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Growth and Characterization of HgI_2, PbI_2 and PbI_2:HgI_2 Layered Semiconductors

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This paper presents a methodology for the preparation of α-HgI_2 by Physical Vapor Transport and of PbI_2 crystals using the Bridgman technique. The results of the growth of HgI_2 diluted in PbI_2 by the Bridgman technique are shown for the first time, its limit of solubility having been determined at 600 ppm of HgI_2 in the PbI_2 matrix. Optical absorption, photoluminescence and electrical conductivity measurements show that the crystals prepared are of good crystalline quality.

Keywords: *mercuric iodide, lead iodide, crystal growth*

1. Introduction

Increasing interest has been focusing on the search for high-energy resolution room temperature X-ray detectors. The development of single detector spectrometers and, lately, of multidetector array systems has been driven by the specific needs of space exploration and synchrotron radiation applications. Recently, layered semiconductors materials have been found to possess a number of properties that make them quite attractive for such applications. Mercuric iodide (HgI_2) and lead iodide (PbI_2) crystals present an excellent response as X-ray and γ-ray detectors at room temperature. Their high density and high atomic number allow one to manufacture small, compact detectors with a very good volume-efficiency ratio[1-4]. The major advantage in using an HgI_2 or PbI_2 system in many applications is that they do not require liquid nitrogen for cooling, as opposed to most commercially available systems, which are composed of cryogenically cooled silicon or germanium X-ray detectors.

Several studies have been carried out on the properties, preparation and application of the HgI_2 layered semiconductor compound and much progress has been made through improved purification of starting materials and growth techniques[5-7]. However, good PbI_2 crystals have only recently been prepared[8]. In this work, we present a methodology for the preparation of α-HgI_2 by Physical Vapor Transport and for PbI_2 crystals using the Bridgman technique. We also show, for the first time, the results of the growth of HgI_2 diluted in PbI_2 by the Bridgman technique. In this specific case, the solubility limit was determined and some electric, structural and optical properties were measured.

2. Experimental Procedure

2.1. Purification and crystal growth

α-HgI_2

Successful growth of high optical and structural quality α-HgI_2 single crystals is largely dependent on the purity of the materials used. Amorphous carbon and carbon complex compounds are present in mercuric iodide and it is necessary to purify the starting materials. All the purification experiments carried out used red HgI_2 from Fluka Chemika (99.5% pure) and from Aldrich Chemical Co. (99.999% pure). The repeated sublimation technique was employed due to the high vapor pressure of mercuric iodide (0.1 Torr at 120 °C). In this technique, the starting materials were placed inside a cylindrical glass ampoule specifically designed to repeat the sublimation cycles after the chemical and vacuum cleaning process. Approximately 15 g of red HgI_2 was used in each experiment. The ampoule was then sealed under high vacuum conditions, and a sublimation cycle was initiated in a homemade vertical furnace. An axial temperature gradient, typically of 20 °C/cm, was imposed to evaporate the mercuric iodide. Approximately

70 h were necessary to evaporate all the HgI_2, which was then deposited in the cold extremity of the ampoule. In each cycle, the impurities (black from red HgI_2 Fluka and grayish from Aldrich) deposited at the hot extremity were eliminated by sealing off part of the glass ampoule. After each cycle, the amount of the impurities decreased drastically. Black and grayish impurities were associated to amorphous carbon and hydrocarbon, as suggested by Piechotka and Kaldis[6].

After the purification process, the mercuric iodide was used as a source in crystal growth runs. Every growth experiments were performed by the Physical Vapor Transport (PVT) technique[9], in a homemade equipment shown in Fig. 1A. This system consisted of a transparent resistive furnace equipped with an 808 Eurotherm temperature controller. Vacuum was used as thermal insulation and the typical temperature fluctuation was 0.5° Celsius. A cold finger was used as a heat exchanger with a temperature control better than ±0.3 °C. The temperature profile of our crystal growth system (Fig. 1B) was measured using a Chromel-Alumel thermocouple when the furnace was empty, that is, without the ampoule. The ampoule with red mercuric iodide was placed in an area of the furnace where the temperature was approximately constant (Fig. 1B). A small area of the cold finger was put in contact with the growth ampoule in a predetermined position. The temperature gradient established in this area was responsible for the nucleation process. Seed selection was carried out by the trial and error procedure. The following growth of the red HgI_2 crystal was possible through a cooling temperature program applied to the cold finger. The optimal mass transport responsible for growth was achieved through maximization of the aspect ratio (height/ radius of ampoule). After some tests, we were able to grow good quality crystals of reasonable size (0.6 cm^3) and with a very well defined external morphology. Figure 2A shows one of the crystals obtained by this technique.

PbI_2 and PbI_2: HgI_2

Lead iodide is a more stable compound than mercuric iodide due to its lower vapor pressure and its stable crystalline structure up to its melting point. These two characteristics make it easier to prepare than red HgI_2. In our experiments we used PbI_2 from Johnson Matthey Co. (99.999% metal pure) which was purified by recrystallization to avoid organic impurities.

A quartz ampoule (8 mm in internal diameter and 95 mm in length) was used in all the crystal growing runs. It was washed with detergent and distilled water, chemically cleaned in a HF and HNO_3 solution (1:1 in volume) for approximately 15 min and thermally treated at 800 °C under high vacuum conditions. After this step, the recrystallized PbI_2 was placed in the ampoule, sealed under high vacuum (~10^{-5} Torr) and put into the Bridgman furnace.

The Bridgman equipment had previously been built and thermally characterized[10]. The axial temperature gradient measured during crystal growth was 35 °C/cm. All the PbI_2 prepared in our system were yellowish and transparent and easily cleaved in the direction perpendicular to the c crystallographic axis. Bubbles appeared only on its external

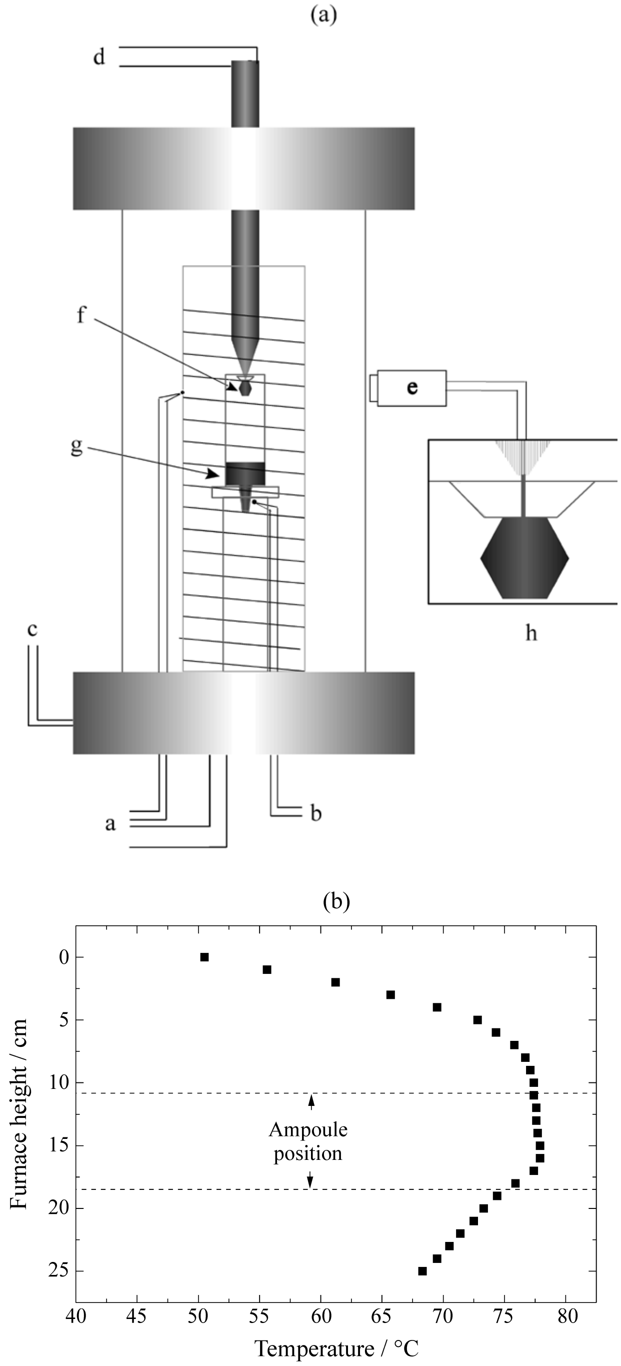

Figure 1. (A) Schematic drawing of the crystal growth furnace. a- temperature controller; b- source material temperature monitoring; c- vacuum system output; d- cold finger temperature controller; e- CCD video camera, f- HgI_2 single crystal, g- source material, h- video monitor. (B) Temperature profile of furnace without the ampoule inside.

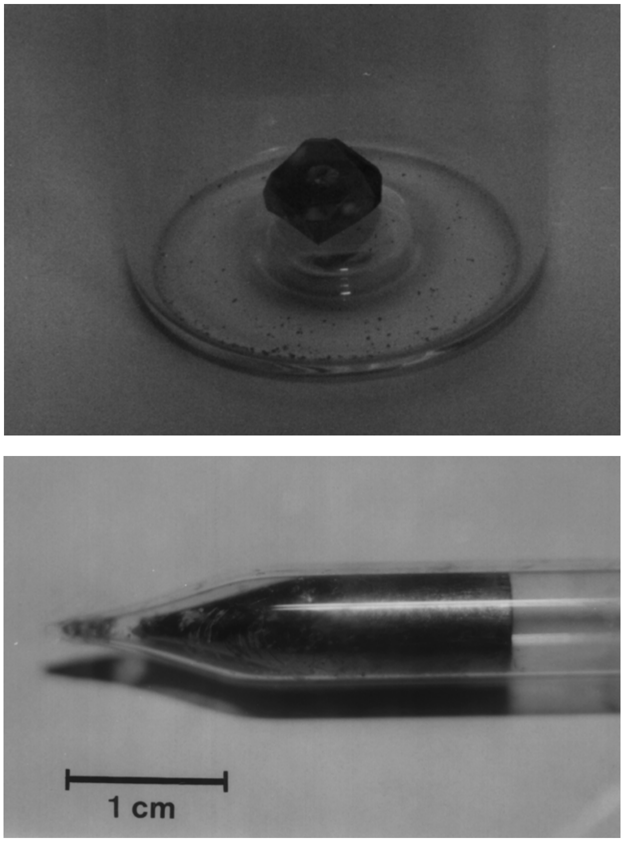

Figure 2. (A) Mercuric iodide single crystal grown by PVT method. (B) PbI_2 crystal grown by Bridgman technique.

surface and there was no adhesion to the quartz ampoule. This last characteristic is an indication of the absence of OH^- impurities in our experiments, as suggested by Eckstein *et al.*[11]. Figure 2B shows a PbI_2 single crystal grown under the experimental conditions described above.

PbI_2: HgI_2 crystals were grown at five different nominal concentrations (50000 ppm, 5000 ppm, 1100 ppm, 680 ppm and 600 ppm) also following the experimental routine of the pure lead iodide. A segregated phase of mercuric iodide was observed in most of the experiments, and it was associated to the structural difference between PbI_2 (hexagonal structure) and HgI_2 (tetragonal structure). Indeed, a large amount of HgI_2 in the bulk and on the surface of the grown crystal was detected at a high nominal concentration. A small amount of segregated phase was detected in the experiment with 680 ppm of mercuric iodide. On the other hand, no segregated phase was detected with a nominal concentration of 600 ppm of red HgI_2. These crystals were transparent and were reddish in color. It was assumed that 600 ppm of HgI_2 in the liquid phase is the solubility limit for PbI_2 crystals.

2.2. Characterization

Photoluminescence (PL) measurements were carried out using an Ar ion laser tuned to 458 nm. The samples were fixed with teflon tape on a cooled copper finger of a closed-cycle helium cryostat to avoid any chemical reaction, and cooled to a temperature of about 15 K. The PL radiation was dispersed in a 0.5 m monochromator with 0.01 nm resolution and detected by a photomultiplier tube using conventional lock-in detection. All the experiments were carried out under very low excitation intensities to avoid thermal heating of the sample and identical optical paths.

The optical band gap of the crystals was determined by absorption measurements, in the visible spectral range, at room temperature (300 K), using Cary 17 equipment.

The DC conductivity measurements were made of all grown crystals at room temperature using a voltage source and an electrometer to detect the current. The electrical contacts were made by pressing the sample between brass plates.

3. Results and Discussion

The low temperature PL spectra of HgI_2 samples grown after three different purification procedures are shown in Fig. 3. In (a), a seed was obtained after one cycle of purification, in (b) a grain of a polycrystalline material was obtained from two purification cycles, and in (c) a single crystal was obtained from three purification cycles. The last two samples were grown by the PVT method. The results

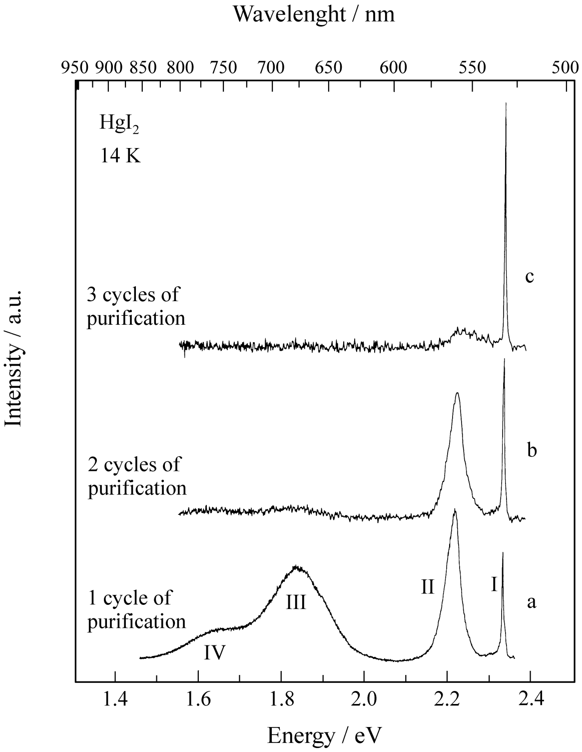

Figure 3. Photoluminescence spectra of α-HgI_2 samples grown after three different purification procedures. Measurements were carried out perpendicularly to the (001) crystalografic plane.

show the effect of purification on crystalline quality. Four bands were observed in the single purification cycle. The broad III and IV bands located at 1.844 eV and 1.646 eV, respectively, are associated to impurities. Band IV and three other bands have already been analyzed by Merz *et al.*[12]. A comparison of their spectra shows that our single cycle purification spectrum is very similar, with a coincidence of bands I, (2. 335 eV) II (2.216 eV) and IV (1.640 eV). Merz *et al.* also labeled a broad band, present only in raw material and located at 2.000 eV, as B3. This band disappeared after the first purification cycle, and was also absent in our spectra. The major difference in our spectra is the presence of the band located at 1.844 eV. We attributed this band to copper, as a result of an accidental contact of the sample to the copper of the cold finger, although teflon tape was used for isolation. This attribution was based on the study performed by Bao *et al.*[13], who first attributed this band to copper. They studied the photoluminescence spectra taken from the same spot on an HgI_2 crystal obtained before and after a semitransparent Cu layer was deposited, where and a broad band centered at 672.0 nm (1.844 eV) appeared after the deposition

A comparison of the (a), (b), and (c) spectra (Fig. 3) shows that the sample with two purification cycles does not present the broad band that is further away from the band edge. Moreover, the band II to band I ratio decreased. There was a further decrease in band II to band I ratio with three purification cycles, and the intensity of band II was also considerably lower. The band II to band I ratio and the absolute intensity of band II were associated to changes in stoichiometry by Merz *et al.*[12] and Schieber *et al.*[14]. They demonstrated that both factors increased in successive sublimation runs, when each run was performed under dynamic vacuum conditions, which might reduce the iodine concentration by preferential removal of the more volatile species. Thus, our results show that the triple purification cycle sample has no impurity bands and is not iodine deficient, as a result of carrying out the sublimation processes in closed tubes. Another feature of these spectra is that band I is, in fact, the predominant line of a great set of lines in the region near the band edge. This region was studied by several authors[15,16], and Bao *et al.*, in 1990[17], identified 26 emission lines from 2.343 eV (529.0 nm) to 2.295 eV (540.0 nm), the predominant line, located at 2.335 eV, being due to zero-phonon line emission of polariton A[15], and other extremely near lines, which are not resolved in our spectrum, are due to bound excitons.

Figure 4 illustrates the PL emissions near the band edge for PbI_2:HgI_2 samples containing nominally 600 ppm, 5000 ppm and 50000 ppm of HgI_2 in the source materials. The same figure also shows a spectrum of pure PbI_2, for comparison. It should be pointed out that although doped PbI_2 samples are more reddish than the pure ones, the PL spectra do not present any detectable red shift. In the 2H polytype of PbI_2, the strongest sharp emission line is located at 2.493 eV, corresponding to a bound exciton recombination, an attribution given by Gähwiller and Harbeke[18], and is seen in the pure PbI_2 spectrum. Another thing that can be seen in the same spectrum is the small emission line due to a free exciton recombination, located at 2.498 eV. In the spectrum with 600 ppm of HgI_2 as well as in the other doped PbI_2 spectra, the intense line of bound exciton is shifted to higher energies located at 2.504 eV, which is characteristic of the 4H polytype[19]. The free exciton line still can be seen, with a much lower intensity, almost as a shoulder of bound exciton peak, located at 2.508 eV, in the 600 ppm doped PbI_2 spectrum. At higher doping concentrations this line is completely destroyed, there is a steady broadening of the emission and reduction of bound exciton line intensity, indicating the deterioration of crystal quality. The pure PbI_2 was only 2H polytype, as demonstrated in a resolved spectrum published elsewhere[20], because it does not have the structures of a sample with more than one polytype, as shown by Levy *et al.*[19]. Hence, the transition of the 2H to the 4H polytype was caused by the introduction of the mercuric iodide in the lead iodide lattice. The broad band located at 2.429 eV in pure PbI_2 is associated to a defect

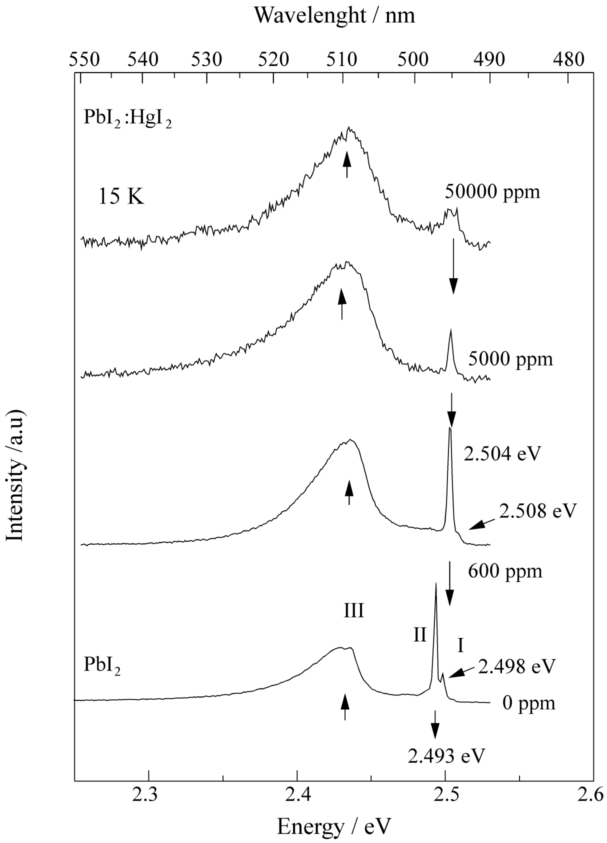

Figure 4. PL emissions near the band edge for PbI_2 and PbI_2:HgI_2 samples.

level recombination[19] and this band shifts to 2.438 eV in doped samples.

The results of electrical conductivity obtained for α-HgI_2 and PbI_2 samples were 1 x 10^{-13} Ω^{-1} cm^{-1} and 3 x 10^{-12} Ω^{-1} cm^{-1}, respectively, coinciding with the best values found in the literature[21]. The electrical conductivities at room temperature in the diluted crystals presented a dispersion of three orders of magnitude (10^{-14} to 10^{-11} Ω^{-1} cm^{-1}), and the sample containing 600 ppm of HgI_2 was the most resistive one, with electrical conductivity of 5 x 10^{-14} Ω^{-1} cm^{-1}, the smallest obtained value for this group of materials. The optical band gap energies determined were 2.10 eV to α-HgI_2 and 2.28 eV to pure PbI_2. These results are very close to the previously published values[13]. The values obtained for the HgI_2 diluted in PbI_2 crystals do not present any difference in comparison to the pure crystal.

5. Conclusions

α-HgI_2, PbI_2 and diluted doped PbI_2 samples were grown, the first by Physical Vapor Transport and the second and third by the Bridgman method. The characterization techniques employed showed that the crystals are of good quality. The PL results from the mercuric iodide samples showed that, after 3 purification cycles, the exciton emission line is sharp and with a high intensity. Moreover, no impurity band was observed and the material was not iodine deficient. Analysis of the PL spectra of doped PbI_2 samples indicated that the introduction of mercuric iodide in lead iodide lattice changed the polytype from 2H to 4H and destroyed the structural quality. It was, nonetheless, possible to determine the solubility limit at 600 ppm of HgI_2, the free exciton line for this sample was still seen in the spectrum and the sample presented the lowest DC conductivity (5 10^{-14} Ω^{-1} cm^{-1}) of this type of material. All the samples measured were very resistive, with values of 10^{-13} Ω^{-1} cm^{-1} of mercuric iodide and 3 10^{-12} Ω^{-1} cm^{-1} of lead iodide, which coincide with the best values reported in the literature. Furthermore, the values obtained for the optical band gap at room temperature are in good agreement with the ones reported previously.

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