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Band gap variation in laser irradiated polytypic crystals of cadmium iodide

A. Nayak, G.L. Bhalla, and G.C. Trigunayat

Department of Physics and Astrophysics, University of Delhi, Delhi-110 007, India

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Abstract. Highly purified single crystals of cadmium iodide obtained through repeated zone refining have been subjected to laser beam exposure (Argon ion laser), both for various time durations and to various beam intensities, and then subjected to band gap determination by UV spectroscopy. The band gap has been found to decrease gradually with increase in the laser beam intensity, whereas its variation with increase in time of exposure shows an unusual behaviour such that it initially falls sharply followed by a gradual rise back to its original value. The results have been analysed and interpreted in terms of indirect band gap character of the material and an unusual variation in phonon frequency. The interpretation is well supported by X-ray diffraction and scanning electron microscopy (SEM) studies.

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1 Introduction

The band gaps of the basic type 2H and four more polytypes, *viz.* 12H, 14H, 18H and 20H, of lead iodide were determined through temperature variation of electrical conductivity [1]. The value, 2.56 eV, for the polytype 2H compared favourably with the known value of 2.53 eV determined by optical absorption. The values for the higher polytypes were found to be much less, *viz.* 1.65, 1.44, 1.07 and 1.01 eV, such that the band gap decreased with increase in the size of the unit cell. The band gap variation was qualitatively interpreted in terms of the division of the original 2H zone into several subzones. Later, Bibik *et al.* [2] observed an unusual irreversible structural phase transition from the PbI_2 polytype 4H to the basic type 2H on laser irradiation. They argued that it could not be attributed to crystal heating as the type 2H is known to be the stable room temperature modification of lead iodide (*cf.* the polytype modifications 4H and 12R, which are known to be the high temperature modifications of lead iodide). They explained the observed transformation in terms of (i) the free energies of the two polytypes having different dependence on temperature and hence having their free energy curves intersecting at the temperature of transition and (ii) the polytype 4H being rendered into an intermediate metastable state by the laser irradiation.

Excitonic peaks have been observed in the UV spectra of thin films deposited on silica substrates, at liquid nitrogen, liquid Helium and room temperature. Kondo *et al.* [3] observed a sharp excitonic peak at 5.676 eV and a prominent peak at 6.15 eV at 77 K in the absorption spectra of amorphous thin CdI_2 films. Crystallization of the film yielded a sharp peak at 3.934 eV. Later, a different spectrum was obtained by Kondo *et al.* [4] for crystalline super thin films (thickness 2.8 nm) at 77 K, with a sharp peak near the absorption edge at 3.912 eV, which is 22 meV less than the previous value. They further confirmed the existence of a very sharp peak at 5.68 eV and a prominent band at 6.15 eV at 77 K for a thin film of thickness 40 nm. Much earlier, Brahms [5] reported a sharp peak at 5.68 eV followed by a broader peak at 6.195 eV, alongwith two sharp peaks at 4.04 eV, 5.228 eV and broad peaks at 3.87, 4.63, 5.39 eV, for CdI_2 crystalline thin films at 80 K. Similarly, for such films Wright and Tubbs [6] reported broad peaks at 4.03 eV, 4.65 eV and sharp peaks at 5.68 eV, 6.19 eV, 5.2 eV, 6.5 eV. They further reported a broad peak at 5.2 eV and sharper peaks at 5.6 and 6.1 eV at room temperature, liquid nitrogen temperature and liquid helium temperature, respectively, in the reflection spectra of single crystals of CdI_2. They stressed the importance of high purity of the material, since small traces of some divalent metals can seriously affect the structure of the absorption edge in CdI_2. Brahms [5] had also observed sharp peaks at 5.68 eV (around 80 K) and 5.76 eV (4 K), with a sharp peak at 6.195 eV both at 80 K and 4 K, in the reflection spectra of CdI_2 single crystals. Fujita *et al.* [7] recorded reflection spectra of single crystals of CdI_2, $CdCl_2$ and $CdBr_2$ at 35 K in the region 3 eV-30 eV, employing synchrotron radiation. For the CdI_2 crystals they reported sharp excitonic peaks at 3.93, 5.69, 6.16, 6.21, 6.49, 15.14, 15.71 eV, broad peaks at 4.06, 4.63 eV and distinct peaks at 8.31, 8.82, 9.30 eV, alongwith plasmonic peaks in the range 16-19 eV. Watanabe *et al.* [8] measured optical absorption spectra of BiI_3–CdI_2 multilayer structures around the band-edge excitonic energy of BiI_3. The excitonic peak was found to exhibit splitting and energy shift, depending on the thickness of the BiI_3 film. They also observed exciton transition in ultra-thin films of thickness just a few layers.

The present work has been concerned with laser irradiation of CdI_2 crystals, which constitute an indirect band gap material [9,10] and are known to be richly polytypic (near 200 polytypes with known crystal structure have been discovered [11]). Some curious changes have been observed in the band gap variation on exposing the crystals to laser beams of varying intensity for various time durations. The results have been discussed.

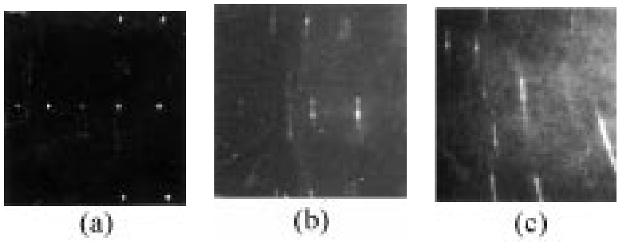

Fig. 1. (a) An a-axis 15°-oscillation photograph of CdI_2 crystal showing reflections of the most common polytype 4H. (b) An a-axis 15°-oscillation photograph of the sample irradiated with 50 mW beam intensity for 7 minutes duration. (c) An a-axis 15°-oscillation photograph of the sample exposed to 50 mW beam intensity for 15 minutes.

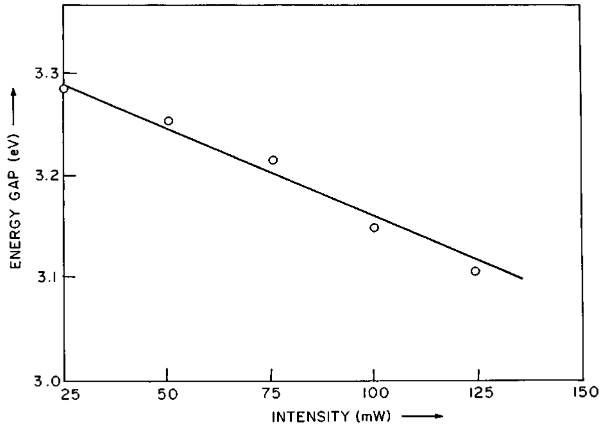

Fig. 2. Variation of band gap with increase in the intensity of laser beam, for a constant time exposure of 7 minutes duration.

2 Experimental

Cadmium iodide was highly purified by zone refining technique, employing fourteen zone passes. After the final zone pass, a single crystal of the purified material was grown using the same experimental set-up by creating an appropriate temperature gradient across the tube containing the material [12]. The semi cylindrical crystal ingot measured nearly 8 cm in length and nearly 1 cm across. Thin sections of thickness around 100 microns could be easily cleaved from the ingot, out of which small pieces measuring nearly 4 mm × 2 mm were cut and exposed to laser beam (argon ion laser), once by varying the intensity of the laser beam and keeping the exposure time fixed and next by varying the exposure time and keeping the beam intensity fixed. The pieces were used in as-grown form, without any specimen preparation.

The laser exposed crystal surface was examined by an optical microscope to locate the region exposed to the beam, which had a different appearence from the rest of the surface. The part comprising this region which measured about 1 mm × 2 mm was cut out of the crystal and subjected to UV spectrophotometry (UV 260) for energy gap determination. The value of the band gap E_g was determined from the plot of photon energy against the square root of absorption coefficient of the material. Towards this end it is essential to employ the initial part of the curve that does not involve any excitonic peaks [9]. As stated earlier, the excitonic peaks in the absorption spectra of thin films of cadmium iodide have been observed to occur at values 3.93 eV onwards. The thickness of the films employed has been a few nanometer to a few tens of nanometer (maximum about 40 nm). The excitonic peaks are not observed in the absorption spectra of CdI_2 single crystals on account of their large thickness (at least a few μm). Since the crystals employed in the present work had thickness of the order of 100 μm, any possible interference of the measurement of band gap with the excitonic peaks was ruled out.

The crystal polytype was identified by X-ray diffraction through oscillation photographs taken about a-axis, employing CuK_α radiation [13].

Finally, the surface of the exposed part was examined by a scanning electron microscope (JEOL, Model HSM 840), which provided much higher resolution and magnification as compared to the optical microscope.

3 Results

(a) The X-ray diffraction revealed all crystal samples to be the basic polytype 4H (Fig. 1a).

(b) The band gap (E_g) varied with increase in the intensity of the laser beam and time exposure as shown in Figures 2 and 3. For estimating the error in determination of E_g the analytical functions $y = a + bx$ and $y = c + d\ln(x)$ were chosen for two part of the curve, $t < 15$ and $t \geq 15$, in Figure 3. Employing the method of least square fitting, the two parts were found to be representated as

$$E_\mathrm{g} = 3.304 - 0.014t \ (t < 15)$$
$$E_\mathrm{g} = 2.657 + 0.156 \ln t \ (t \geq 15).$$

Comparison of the calculated value of E_g with observed value showed that the choice of the function were perfect for the part $t \geq 15$ and was nearly perfect for the part $t < 15$. The average percentage error for the two cases was found to be 0.3% and 0.7% respectively. Similarly, for Figure 2 the analytical function $y = e + fx$ was chosen.

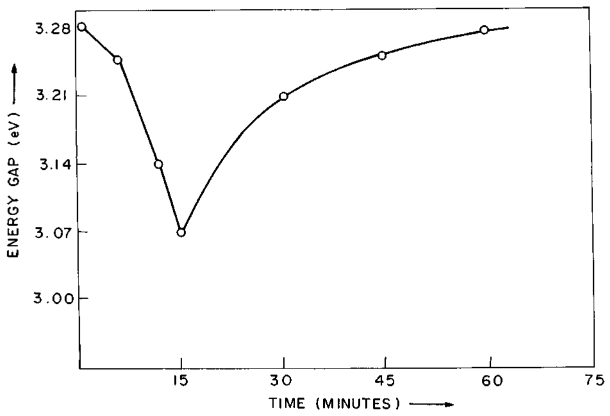

Fig. 3. Variation of band gap with increase in the time of exposure for a constant laser beam intensity of 50 mW.

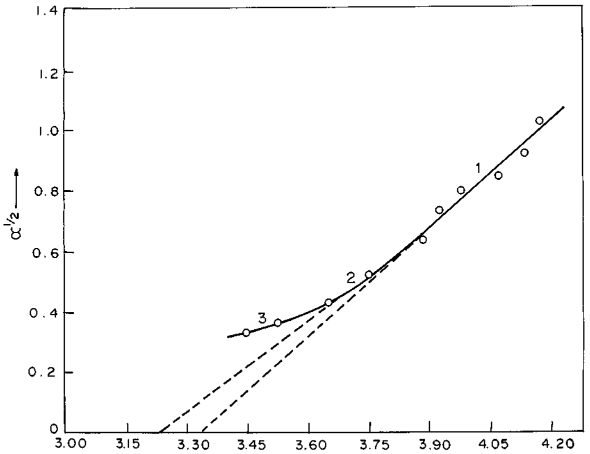

Fig. 4. Plot of photon energy *versus* square root of the absorption coefficient α, for the unexposed sample. The band gap is found by taking average of the intercepts made on the x-axis by extending the parts (1) and (2) of the curve.

Employing the method of least square fitting the curve was found to be representated by

$$E_g = 3.3 - 1.4 \times 10^{-3}\ I$$

and percentage error is found to be 0.1%.

The value of E_g for the unexposed sample is found to be 3.28 eV as shown in Figure 4. The parts (1) and (2) of the curve correspond to emission and absorption of phonons [14]. With increasing beam intensity it gradually falls, down to 3.11 eV for the intensity 125 mW. The exposure time was restricted to 7 minutes, because longer exposure with beam intensities of 100 mW and more damaged the crystal by deforming it and/or piercing a hole through it and irradiation time of less than 7 minutes were found to produce no significant structural changes. With the beam intensity fixed at 50 mW, its variation with exposure time has a curious behaviour. Initially it falls to a strikingly low value of 3.07 eV with just 15 minutes of exposure and then gradually rises to the normal value of 3.28 eV for the unexposed sample.

Fig. 5. SEM photograph of the sample exposed for 15 minutes duration with beam intensity of 50 mW.

(c) The oscillation photograph of the sample irradiated with 50 mW beam intensity for 7 minutes shows the reflections lying along highly discontinuous powder rings of Cadmium iodide (Fig. 1b). Keeping the exposure time same and increasing the beam intensity gradually reduced the discontinuity. It follows that the polycrystallinity of the material progressively increases with increasing beam intensity.

The oscillation photograph of the sample exposed to 50 mW beam intensity for 15 minutes (Fig. 1c) displayed far less discontinuity of the powder rings as compared to the sample exposed for 7 minutes (Fig. 1b), thus implying transformation of the irradiated part of the sample into a material of considerably high polycrystallinity. However, on increasing the exposure time in steps for the same beam intensity, the discontinuity steadily increased, so much that after 60 minutes exposure total discontinuity was achieved, like in Figure 1a, meaning thereby that the exposed part had attained single crystal character.

(d) Exposure of the crystal for 15 minutes with 50 mW beam intensity considerably obliterated the surface over a pear-shaped region around the site of impingement of the beam (Fig. 5). On raising the exposure to 30 minutes for the same beam intensity the region of obliteration was seen to widen, with the formation of randomly scattered grains of various sizes and shapes inside it. Further raise to 45 minutes exposure led to mutually joined neighbouring grains all over a further extended region. Finally, an exposure time of 60 minutes made the grains to join perfectly to produce a smooth surface with a few slip lines running over it. Exposure of the crystal for less time, *viz.* 7 minutes, to 50 mW intensity beam produced fragmentation in the region of impact of the beam. A stepwise increase in the beam intensity led to widening of the affected area. The exposure to 100 mW and 125 mW beams also produced thermal etch pits within the affected region.

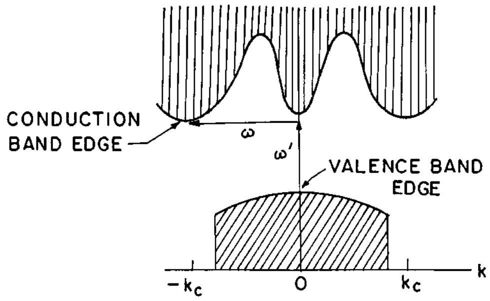

Fig. 6. Energy band diagram for an indirect gap material separated by a wave vector $\mathbf{k}_c$; ω: phonon frequency, ω': photon frequency.

4 Discussion

The CdI_2 crystals are known to have indirect band gap [9,10]. For an indirect gap material, the minimum energy gap of the band structure involves electrons and holes separated by a substantial wavevector $\mathbf{k}_c$ (Fig. 6). Further, unlike a direct gap material, the edges of the conduction band are widely separated in the **k**-space. For satisfying the requirement of conservation of wavevectors it is not enough to merely visualize a direct photon transition at the minimum gap energy. It becomes imperative to invoke the creation of a phonon in the process, whereby the condition of conservation is met as [15]

$$\mathbf{k}(\text{photon}) = \mathbf{k}_c + \mathbf{K}; \quad \hbar\omega' = E_g + \hbar\omega$$

($\mathbf{K}$: phonon wavevector; ω': photon frequency; E_g: band gap; ω: phonon frequency).

Assuming that all atomic plane displacements have the time dependence $e^{-i\omega t}$ the solution of the equation of motion of the phonons is obtained as

$$-M\omega^2\, U_s = \sum_p C_p(U_{s+p} - U_s)$$

where M is the phonon mass, U_s and U_{s+p} are the displacements of the atomic planes s and s + p, and C_p is the force constant between the planes mutually removed by the distance p [15].

On the left hand side ω^2 has a positive value for both + and − sign of ω. However, since physically a phonon must have positive value of energy it is both suitable and conventional to take ω as positive. Yet it is possible that at some instant of time the crystal structure is rendered unstable due to an unusual dependence of the force constants on temperature, which will make ω^2 negative. Then ω becomes imaginary. However, since the corresponding structural mode is unstable, the crystal will spontaneously tend to transform into a stable structure. An unusual temperature dependence of the force constants may result from a unusual supply of the energy to the crystal.

When the exposure time of the crystals is varied, with the beam intensity fixed as 50 mW, the band gap initially drops to a low value, *viz.* 3.07 eV (exposure: 15 minutes) and then gradually rises to be ultimately restored to the original value, *viz.* 3.28 eV (exposure: 60 minutes). The large initial drop indicates an unusual disturbance in the crystal structure which affects the stability of the structure. As mentioned earlier, in theoretical terms it implies that in the equation of motion for the phonons ω^2 becomes negative, which physically means that the structure is rendered unstable. Since the energy of phonons must be positive, the lattice will spontaneously tend to acquire stability. However, only a quasi-stable structure is likely to be formed, as the extreme rapidity of the process may not permit the formation of a fully stable structure at once. The opportunity for acquiring stability is presented upon increasing the time of exposure of the sample to the laser beam, which tends to melt the material locally at an around the position of the beam. The melting is naturally followed by a tendency of the material to recrystallize and thus to be restored to the original stable structure. Longer exposure times lead to more complete local melting, which in turn promotes better recrystallization, so much so that for a prolonged exposure of about one hour complete recrystallization back to the parent structure becomes possible.

With reference to the energy band diagram (Fig. 6), the initial marked drop in the value of the band gap from 3.28 eV to 3.07 eV implies that the shape of the conduction band has suitably changed to produce the observed drop. The subsequent changes in the band gap resulting from progressively increasing exposure time of the sample similarly imply further appropriate changes in the shape of the conduction band.

The SEM photographs of the sample surface exposed to the laser beam confirm the said process of melting followed by recrystallization. As seen in Figure 5 the 15 minutes exposure melts the material and considerably obliterates the surface around the position of impingment of the beam. After the exposure, the sample gradually cools down to the room temperature. After 30 minutes exposure, the obliterated region is widened and recrystallized grains of various sizes and shapes are formed. The crystallization apparently takes place after the exposure when the sample cools down to the room temperature. A longer exposure of 45 minutes helps to enhance recrystallization with the recrystallized grains tending to join each other. Further increase in the exposure to 60 minutes helps to join the grains together almost completely to produce a smooth surface. The presence of slip lines now on the surface confirms that the crystallization has nearly completed.

The foregoing inferences are further supported by the X-ray diffraction data. On the oscillation photograph of the sample exposed to 50 mW beam intensity for 15 minutes, the reflection are found to be elongated along the powder rings, thus implying that the exposed portion of the sample possesses polycrystallinity but to a limited extent. On increasing the exposure time in steps the elongation progressively decreases until after 60 minutes exposure it totally vanishes, meaning thereby that the exposed part attains a truly single crystal character. Thus the X-ray photographs substantiate that the crystal structure tends to acquire progressively greater stability with increase in the exposure time.

When the crystals are exposed to varying laser beam intensity for a fixed value of exposure time, *viz.* 7 minutes, the band gap is found to reduce slowly but steadily (Fig. 2). Apparently, the incident beam disturbs the crystal structure, but not drastically, as before. The disturbance presumably causes alterations in the shape of the conduction band, leading to a different value of the band gap after each exposure. Expectedly, the change in the band gap is unidirectional, such that the greater is the disturbance in the crystal structure the lower is the value of the gap.

The SEM photograph of the crystal exposed to 50 mW intensity for 7 minutes reveals fragmentation on the surface in the region of impact of the beam. A stepwise increase in the beam intensity leads to a progressive widening of the fragmented area. On the corresponding X-ray photographs the powder rings tend to become less discontinous, *i.e.* the continuity of the powder rings tends to increase, until finally they look quite continuous. It follows that the exposed part of the crystal tends to become increasingly more polycrystalline with progressive increase in the laser beam intensity. Such progressive alterations in the crystalline character of the exposed part presumably lead to corresponding gradual change in the shape of the conduction band, bringing about in turn a gradual unidirectional change in the value of the band gap, as actually found.

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