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Stress effects on HgI_2 optical properties

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The effect of small deformations on the optical properties of HgI_2 is measured in this work in a qualitative way. It has been found that the gap position slightly decreases with pressure, whereas the photoluminescence associated with the presence of intrinsic defects increases more than three orders of magnitude.

Over the last few years there has been a renewed interest in mercuric iodide (HgI_2) in order to obtain further knowledge about its structural and physical properties. The material is an intrinsic semiconductor characterized by a wide band gap (2.11 eV) at room temperature and high atomic weight (Hg:200.6, I:126.9). These features lead to a photoconducting material in which all the crystal volume is effective, low dark current, and high radiation stopping power, all of which make this material suitable for x-ray and gamma-ray detection. Unfortunately besides these interesting properties, it presents some disadvantages which make it difficult to obtain single crystals with good radiation response: above 400 K, the stoichiometric compound suffers a destructive phase transformation from the red tetragonal (α) to the yellow orthorhombic (β) structure. Also, mercuric iodide has a high vapor pressure, which means that crystals should not be exposed to vacuum during measurements. For these reasons, there are still only a few papers concerning this material in which some discrepancies between authors still exist. Many of these works focused on the determination of optical properties, such as optical absorption and photoluminescence.

Over the last 40 years, the HgI_2 band-gap energy has been measured at different temperatures by optical or electrical methods.[1–4] Values of about 2.1 eV at room temperature are obtained and, in general, it is assumed that the observed transition is related to exciton formation. In spite of this, there is some controversy about the direct or indirect character of the transition. The temperature dependence shows a T^2 law following the Varshni formulation,[5] with coefficients of approximately 1.7×10^{-3} eV/K.

Mercuric iodide also exhibits photoluminescence at low temperatures. This behavior was first systematically studied by Bube.[1] On illumination with 3.40-eV (365-nm) light, the emission spectrum obtained at 77 K consists of three main bands at 2.31 eV (536 nm), 2.19 eV (567 nm), and 2.00 eV (620 nm), called bands I, II, and III, respectively, the latter being the more intense. It was later found that at 4 K band I shows a fine structure composed of up to 26 peaks.[6–9] The origin of this emission is related to the radiative recombination of free and bound excitons.[6] Above 35 K, band I consists only of free exciton recombination and its phonon replicas, with a calculated exciton binding energy of about 3–4 meV.[6] To explain the observed number of peaks, the existence of two close energy minima near the conduction band has been proposed, which would give rise to direct and indirect transitions.[8] This model would also explain the unclear results about the direct or indirect character of the optical-absorption measurements of the band gap.

In general, it is accepted that bands II and III are related to emissions resulting from radiative recombination of electron-hole pairs at defects. Defects associated with stoichiometric deviations (iodine and mercury vacancies) could be responsible for band-II emission,[7] and the existence of impurity centers could lead to luminescence radiation at 2.00 eV (620 nm, band III).[6] Besides these bands, a low-energy broadband has been observed,[10] with its maximum located at 1.77 eV (700 nm), associated with strongly deformed crystal regions.

The aim of this work is to study the effect of small deformations on the optical properties of HgI_2 single crystals. It will be shown that these deformations induce dramatic changes.

Crystals used in this study were from two different origins. The majority were grown at the Crystal Growth Laboratory of the Universidad Autonoma de Madrid by the Temperature Oscillation Method (TOM).[11] The Baker HgI_2 starting material is first purified by a sequential sublimation procedure at 150 °C under continuous vacuum, followed by a close-tube melting at 300 °C and a subsequent close-tube sublimation at 150 °C. A cylindrical ampoule is then filled with the purified material and closed in dynamic vacuum. Growth begins with the condensation of a nucleus on a cold finger. Typical crystals of $5\times5\times3$ cm^3 are obtained. Thin single-crystal samples ($5\times5\times0.5$ mm^3) were wire-saw cut normal to the (001) direction in 5% KI, mechanically polished in 5% KI, and preserved in the dark in a desiccator. Commercial crystals (EG&G) were also used to confirm the results.

Optical-absorption and luminescence measurements were performed in a specially designed sample holder. It consists of a sandwichlike structure in which the sample is inserted between two optical sapphire windows,

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separated by a Teflon layer, to avoid the exposure of the crystal to the cryostat atmosphere. The whole system is fixed by metal screws to the cryostat finger using two brass supports. Turning the screws or modifying the thickness ratio between the Teflon sheet and the crystal, the later may be submitted to different uniaxial compression stresses.

Optical-absorption measurements were made with a Cary 17 spectrophotometer. A small cryostat, designed to be inserted into its measuring cell and able to hold the previously described sample holder, was used for low-temperature studies. The sample temperature is measured by a type-*K* thermocouple and can be varied between 90 and 400 K with a small oven attached to the cold finger. Measurements are made between 0.49 and 3.10 eV (2500 and 400 nm, respectively).

Photoluminescence measurements were performed using a 6-W Ar-ion laser as the excitation source. Wavelengths at 2.41, 2.47, and 2.50 eV (514, 502, and 496.5 nm, respectively) were used. Light emitted from the sample was collected with a 52-mm-diameter lens and focused on the input of a quartz optical fiber, guided to a 0.5-m-high-resolution monochromator and measured with a cooled EMI9659QB photomultiplier with S20 response. The emission spectra have been corrected from the system response. For low-temperature measurements, the sample holder was installed on the cold finger of a close-cycle helium gas cryostat able to work between 30 and 700 K.

A typical optical-absorption spectrum of a HgI_2 single crystal is shown in Fig. 1 (curve *a*). No significant differences have been observed between the different single crystals analyzed in this work. The spectra show no features with the exception of the sharp increase of absorption around 2 eV, related to the absorption edge. As temperature decreases, the edge moves toward higher energies. Fitting the spectra obtained to the Urbach and Varshni formulas it is possible to calculate the band-gap energy and the steepness constant as a function of temperature. The results obtained both at room temperature and as a function of temperature are in close agreement with those found by other authors.[2,4]

When the crystal is deformed (by tightening the screws of the sample holder) the absorption spectra slightly modifies in the gap region. It is observed that the gap and the steepness constant decreases. Figure 2 shows these results for different degrees of deformation. This effect has been observed on many other semiconductors and, in general, it can be associated with a change of the lattice dimensions induced by deformation. Concerning mercuric iodide these results are in agreement with those of Kuroda, Inabuchi, and Nishina,[12] who observed redshifts in the fundamental absorption edges of tetragonal crystals when hydrostatic pressure was applied. They concluded that the decrease of the energy gap with pressure is related to relative energy gains of bonding and antibonding states, which is accompanied by a decrease in the ionicity.

Figure 2 (curve *a*) shows a typical photoluminescence spectrum at 30 K. The sample was excited at 2.41 eV (514 nm) with a power of about 30 mW. It was taken on a crystal free of induced stresses. In these conditions, the overall intensity is very low. Band I could not be well defined, but, if it is magnified, those peaks located at 2.34 and 2.33 eV (529 and 532 nm, respectively) can be observed above the background. Band II presents a maximum at about 2.21 eV (560 nm), and band III also appears around 2.00 eV (620 nm). This spectrum has a very marked time dependence, and disappears completely below detection limit after a few seconds. This time

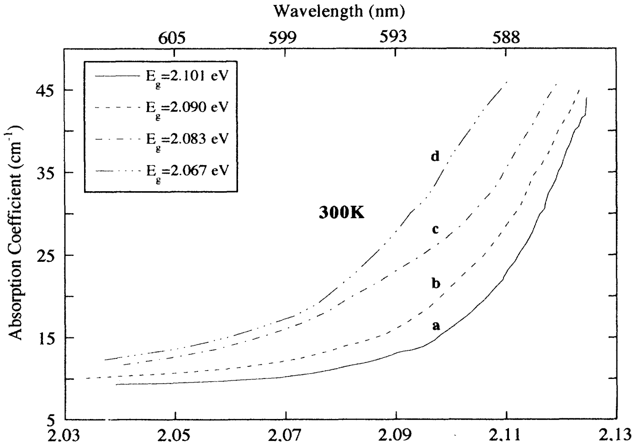

FIG. 1. Optical-absorption spectra at room temperature of a mercuric iodide single crystal as a function of increasing induced pressure: (curve *a*) no pressure (——), (curve *b*) low pressure (— — —), (curve *c*) intermediate pressure (—·—·—·), (curve *d*) high pressure (——-).

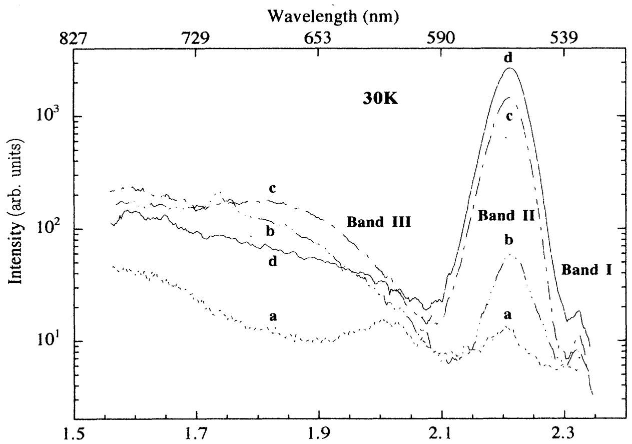

FIG. 2. HgI_2 photoluminescence spectra at 30 K obtained under induced pressure during excitation at 514 nm: (curve *a*) no pressure (——), (curve *b*) low pressure (— — —), (curve *c*) intermediate pressure (—·—·—·), (curve *d*) high pressure (——-).

dependence was observed in one of the first works on HgI_2 photoluminescence,[13] but has not been mentioned since.

If luminescence is measured when the crystal is deformed, large changes are observed in the emission. Figure 2 shows the spectra obtained for increasing deformation of the crystal. The absolute intensity of the whole spectrum increases notably, although the effect is larger for band II. In the extreme case, the band-II intensity was enhanced by more than three orders of magnitude. An additional structure can be found around 1.77 eV (700 nm), in which an intensity increasing effect with induced deformation is also present. The evolution with time also changes drastically, showing no time dependence in the samples under stress. The temperature dependence has also been studied. It has been found that band II decreases much faster than the others upon raising the temperature. In fact, at a temperature around 90 K band II decreases by more than two orders of magnitude, whereas band I decreases by only a factor of 2 and the structure around 1.77 eV (700 nm) remains almost constant.

When pressure is removed (by loosening the screws) the crystal completely recovers its absorption and emission characteristics. This means that the observed effect in the absorption and luminescence characteristics is not permanent, but only appears under pressure.

Taking into account the optical-absorption results and band-edge fittings presented above, it is possible to estimate the optical-absorption spectrum at 30 K. At this temperature the laser excitation lines are completely absorbed on the crystal near-surface region, which must therefore be the origin of the observed luminescence. To check if the observed results are associated with impurity defects on the surface, the same experiment has been repeated after removal of thin layers of the crystal. Chemical etching with 5% KI at 273 K were performed on crystals with photoluminescence spectra previously characterized. In 20 s about 100 μm are removed in these conditions. After treatment, crystal was again compressed and the emission response recorded at 30 K. The spectra obtained were similar to those plotted on Fig. 2, where the band-II maximum is greater than 10^3. The same behavior was found after different etching times. That means that the effect is not related to surface impurities, but probably a bulk effect.

Very similar results are obtained for the samples of commercial origin. The only difference is that the relative heights of bands I, II, and III are different, probably indicating a different concentration of the luminescent centers. Under compression the intensity of the whole spectrum increases with an enhancement of a factor of 1000 on band-II intensity, and again the original spectrum is recovered after compression. These results clearly indicate that the observed behavior is a general one and is not related to the growth method.

Taking into account that the observed effects only appear under stress, it is clear that they are not related to permanent defects induced by deformation. It is well known that bands II and III are related to electron-hole recombination at both intrinsic and extrinsic defects. Experimentally, it is shown that the enhancement is more pronounced in the band related to electron-hole recombination in intrinsic structural defects (band II), which indicates that the defects involved are the same as in the as-received condition, the only difference being the efficiency of the process. It seems reasonable to suggest that in mercuric iodide single crystals the uniaxial stress decreases the gap and in some way enhances the radiative emission processes. To our knowledge this is the first time that this effect has been observed in HgI_2, but not in the best known semiconductors.

From the results obtained, mercuric iodide seems to be a good system to test electron-hole recombination processes, due to its high sensibility response to pressure variations. Also, our results point out that any applied stress, even at very low levels, should be considered as a variable on the interpretation of HgI_2 photoluminescence spectra.

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