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Research Paper

Confinement and IR Induced Optical Nonlinearity and Enhanced Second-Order Susceptibility in Nano-Sized Crystals

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Abstract
Cadmium iodide bulk- and nano-crystals are grown and doping defect and quantum-confinement effects in IR-induced optical susceptibility in the nanocrystals are investigated. Bulk-sized and intrinsic crystals are also investigated as of reference. The nanomaterials with various crystal sizes are pumped with an IR laser beam. This pump-probe experiment probes the doubled-frequency IR-induced second harmonic optical beam. The expression for the second harmonic intensity is obtained from the electric polarization of the nanomaterial process subjected to high intensity illumination. The second–order susceptibility is calculated from the experimentally measured data. The results show that a significant enhancement in the optical susceptibility is achieved in nanomaterials with moderately doping. The maximum second–order optical susceptibility is found to 0.65 pm/V. However, bulk and intrinsic crystals show no considerable second harmonic effect. A nonlinear transmittance measurement for the determination of the second-order contribution in absorption supports the effect.

Keywords
Nanomaterials, Nano-Confined Effect, Doping Effect, Optical Susceptibility

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1. INTRODUCTION

Multiphoton spectroscopy (Miah, 2001), multiphoton spin spectroscopy (Miah, 2009b) and the second harmonic generation (SHG) (Mahr, 1975; Haug, 1988; Miah, 2008) in materials have widely been used to study the optical nonlinear processes. Of them, the SHG is a tool to study the optical nonlinearity, particularly the surface effects of the noncentrosymmetric materials.

There are some possibilities of breaking the symmetry property in a centrosymmetric material by means of inducing the noncentrosymmetricity in the material's processes (Cazzanelli and Schilling, 2016; Miah, 2009a). For example, this property is generally broken at the surface of a material. Any other mechanisms that break the symmetry may allow the processes for the observation of the SHG (Kityk et al., 1998; Miah, 2019).

A cadmium iodide (CdI_2) single crystal is an indirect and wide-bandgap semiconductor (Eg = 3.7 eV) possessing layered crystal ((Kityk et al., 1998)). Bulk crystals CdI_2 are symmetric. Recent research records predict that bulk CdI_2 process the third-order optical nonlinearities (Slater, 1956; Nakagawa and Kitaura, 1995; Miah, 2011). The band structure calculations for the CdI_2 crystals show the similar results (Kityk et al., 1998; Mott and Davis, 1979). It makes CdI_2 nanocrystals promising material's process for the study of SHG.

We consider the high intense light response of the material. We take this nonlinear response of the material by relating the D and E fields with the nonlinear polarization (P) given by Equation (1),

$$\vec{D} = \varepsilon_0 \vec{E} + \vec{P}. \tag{1}$$

If we follow the method for the derivation of the wave equation Equation (2), we obtain

$$\vec{\nabla} \times \vec{\nabla} \times \vec{E} + \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = -\frac{1}{\varepsilon_0 c^2}\frac{\partial^2 \vec{P}}{\partial t^2} \tag{2}$$

which, after simplification using the identity $\vec{\nabla} \times \vec{\nabla} \times \vec{E} = \vec{\nabla}(\vec{\nabla} \cdot \vec{E}) - \nabla^2 \vec{E}$, we obtain the inhomogeneous wave in equation (3)

$$\nabla^2 \vec{E} - \frac{1}{c^2}\frac{\partial^2 \vec{E}}{\partial t^2} = \frac{1}{\varepsilon_0 c^2}\frac{\partial^2 \vec{P}}{\partial t^2}. \tag{3}$$

Following (Kivshar and Agrawal, 2003), polarization can be written with the following Equation (4)

$$\begin{aligned} P(\vec{r}, t) &= \varepsilon_0 \left\{ \chi^{(1)}_{ij} E_j(\vec{r}, t) + \chi^{(2)}_{ijk} E_j E_k(\vec{r}, t) + \chi^{(3)}_{ijkl} E_j E_k E_l(\vec{r}, t) + .. \right\} \\ &= P^{(1)}(\vec{r}, t) + P^{(2)}(\vec{r}, t) + P^{(3)}(\vec{r}, t) + ... + P^{(n)}(\vec{r}, t) \end{aligned}$$

(4)

where E_j, E_k, and E_l are the field components of the light wave interacting with the material. Here $P^{(n)}$ and $\chi_{ij}^{(n)}$ are the nth order polarization and susceptibility, respectively, of the material. The first term Equation (5),

$$P^{(1)}(\vec{r},t) = \varepsilon_0 \chi_{ij}^{(1)} E_j(\vec{r},t) \tag{5}$$

is the linear term. The susceptibility tensor $\chi_{ij}^{(1)}$ is responsible for most of the interactions of light with materials. The subject is, more specifically, called Linear Optics. However, the higher-order susceptibility tensors are responsible for nonlinear phenomena. The susceptibilities are very small compared to the linear one. The second part of Equation (6)

$$P^{(2)}(\vec{r},t) = \varepsilon_0 \chi_{ijk}^{(2)} E_j E_k(\vec{r},t) \tag{6}$$

is the first nonlinear term that describes the second-order optical effects. We can write the nonlinear polarization (Ablowitz and Clarkson, 1991) as

$$P^{(2)}(\vec{r},t) = \varepsilon_0 \chi^{(2)} E^2(t). \tag{7}$$

For the centrosymmetric material (Kivshar and Agrawal, 2003),

$$-P^{(2)}(\vec{r},t) = \varepsilon_0 \chi^{(2)} \{-E(t)\}^2 = \varepsilon_0 \chi^{(2)} E^2(t). \tag{8}$$

Substituting Equation (8) into Equation (7) we get $P^{(2)}(\vec{r},t) = -P^{(2)}(\vec{r},t)$. We now obtain (Equation 9)

$$\chi^{(2)} = 0 \tag{9}$$

which demonstrates that for a centrosymmetric process the SHG is forbidden.

If we describe the second harmonic polarization in frequency space, we can write (Equation 10)

$$P_i^{(2)}(2\omega) = \varepsilon_0 \chi^{(2)} E_j(\omega) E_k(\omega). \tag{10}$$

After doing some algebra, a relation for the double-frequency SHG beam may be found (Miah and Kasperczyk, 2009) as

$$I(2\omega,t) = \frac{2\mu_0^{3/2}\omega^2 T^2 \zeta^2 \left(\chi^{(2)}\right)^2 I^2(\omega, t-\Delta t)}{\pi\, \varepsilon_0^{3/2} R^2 n(2\omega) n^2(\omega)} \tag{11}$$

where

$$\zeta = \frac{\sin\left(T\Delta k(t)/2\right)}{T\Delta k(t)/2} \tag{12}$$

R is the radius of the pumping beam, T is the length of the nonlinear medium (thickness of the crystal), $n(\omega)$ and $n(2\omega)$ stand for, respectively, the refractive indices for the pumping and the SHG, and $\Delta k = k(2\omega) - 2k(\omega)$.

We can see the second-order optical effect by considering the nonlinear beam propagation in the medium, where the optical transmission is written (Miah, 2009c) as

$$I_0 = I \exp(\alpha T) + \frac{2\beta I_d}{\alpha}\{\exp(\alpha T) - 1\} \tag{13}$$

where α and β are, respectively, the first-order and second-order contributions to the absorption. Here I and I_0 are, respectively, the incident and transmitted intensities. If α is negligible, Equation (13) can approximately be written for the reciprocal transmittance (I_0/I) (Miah, 2010) as

$$\frac{I_0}{I} = 1 - \beta I_0 T. \tag{14}$$

Previously, a study was conducted on the photoinduced SHG in Cu-CdI_2 single crystals (Herest and Voolless, 2004), where they found the maximum SHG effect for the copper content of about 0.4%, but they did not systematically study the doping dependence. The photoinduced electron-phonon anharmonic interactions in the copper-doping responsible for the enhanced SHG effect was explored in (Miah and Kasperczyk, 2009). Recently, we experimentally introduced novel processes of inducing the noncentrosymmetricity (Miah, 2009b), where the involvement of the interlayer phonons for the photoinduced electron-phonon (e-ph) anharmonic interactions was also confirmed by the examination of the phonon modes in Raman spectrum.

In the present study, we induce the noncentrosymmetricity in CdI_2 by inserting the copper doing into the crystals and lowering the size of the crystals. The output SHG signal is measured from the nanocrystals with various sizes, pumped with an IR laser. The susceptibility is evaluated from the measured signal using the equation derived. A significant enhancement in the optical susceptibility is achieved in nanocrystals. We then explore the doping defect and nano-confined effects in the optical susceptibility of the materials. In order to have an additional support of findings, a nonlinear transmittance measurement is also performed. From the measured data the second-order absorption coefficient is calculated.

2. EXPERIMENTAL SECTION

For the present investigation, copper-doped cadmium iodide ($Cu-CdI_2$) nanocrystals were synthesized from the mixture of cadmium iodide (CdI_2) and cuprous oxide (CuI) using a standard method (Bridgman, 1952). Crystal structure was monitored using an X-ray diffractometer and a tunnelling electron microscopy. We used an Nd laser. We used a monochromator to spectrally separate the output SHG signal at 530 nm and the fundamental signal at 1064 nm. Detection of the SHG signal was done by a photomultiplier coupled with an electronic boxcar integrator. The setup used in the experimental was reported elsewhere (Miah and Kasperczyk, 2009). The second-order susceptibility

$X^{(2)}$ for samples with different T was calculated from the experimentally measured second harmonic data using Equations (11), (12), and (13). The second-order optical effect was investigated by measuring the nonlinear transmittance (Miah, 2001) of the sample. The second-order absorption coefficient was calculated using the Equation (14).

3. RESULTS AND DISCUSSION

Figure 1 shows the second harmonic signal. This delay dependence in the second harmonic signal shows a relatively large relaxation time, which demonstrates the long-lived e-ph states. This can be explained in terms of the e-ph anharmonicity (Miah and Kasperczyk, 2009), where the relaxation time plays the crucial role in the nanosize-confined effect.

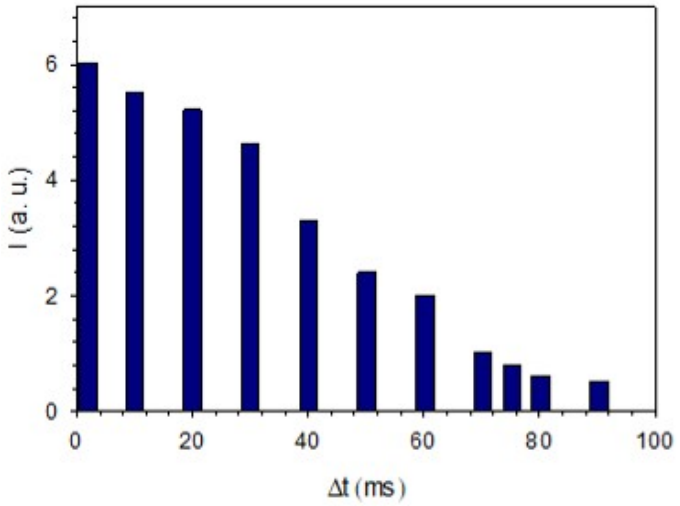

Figure 1. Second Harmonic Signal as A Function of the Time Delay Between the Pump and Probe Beams for A Typical Doped Nanocrystal

Figure 2 shows the power (P) and thickness dependences of the second harmonic signal at low temperature. It is seen that the signal increases with decreasing the thickness T of the nanocrystals. It also shows that the signal first increases with increasing the pumping power up to the maximum (24 GW/m^2) and then it decreases for all the sizes of the nanocrystals. The background signal is obtained for the intrinsic CdI_2 crystals or the bulk.

This nano-sized dependence optical effect is supported by a nonlinear transmittance measurement. Equation (14) says that the second-order contribution characterized by the absorption coefficient β can be obtained from the slope of the plot of the reciprocal transmittance. The results are pictured in Figure 3. As seen, the nano-sized dependence of the second-order optical effect shows a decrease of the β-value, agreeing with the literature reported earlier (Miah, 2001; Gopalan et al., 2007).

The optical susceptibility as a function of the nanocrystal size and copper-impurity content was calculated and was plotted in Figure 4. It is seen that the susceptibility increases with

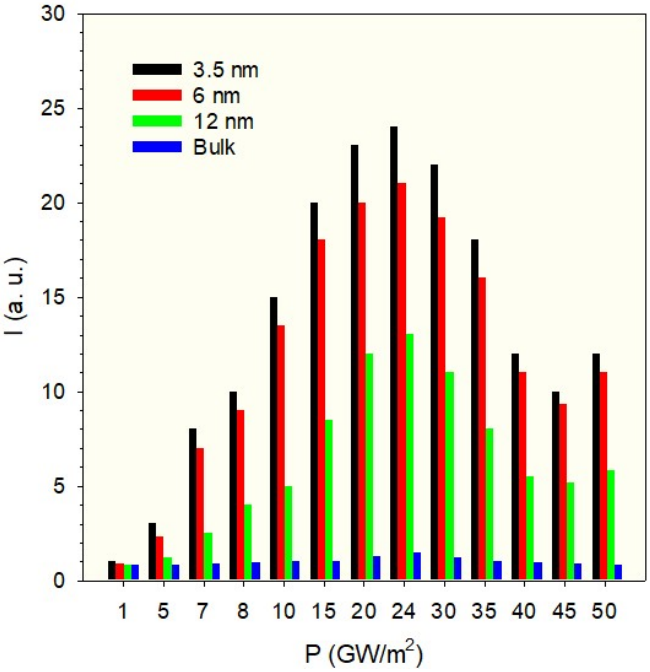

Figure 2. Second Harmonic Signal as A Function of Pumping Power. The Background Signal is for the Bulk Crystal (Green Bars)

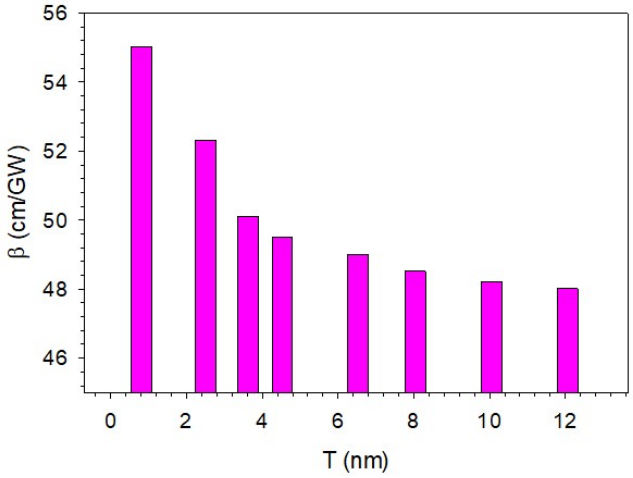

Figure 3. Second-Order Absorption Coefficient β as a Function of the Size of the Nanocrystals

decreasing the crystal size. Figure 5 shows the susceptibility in dependence of the size of thick crystals. As can be seen, the susceptibility for the crystal sizes larger than T = 250 nm gives the value at the background level (0.355 pm/V). Therefore, the size T >250 nm may be identified as the bulk. It was found that the bulk and intrinsic crystals show no considerable second harmonic effect.

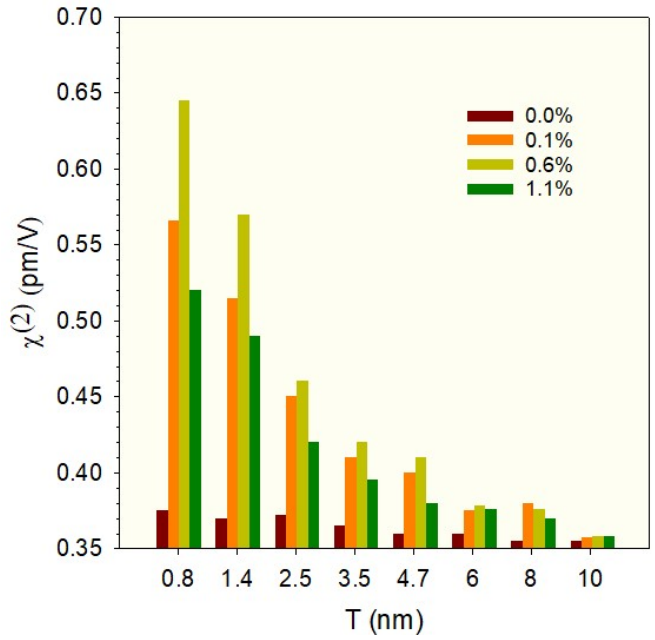

Figure 4. Second-Order Susceptibility as a Function of the Size and Impurity Content of the Crystals. The Background Signal is for the Intrinsic Crystal (Black Bars)

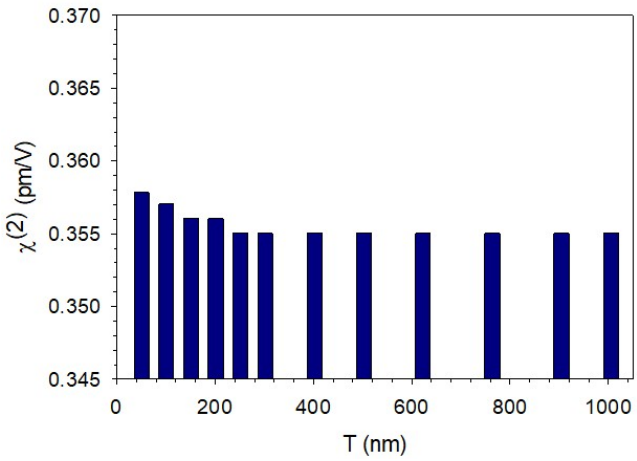

Figure 5. Second-Order Susceptibility as a Function of the Size of Thick Crystals (With Impurity Content of 0.6%). Bars Show the Deviations from the Average

The doping plays the role to enhance the anharmonic e-ph interaction (Barbagiovanni et al., 2014). In the in disordered systems, it is described by the third-order rank tensor, which was confirmed by observing the enhanced fluorescence yield of the intrinsic CdI_2 crystals (Miah, 2018), where the dependence was three orders of magnitude in optical power density.

It can be seen that the second-order susceptibility decreases for higher doping concentration, and it reduces almost to that for the intrinsic CdI_2 crystals. This might be due to the aggregation of the copper impurities. This defect-assisted effect might be explained as the influence of the doping mediated metallic-aggregators (Cazzanelli and Schilling, 2016; Kityk et al., 1998; Miah, 2009d). The generation of the aggregators can deduce active e-ph centres (Adduci et al., 1977; Catalano et al., 1985; Mott and Davis, 1979).

Thinner nanocrystals are also found to significantly enhance the effect in inducing the noncentrosymmetricity in the crystals. The SHG confidently probes the surface effects of the nanomaterial. Here, in these optical processes, quantum confinement dominates the material's nonlinear optical properties, in particular the second-order effect (Zhanga et al., 2020; Khlebtsov et al., 2005; Mott and Davis, 1979).

4. CONCLUSIONS

Doping defect and nano-confined effects in IR-induced optical susceptibility in cadmium iodide nanocrystals were investigated using a pump-probe experiment. The experiment probed the doubled-frequency IR-induced SHG. The expression for the second harmonic intensity was obtained from the polarization of electric field in the nanomaterial process. The optical susceptibility responsible for the SHG was obtained from the experimentally measured second harmonic data. A significant increased of the optical susceptibility was achieved. However, bulk and intrinsic (or pure) crystals showed no considerable second harmonic generation effect. The observed results demonstrated the copper doping and nano-sized quantum-confinement effects in IR-induced optical susceptibility in nanomaterials. As a support of the results, a nonlinear transmittance measurement for the determination of the second-order contribution characterized by the absorption coefficient was also performed.

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