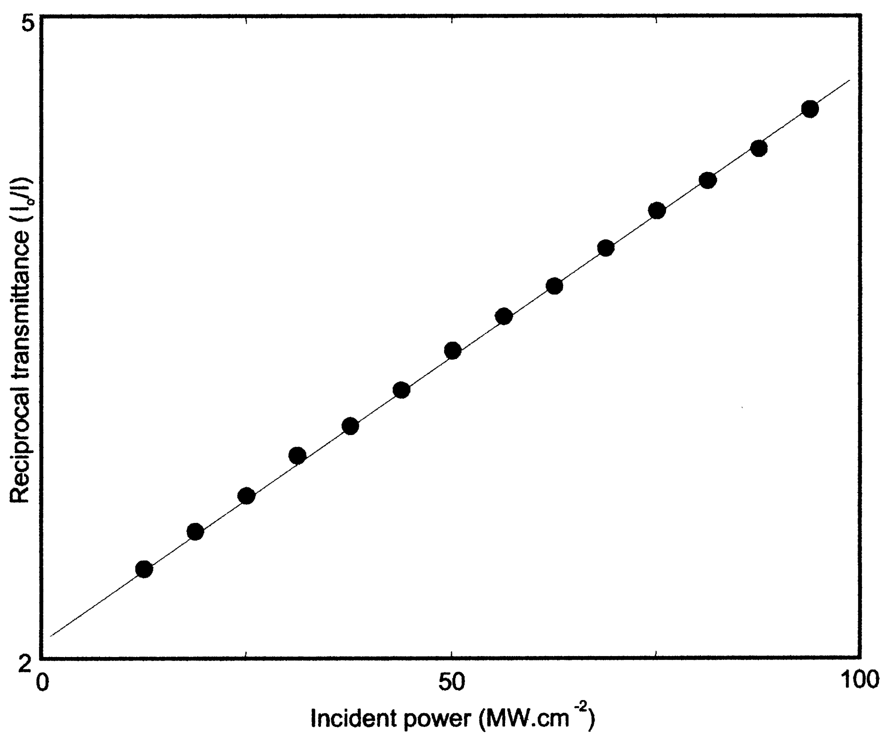

Figure 4. Reciprocal transmittance as a function of the incident power of ruby laser. A straight line with a slope of 0.025 ± 0.001 is fitted to the data.

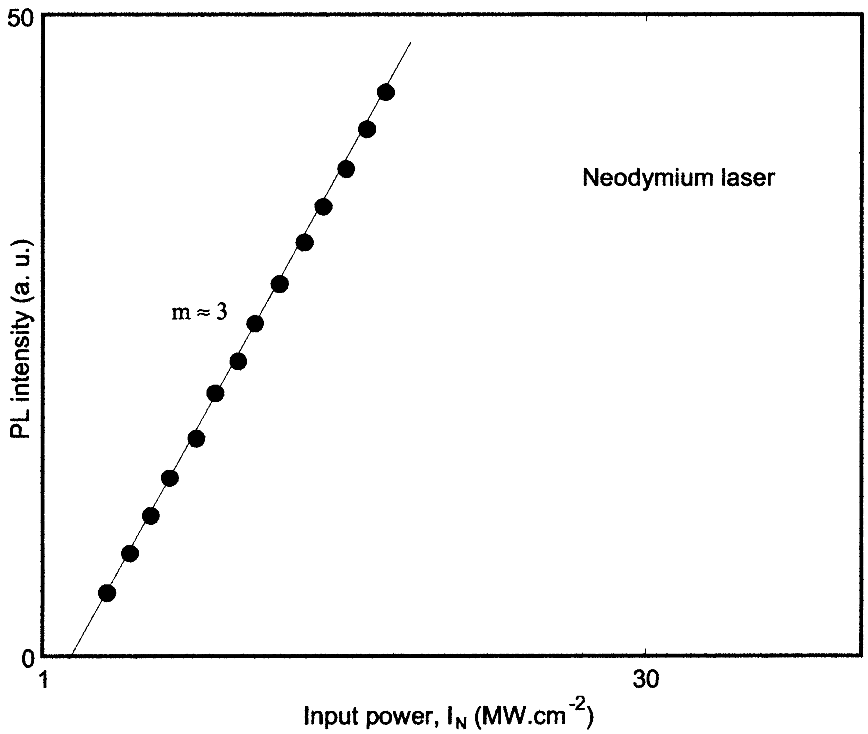

Figure 5. PL peak intensity as a function of the incident intensity of neodymium laser in the desired energy range of interest. The slope of the straight line is 2.8 ± 0.1, indicating that the nonlinearity is a third-order process, i.e., three-photon absorption process.

quantitative determination of the 3PA coefficient. The band gap energy (E_g) of CdI_2 at 80 K is approximately in resonance with the two-photon of ruby $(2h\nu_R = 3.56$ eV) and three-photon of neodymium $(3h\nu_N = 3.51$ eV) laser. If the photon energies of the two-photon excitation flux of ruby (I_R) and three-photon excitation flux of neodymium (I_N) are such that $2\hbar\omega_R \approx 3\hbar\omega_N$, the same quantum yield can be assumed in both absorption processes. Then the expression[13] for the 3PA coefficient becomes

$$\gamma = (I_3/I_2)(I_R^2/I_N^3)\beta(1 - \alpha x) \tag{2}$$

where I_2 and I_3 are the peak PL intensities at the ruby and neodymium frequencies respectively. The dependence of the peak PL intensities on the excitation fluxes I_R and I_N are shown in Figs. 3 and 5. Assuming the same PL intensity for both the processes ($I_2 = I_3$) in Figs. 3 and 5 and by knowing the 2PA coefficient (β) at the ruby frequency, the 3PA coefficient (γ) at neodymium frequency was calculated from Eq. (2). The value was found to be 4.5×10^{-2} cm^3 GW^{-2}.

CONCLUSION

A broad-band luminescence spectrum with its peak emission around 522 nm was generated from the crystal at 80 K by the two- photon pumping and the PL studies showed a super quadratic dependence of the PL peak intensity on input laser energy, indicating also under two-photon pumping, the optical amplification processes due to the self-trapped excitons work properly. The result of optical amplification under two-photon pumping is quite analogous to that under one-photon excitation using N_2 laser[8]. The dependence of PL peak intensity on input energy in the desired range of interest for ruby and neodymium lasers has been studied. A straight line was fitted to the data for each laser excitation by using a least-squares linear regression analysis. In the ruby excitation case, the straight line causing the experimental data points has a slope (m) around 2, which is consistent with the two-photon absorption process. On the other hand, the slope of about 3 obtained for neodymium excitation indicates a three-photon process. Thus by monitoring the dependence of PL peak intensity on pump energy one can identify the occurrence of different processes, such as one-photon absorption ($m = 1$) and multiphoton absorption ($m > 2$). The 2PA coefficient obtained in the present study is comparable with that as found by other investigators[10]. A combination of nonlinear transmittance and luminescence technique was used to measure the 3PA coefficient.

ACKNOWLEDGMENTS

The author is grateful to Professor T.B. Melø of Norwegian University of Science and Technology for useful discussions with him.

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Received January 15, 2001
Accepted August 20, 2001