Optical Properties of Tetragonal HgI_2 and PbI_2: the Relationship With Crystalline Quality

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We present the main low temperature photoluminescence (PL) features in HgI_2 and PbI_2 related with its crystal and electronic structures. The properties of diluted $Pb_{1-x}Hg_xI_2$ ($0.0005 < x < 0.05$) are also presented. We try to establish a connection between optical properties and structural quality and impurity content in the crystals.

I. Introduction

Mercury iodide is a tetragonal red semiconductor with a relatively large band gap of 2.13 eV at 20 °C. The recent growth [1] of single crystals of HgI_2 has been motivated by the important applications in photocells, room temperature x-ray and g-ray radiation detectors and spectrometers, due to low thermal noise, high resistivity, large average atomic mass and lifetimes of both electrons and holes[2]. Similar properties can be found for the hexagonal PbI_2. In particular, special attention has been given to the interesting properties of excitons[3-4] in both materials, such as the very narrow luminescence emissions (about 1meV), the high value of the free-exciton binding energy (≈35 meV) and the possibility of obtaining Bose-Einstein condensation in such materials[5]. However, there still remains many material and processing issues that are of concern for further development and application[2].

The combination of the interest in improving the material properties for applications and in studying the growth of two similar substances to form a diluted compound, although it appears to be difficult to crystallize from the structural point of view, has put the $Pb_{1-x}Hg_xI_2$ in the list of material used in this work. Taking this into account, we present in this investigation the synthesis of diluted $Pb_{1-x}Hg_xI_2$ ($0.0005 < x < 0.05$) and its related optical properties, looking for a further improvement of these crystals for device application.

II. Experiments

II.1. Synthesis of samples

The α-HgI_2 crystals used in our investigation have been grown from the vapor phase through the method of physical vapor transport (PVT) in a properly evacuated ampoule. This method has been used to produce bigger crystals with superior quality than others. Before the growth, the starting materials were submitted to purification procedures, which consist of repeated sublimation cycles in a special designed ampoule. Purification procedures composed by one, two and three cycles are compared in this work. The crystals were cut perpendicular to the c optical axis.

We used the Bridgman method to the growth of the PbI_2 and $Pb_{1-x}Hg_xI_2$ crystals. The source material (5N) was sealed in an evacuated quartz ampoule and the growth temperature was held at 50 oC above the melting point. The $Pb_{1-x}Hg_xI_2$ crystals used in the present work were grown with a HgI_2 content varying nominally in the proportions between 5% and 0.05%. The studied samples were obtained by cleaving the bulk crystal perpendicular to the c axis.

II.2. Optical measurements

The PL measurements were carried out using an Ar-ion laser emitting at 458 nm. The samples were fixed with Teflon tape on a cooled copper finger of a closed-cycle helium cryostat to avoid thermal stress and any chemical reaction and cooled to a lattice temperature of 15 K. Temperature dependent measurements were carried out in the temperature range from 15 to 200 K. The PL radiation was dispersed in a 0.5 m monochromator with 0.01 nm resolution and detected by a S1 photomultiplier tube using conventional lock-in detection. All experiments were taken under very low excitation intensities to avoid thermal heating of the sample and identical optical path.

III. Results and Discussion

III.1. The HgI_2 crystals: purity and structural quality

Recognizing the importance of obtaining very pure material, we have studied and optimized the purification procedure of the source elements for the PVT growth method. Usually, material with claimed purity of 5N is evidently not pure as far as organic impurities are concerned. Incidentally, even in the advance purification method, like the sublimation method used here, organic molecules (such as hydrocarbons) cannot easily be removed because they sublimate and contaminate the already purified part of the material. Taking this into account, the starting materials were submitted to repeated steps of sublimation.

Fig. 1 shows the low temperature near band edge PL spectra of HgI_2 samples grown after three different purification procedures. As expected, the results show that the success of growing good quality single crystals depends strongly on the purification cycles of the starting materials. We found that three purification cycles are sufficient to obtain high purity samples, as demonstrated by the very intense, yellow excitonic emission about 2.32 eV in the PL spectrum (Fig. 1.a). PL features related with iodine deficiency or impurities (2,2 eV) and structural defects (around 1.8 eV), shown in spectra b and c, are almost absent in high quality samples.

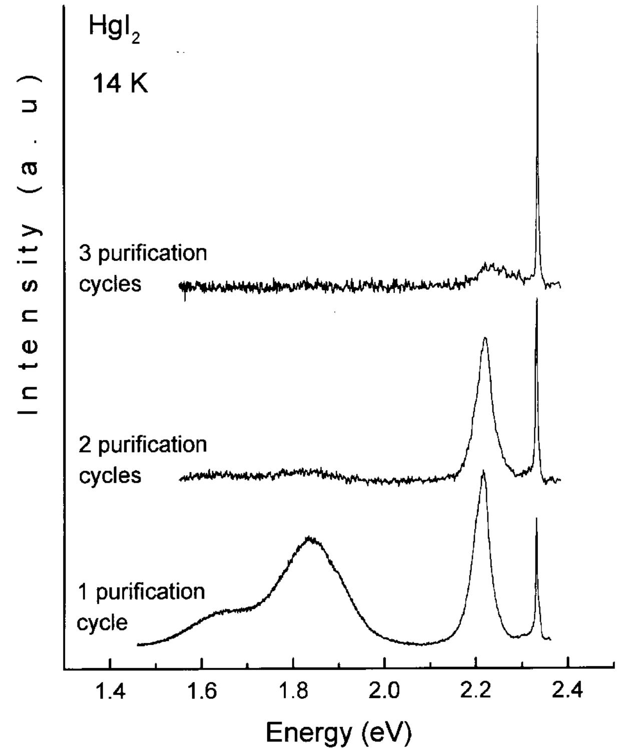

Figure 1. Dependence of the near band edge luminescence (15 K) of the HgI_2 crystals on the purification procedure of the starting materials: after one, two, and three purification cycles.

Fig. 2 resolves the spectrum of the good quality sample (Fig. 1.a) in the spectral range of excitons. In Fig. 2.b, the sole line of tetragonal crystals has intrinsic nature (free exciton) and depends on the orientation of the electric field vector of the incident radiation with respect to the c-axis of these crystals. After rotating the sample 45^o with respect to the c-axis (Fig. 2.a), the single excitonic line splits in its phonon replicas[3]. This well resolved spectrum and the narrow line width (around 3 meV) also demonstrate the good structural quality of our samples. This result is also confirmed by the temperature dependent measurements which show the same strong and symmetrical emissions even at high temperatures (200 K). In general, semiconductors present emissions with very asymmetrical high energy Boltzman tail at high temperatures.

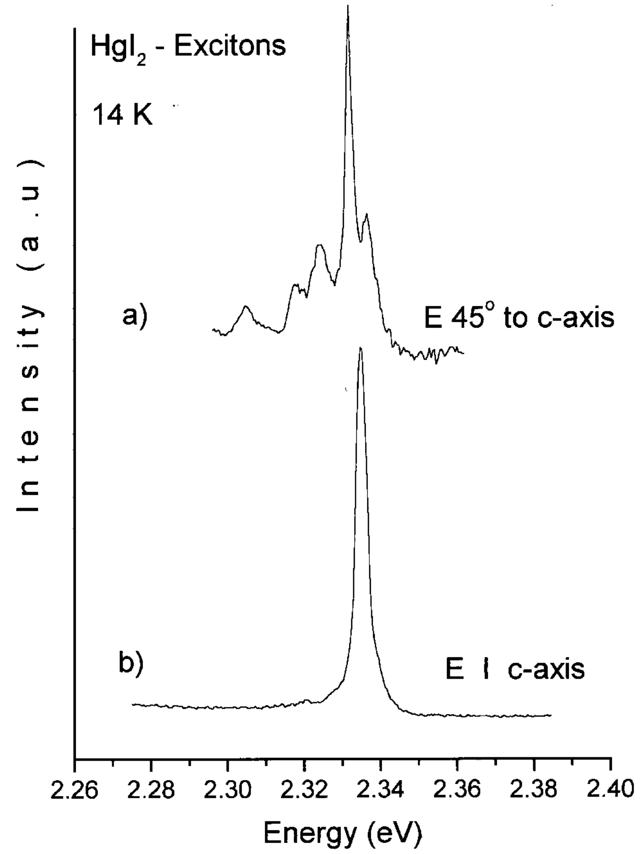

Figure 2: Resolved spectral region of excitons for the HgI_2 showing the dependence with the orientation of the electric field of the incident radiation with respect to the optical c-axis: a) $\vec{E}$ 45° to c-axis and b) $\vec{E}$ $\perp$ to c-axis.

III.2. The PbI_2 crystals: purity and structural quality

Fig. 3 shows the near band edge luminescence of two PbI_2 crystals resulting from different purification cycles of the starting materials before growth. Spectra a and b correspond, respectively, to crystallization from a pure powder material (5N) and from a crystal, resulting from one recrystallization step. One observes for the spectrum b that the strongly amplified defect peak around 2.44 eV and low energy bound excitons by 2.48 eV are almost absent. This result shows that very pure crystals grown from the melting can be obtained even with just one purification step. Details of the excitonic peaks and their relationship with the crystal quality will be given in the following.

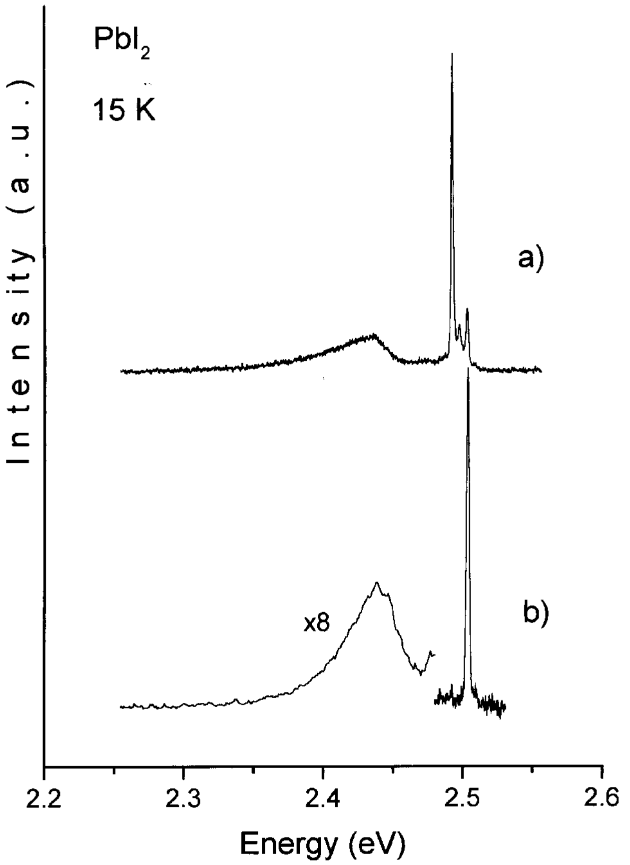

Figure 3. Dependence of the near band edge luminescence (15 K) of the PbI_2 crystals on the purification procedure of the starting materials: (a) crystallization from the powder material and (b) from a pure crystal resulting from one step of recrystallization.

III.3. Optical properties of diluted $Pb_{1-x}Hg_xI_2$

The combination of the interest in improving the material properties for applications and in studying the growth of two similar substances to form a diluted compound, although it appears to be difficult to crystallize from the structural point of view, has put the $Hg_xPb_{1-x}I_2$ in the list of material used in this work. In spite of the difficulties, the relevance of these experiments seems to be unique and we decided to begin the work with very diluted $Hg_xPb_{1-x}I_2$.

In Fig. 4 we present the PL emissions near the band edge for $Hg_xPb_{1-x}I_2$ samples containing nominally 0.05, 0.5 and 5% of Hg in the source materials. For comparison, we also show in the figure a spectrum of pure PbI_2. It should be pointed out that, although crystals have changed its yellow-green color in direction to the red HgI_2, the PL spectra does not present any detectable red shift. On the contrary, we observe a blue shift of the excitonic features with respect of the pure PbI_2 ones. In addition, there is a steady broadening of the emissions and a diminution of the excitons intensity, indicating the deterioration of the crystal quality.

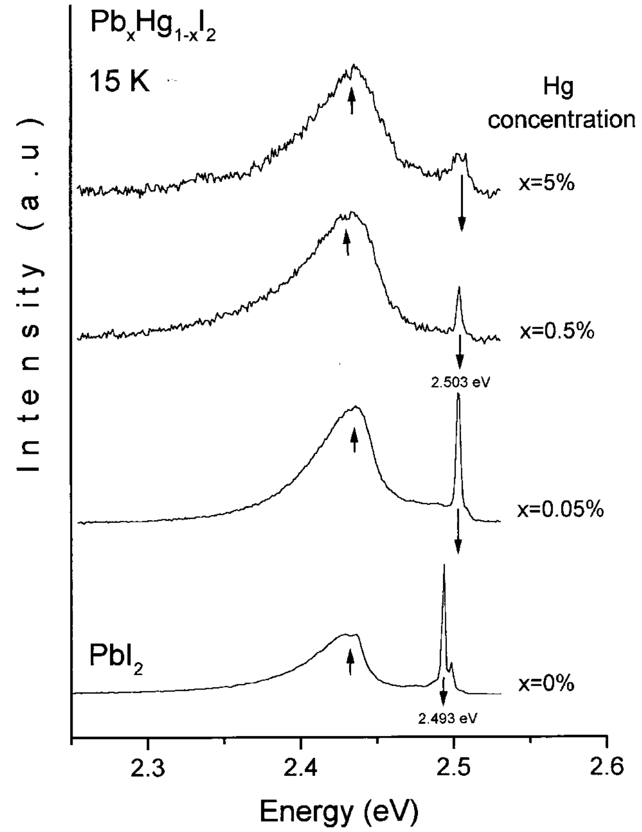

Figure 4: PL emissions near the band edge for $Hg_xPb_{1-x}I_2$ samples containing nominally 0, 0.05, 0.5 and 5% of Hg in the source materials. For comparison, we show also a spectrum of pure PbI_2.

For a better understanding of such phenomena, we show in Fig. 5 the region of excitons for the pure PbI_2 and $Hg_xPb_{1-x}I_2$ (x=0.05%). As mentioned before, the excitonic features for the $Hg_xPb_{1-x}I_2$ are blue shifted with respect of the PbI_2 ones. We carried out temperature dependent measurements which revealed that the high intensity peaks at 2.493 eV and 2.504 eV for both spectra in Fig. 5 are related to excitons bound to an impurity. On the other hand, the small features located at the side of higher energies (assigned by arrows at 2.4898 eV and 2.509 eV) are intrinsic in nature and correspond to the ground state of free excitons. The exciton line width for the pure PbI_2 is 1.8 meV, which is an indication of good crystal quality.

From these results we believe that Hg atoms are incorporating interstitionally in the PbI_2 crystal matrix causing strain which produces the blue shift of the exciton energy.

In addition, for nominal Hg concentrations higher than 0.05%, we observe a segregated red HgI_2 phase in the growth ampoule, that certainly increase the structural defects as shown in Fig. 4. The study of the nature of such defects and their density is being proceeded.

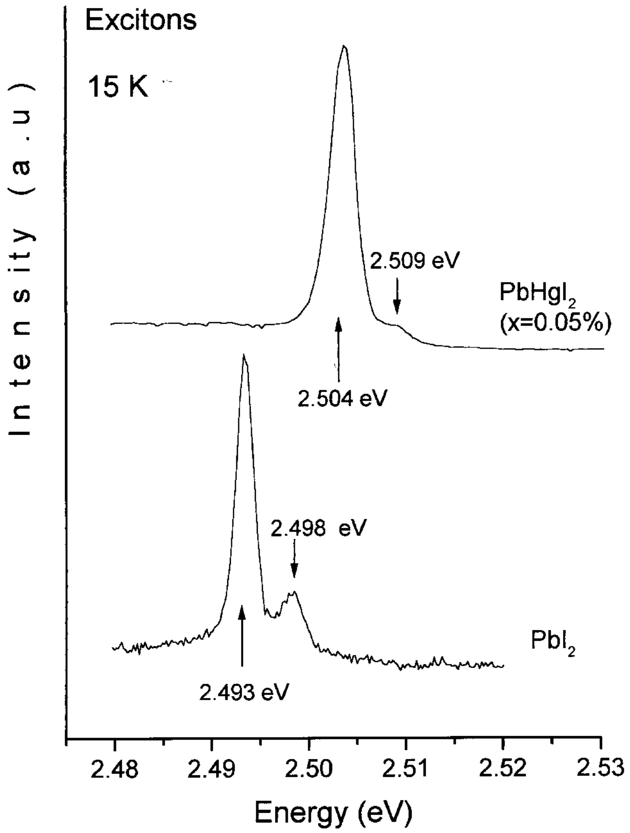

Figure 5: Resolved region of excitons for the pure PbI_2 and $Hg_xPb_{1-x}I_2$ (x=0.05%).

IV. Conclusions

A detailed study of the optical properties of tetragonal HgI_2 and its related compound PbI_2 and $Pb_{1-x}Hg_xI_2$ is presented in this work in relationship with the applied growth method and crystal qualities, such as impurity incorporation and stoichiometry and structural perfection. In the characterization we use low temperature photoluminescence where special attention was given to the properties of excitons in such materials. We found the necessary conditions for the purification of the source material for both PVT and Bridgman method. After few purification cycles of the starting materials we obtain samples with good crystalline qualities and with very low content of impurities. We show also unique results of the growth of diluted $Hg_xPb_{1-x}I_2$. The PL measurements indicate that Hg incorporates in the PbI_2 crystal matrix mainly as interstitial atoms. For Hg concentrations higher than 0.05% it appears a segregated HgI_2 phase during the crystal growth process.

Acknowledgments

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