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Non-linear optical processes in CdI_2*

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In honor of Emanuel Mooser's 60th birthday

Abstract. Cadmium Iodide has been studied from the point of view of non-linear processes by performing Raman spectroscopy measurements and experiments of optical amplification under either one or two photon excitation and of second harmonic generation.

Our experimental results give new information on the phonon structure, on the optical gain spectral dispersion and on the phase-matching conditions for second harmonic generation in CdI_2. The optical amplification, extended in a wide spectral range, is discussed on the basis of a model involving self-trapped excitons.

Introduction

The luminescence of self-trapped excitons (STE) in ionic crystals consists of broad bands in the near ultraviolet and visible spectral region. The calculated threshold for laser action from STE requires a population inversion $\Delta N \simeq 10^{16}\,\mathrm{cm}^{-3}$ in order to obtain an optical gain of $1\,\mathrm{cm}^{-1}$ [1]. At present such a population threshold can be achieved under one and two photon excitation by means of high peak power pulsed laser sources.

The laser action involving STE transition is worth interesting for the development of new tunable laser sources; the tunability results from the homogeneously broadened emission linewidth.

In order to study laser action from ionic crystals a good candidate is CdI_2, a layered compound that shows a broad spontaneous emission from STE [2]; its direct energy gap ($E_g = 3.5$ eV at 4.2 K) is approximately in resonance with one photon of nitrogen laser ($h\nu = 3.68$ eV) and two photon of ruby laser ($2h\nu = 3.56$ eV).

Moreover CdI_2 is a non-centrosymmetric material, belonging to the 6 mm symmetry group, that shows a strong birefringence and a large range of transparency from 0.4 to 40 μm. Therefore we expect it should have good performances as second harmonic generator.

In this paper we report the results of non-linear optics experiments on CdI_2. Particularly, we have performed measurements of: 1) spontaneous Raman spec-

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troscopy at high sensitivity; 2) optical gain spectroscopy at high excitonic density under either one photon or two photon optical pumping; 3) second harmonic generation in phase-matching conditions.

Experimental

The CdI_2 single crystals were grown from the melt by using the Bridgmann technique. Among the various polytypes of the layered structure, the crystal grown from the melt have been reported to be predominantly of the 4H type [3]. This is confirmed by the Raman spectrum reported below. Optical absorption measurements performed in our samples by means of photoacoustic spectroscopy show an impurity absorption band below the indirect energy gap [4]. This band (centered at 3.1 eV at RT) is due to the presence of Pb^{++} impurities; this nature is confirmed by measuring the spontaneous luminescence spectrum of CdI_2 at 10°K under PPO dye laser optical pumping in resonance with the impurity band. In fact the spectrum shows the three typical emission band of Pb^{++} in CdI_2, [5], i.e. two narrow bands at 388 and 397 nm respectively and another broad band centered at 518 nm.

The Raman scattering was excited by the lines 514.5, 488 and 476.5 nm of an Argon laser operating in single longitudinal and transverse mode at a power of 500 mW. The spectral analysis was performed by a high sensitivity spectrophotometer (Ramanor HG2 S), equipped with holographic gratings. The measurements were carried out between 80 and 300 K by means of a LN cryostat with the sample immersed in exchange gas.

To achieve the one photon high excitation density in CdI_2 we used two different laser sources: 1) a nitrogen laser ($I_{max} = 10\ MW/cm^2$) whose 337.1 nm light lies in the direct excitonic absorption region of CdI_2; 2) a flow-type nitrogen pumped dye laser ($I_{max} = 1\ MW/cm^2$) tuned at 367 nm, i.e. in the indirect energy gap absorption region [6].

The stimulated emission experiments were carried out at temperature between 10 and 300 K and an orthogonal excitation-collection geometry was adopted. The photoelectric detection apparatus was described elsewhere [7]. The experimental technique to measure the unsaturated optical gain was similar to that developed in Ref. 8; the sample excited length was controlled down to 0.1 μm.

Two photon excitation was obtained by means of a Q-switched ruby laser ($I_{max} = 100\ MW/cm^2$) operating in TEM_{00}. Complementary two photon transmittance measurements were also carried out. The two photon apparatus used for measuring the stimulated emission and the non-linear absorption has been described in Ref. 9.

The second harmonic generation measurements in CdI_2 were carried out by using as fundamental frequency source a Q-switched Nd:YAG laser ($I_{max} = 50\ MW/cm^2$). The second harmonic intensity $I(2\omega)$ was measured either as a function of the angle ϕ between the electric field vector of the laser beam and the (001) axis of the crystal or as function of the angle θ between the laser beam and the normal to the surface of the sample. Taking ϕ and θ constant, the intensity $I(2\omega)$ was measured as a function either of $I(\omega)$ or of the path length L in the sample, by means of an experimental set-up like that of Ref. 10.

Results and discussion

Figure 1a shows the Raman spectrum of CdI_2 at 80°K under 488 nm 500 mW Argon laser excitation. In this spectrum there is evidence of the well known and strong E_2^3, E_1^1 and A_1^1 lines [3]. Moreover in Fig. 1b Raman spectra, recorded at higher sensitivity under 476.5 nm 500 mW Argon laser excitation, show further six weak lines at 75, 85, 138, 178, 210 and 220 cm^{-1} respectively. When the temperature increases, the amplitude of the lines at 75, 178, 210 and 220 cm^{-1} increases as $(1+n_0)^2$ where $n_0=[\exp(E/KT)-1]^{-1}$ is the Bose factor; this shows that they are due to a two-phonon scattering. On the other hand the two weak

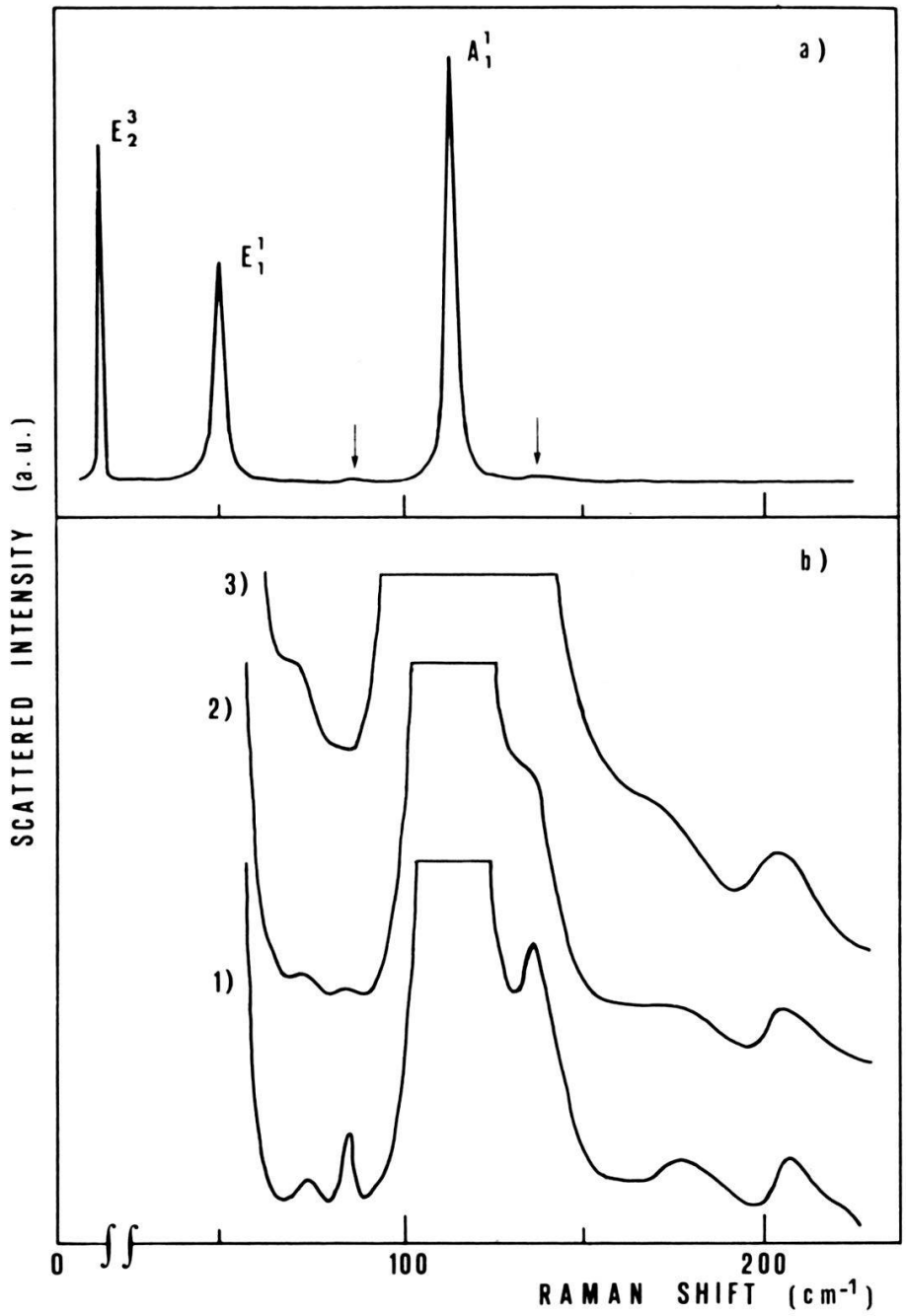

Figure 1
Raman spectra CdI_2 under 500 mW Ar^+ laser excitation: a) typical spectrum at 80 K excited at 488 nm; b) spectra recorded at high sensitivity under 476.5 nm excitation: (1) $T=100$ K; (2) $T=200$ K; (3) $T=300$ K.

peaks at 85 and 138 cm^{-1} have the same dependence of the strong lines E_2^3, A_1^1 and E_1^1 that grow with T as $1+n_0$; then they are due to a first order Raman scattering. The weak bands at 85 and 138 cm^{-1} can be assigned by taking into account the similarity between the Raman spectra of CdI_2 and those of $CdBr_2$ and $CdCl_2$. Particularly both $CdBr_2$ and $CdCl_2$ crystals are characterized by the Raman modes A_1^1 and E_1^1 and by the polar optical modes $A_1(TO)$ and $E_1(TO)$ [11]. It has been shown that the frequencies of A_1^1 and E_1^1 modes in CdI_2, $CdBr_2$ and $CdCl_2$ decrease with the increase of the atomic weight M_x of the halogen [3] as $M_x^{1/2}$. Similar dependences have been found for the Raman mode at 85 cm^{-1} of CdI_2 and the $A_1(TO)$ modes of $CdBr_2$ and $CdCl_2$ and for the Raman mode at 138 cm^{-1} of CdI_2 and $E_1(TO)$ modes of the same Cadmium halides.

Practically, our experimental results show that one phonon Raman spectra of 4*H* CdI_2 are characterized by five lines according to the irreducible representation of space group $C_{6v}-6\,mm$. Three of these lines are the well known E_2^3, E_1^1 and A_1^1 modes, while the other two lines can be assigned to $A_1(TO)$ and $E_1(TO)$ modes.

In Fig. 2 we report the unsaturated optical gain spectrum of CdI_2 at 80 K under N_2 laser excitation at $I_0 = 1\,MW/cm^2$. It is worth noting that the gain coefficient $g(\lambda)$ holds values above $10^3\,cm^{-1}$ in a broad range between 420 and 630 nm. Moreover $g(\lambda)$ depends linearly on the excitation intensity up to the maximum delivered by the nitrogen laser. On the contrary, no evidence of optical gain was achieved by means of optical pumping resonant either with the indirect gap or with the Pb^{++} impurity band. This proves that the optical amplification effect is related to the generation of a high excitonic density. The highest value of

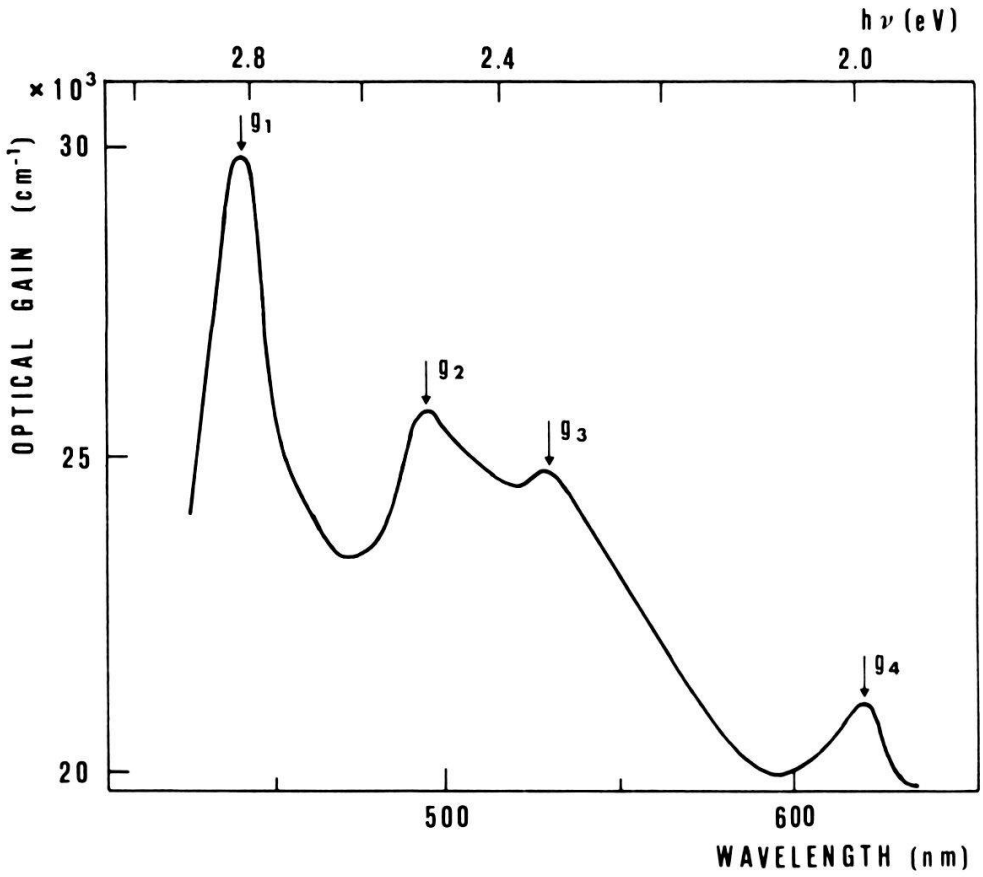

Figure 2
Unsaturated optical gain spectrum of CdI_2 at 80 K under 1 MW/cm^2 nitrogen laser excitation (one photon pumping).

g is achieved at LNT, whereas at 10 K also the maximum value is below 600 cm^{-1}; on the other hand at $T > 80$ K, at fixed I_0, the optical gain decreases quickly. In Fig. 2 four main peaks can be recognized: g_1 at 2.81 eV, g_2 at 2.53 eV, g_3 at 2.37 eV and g_4 at 2 eV. Experimental evidence of g_1 and g_3 was reported in Ref. 12, though the value of g_1 resulted to be one half of g_3.

In common opinion the self-trapped excitons in CdI_2 are well approximated by the excited states of the $(Cd^{2+}X_6^-)^{-4}$ complex molecular ions, where X^- is a halogen ion [12]. The energy diagram of this complex ion could allow us to associate g_1, g_3 and g_4 to the transitions called V, G and Y [13], experimentally observed at low excitation intensity. In our spontaneous emission spectra of CdI_2, at suitable excitation intensity and temperature, we also observe V, G and Y bands and, moreover, the band associated to g_2. Anyway, since the Raman spectra have shown that our CdI_2 samples belong to the C_{6v} symmetry group, the energy diagram of $(Cd^{2+}I_6^-)^{-4}$ complex molecular ion, developed in D_{3d} symmetry field, cannot apply to our experimental results.

In Fig. 3 we report the dependences of the stimulated emission intensity at the wavelengths of the gain peaks g_1, g_2, g_3 and g_4 on the excited length l of the sample from 10 to 70 μm. In the inset of Fig. 3 we show the broad stimulated emission spectrum of CdI_2 obtained in the same experimental conditions of Fig. 2 with an excited length $l = 3$ mm. This spectrum show only a broad band with its maximum at about 2.3 eV.

It is evident from Fig. 3 that the stimulated emission saturation depends strongly on the wavelength. Particularly it must be noted that at $\lambda_1 = 440.5$ nm the

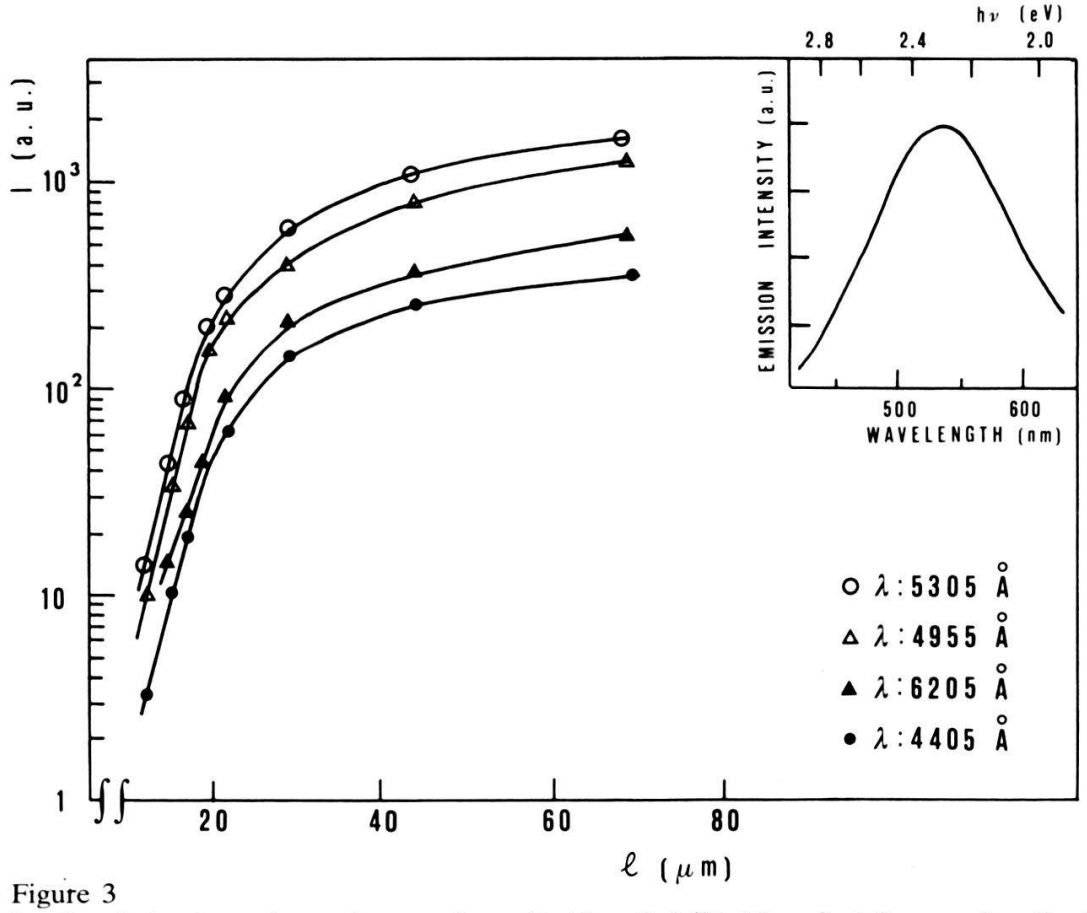

Figure 3
Stimulated emission intensity vs the sample excited length l ($l > 10$ μm) at the wavelength of the gain peaks of Fig. 2. The inset shows the stimulated emission spectrum obtained at an excited length $l = 3$ mm.

stimulated emission intensity quickly grows with l and shows a large gain (g_1), though it saturates at relatively small levels of emitted intensity or of excited length. On the contrary, at larger wavelengths (i.e. $\lambda_2 = 495.5$ nm) the optical gain $g_2 < g_1$, but the saturation effect is observed at an emission intensity which is almost an order of magnitude larger than at λ_1. Moreover for $\lambda = 530.5$ nm and $\lambda = 620.5$ nm we obtain $g_4 < g_3 < g_2$, but the saturation for $\lambda = 530.5$ nm is achieved at higher values of l. Such a spectral behaviour of the optical gain explains why the unsaturated optical gain spectrum shows four well-distinguishable peaks, whereas the stimulated emission spectrum obtained at $l > 100\ \mu$m results always in one only broad band centered on the wavelength with the highest saturation threshold.

Under two photon pumping by means of ruby laser the spontaneous emission spectra of CdI_2 at 80 K are quite similar to those recorded under N_2 laser excitation. The dependence of the emission intensity at $\lambda = 530$ nm of CdI_2 at 80 K on the excitation intensity of ruby laser is reported in Fig. 4. Above the threshold of about 7 MW/cm^2 the slope becomes super-quadratic and the emission shows lasing features, up to the saturation threshold of about 50 MW/cm^2. This means that also under two photon pumping the optical gain process due to self-trapped excitons works properly. The two photon absorption coefficient α_2 of CdI_2 at the wavelength of ruby laser can be calculated by means of the non-linear transmittance experimental data reported in the inset of Fig. 4, where the ratio

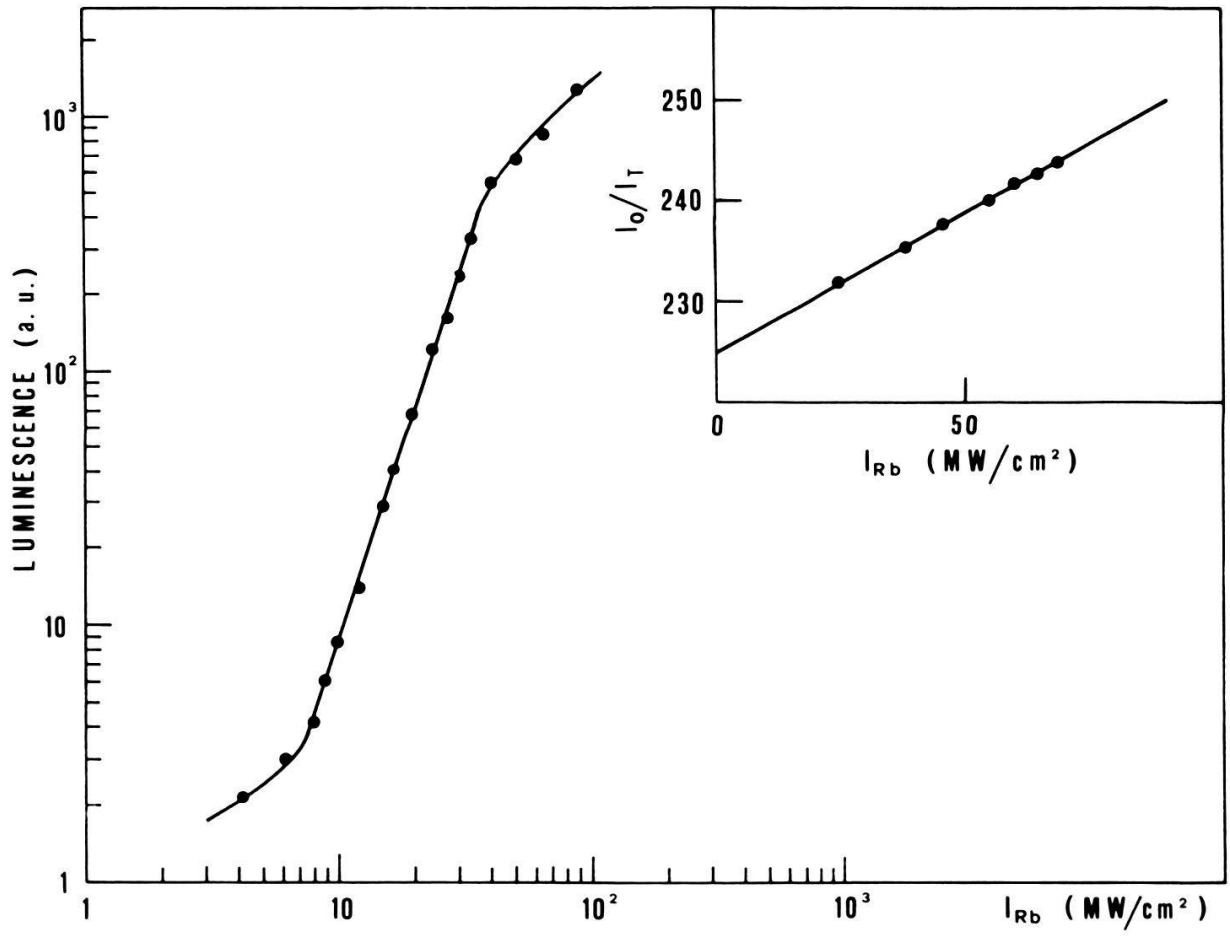

Figure 4
Stimulated emission intensity at $\lambda = 530$ nm vs the two photon pumping intensity I_{Rb}. The inset shows the reciproc of transmittance of CdI_2 vs I_{Rb}.

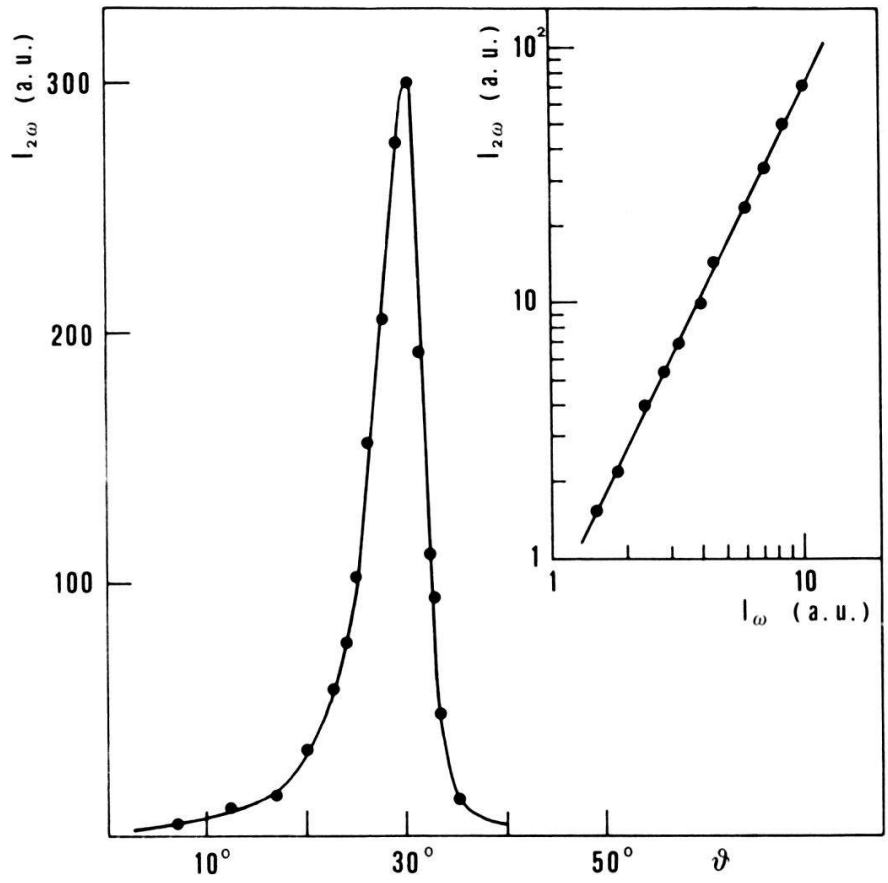

Figure 5
Second harmonic intensity from CdI_2 as a function of the angle θ, at the wavelength of Nd:YAG laser. In the inset the dependence of I (2ω) vs I (ω) is shown.

between impinging and transmitted intensity is plotted as a function of ruby laser intensity: in this way we find that $\alpha_2 = 4 \cdot 10^{-2}$ cm/MW and then, the non-linear cross section γ_2 of CdI_2 has a value of $1{,}2 \cdot 10^{-48}$ cm^4 sec.

According to Ref. 1 the required self-trapped excitons density δ_{STE} for stimulated emission is of about 10^{16} cm^{-3}. Then to achieve the population inversion the two photon pumping generation rate must exceed the recombination rate, i.e. $W = N\gamma_2 I^2 > \delta_{STE}/\tau$. By assuming $\tau \simeq 10^{-8}$ sec and for γ_2 the value above reported, we find that the calculated excitation threshold is of about 10^7 W/cm^2, in good agreement with our experimental data.

Since we expected, on the basis of its group of symmetry, that CdI_2 was a good second harmonic generator, we have measured the second harmonic intensity as a function of the angle θ between the laser beam and the c-axis of the crystal, as reported in Fig. 5. From our experimental data it appears that the phase-matching angle of CdI_2 at the wavelength of the Nd:YAG laser is $\theta_m = 30°$. The inset of Fig. 5 shows the quadratic dependence of the second harmonic intensity vs the fundamental one. Unfortunately up to now the dispersion curves of both ordinary and extraordinary refraction indices of CdI_2 are not known; therefore it is not possible to calculate the values of the nonvanishing terms of the second harmonic tensor of this material and then to evaluate quantitatively the performances of CdI_2 as second harmonic generator. Anyway, since CdI_2 is transparent from 0.4 to 40 μm and the second harmonic intensity is comparable with that one generated in the phase-matching conditions by a good second

harmonic generator as GaSe [10], we can infer that CdI_2 is a second harmonic generator of quite high efficiency.

In conclusion our experimental measurements on CdI_2 give new information on the non-linear processes and properties of this material. Particularly our results show for the first time that CdI_2 has a relevant practical interest either as a tunable laser emitter or as second harmonic generator.

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