# NON-DESTRUCTIVE EVALUATION OF PURIFIED HgI<sub>2</sub> STARTING MATERIALS

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In order to prepare high purity starting materials it is necessary to make thorough impurity analyses. The chemical analytical methods which were used during 25 years at EG&G, EM, Inc. and at Sandia National Laboratories-Livermore Ca. to identify these impurities were ICP or SSGMS. However despite the many impurities identified in the ppm and even in the ppb level no direct correlation could be obtained between the impurity content and the performance of the nuclear radiation detectors investigated. The present paper will review results obtained on various purified HgI<sub>2</sub>, using a non-destructive method like photoluminescence that correlates with detector performance. In fact, it is possible to correlate the presence and the intensity ratio of specific bands in the photoluminescence spectrum of a HgI<sub>2</sub> crystal to its impurity content and stoichiometry.

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## 1. Introduction

Mercuric iodide, due to high atomic numbers of the elements (80-53), large band gap (2.15 eV) and the low energy needed to generate one electron-hole pair, is one of the most interesting materials for  $\gamma$  and X-rays detectors at room temperature [1]. The potential for manufacturing spectrometer from HgI<sub>2</sub> has been demonstrated [2], but the role of defects and impurities in the asgrown crystals is not well understood. What is well known is the fact that by improving the purification and/or by adding new purification steps the quality of the nuclear detector response was improved. Which is the bad impurity, which can be accused to be the major culprit for carrier recombination and trapping is not known very accurately. Correlation between detector quality and stoichiometry, structural imperfections in the crystal and impurity contamination have been, extensively studied [3-7]

Mercuric iodide having an adequate purity for successful crystal growth and device preparation can be prepared with a certain sequence of well established purification steps [1]. However, the optimization of the purification process is limited by the lack of reliable analytical methods for measuring impurities in this material. As shown by Merz and al. [8] Bao et al. [9], Schieber et al., [10], the HgI<sub>2</sub> ability to produce high-quality detectors [11] may be tested by a non-destructive method like photoluminescence (PL). In particular, it is possible to correlate the presence and the intensity ratio of specific bands in the PL spectrum of HgI<sub>2</sub> crystal to the detector grade that may be correlated by using that starting material. Examples will be given to show the PL Merz-Bao procedure is used to characterize HgI<sub>2</sub> crystal growth starting materials.

#### 2. Photoluminescence studies

The classical paper by Merz [8] showed that the PL bands change with purification sequence as given in Fig. 1 One could clearly see that band # 2 increases with each step of sublimation of a commercial starting material, by which every x represents one cycle of sublimation and 4x means four cycles of sublimation. Band #3 decreases while band #1 is also changed.



Fig. 1. Photoluminescence at 90K of  $HgI_2$  powders, commercially purchased (0x) and after several cycles of sublimation, 1x, 2x, 3x and 4x meaning the number of sublimation cycles that the material underwent. (reprinted from Ref. 14).

The PL spectrum of HgI<sub>2</sub> is usually divided in two main regions. The near band gap region, or band-1, dominated by excitonic transitions, and the long wavelength region, which includes several broad emissions labeled band-2, band-3 and band-4. The excitonic region consist of at least 26 narrow emission lines [13], attributed to free excitons, bound excitons and excitonic phonon replicas [14]. The band-2, centered at about 560 nm, is the main spectral component of the PL spectra of HgI<sub>2</sub>. It is attributed to iodine deficiency [8]. A third and a fourth band (band-3 and band-4), attributed to impurities present in the material [14], have been observed in the spectra at 620 and 775 nm, respectively.

The defects and impurities responsible of these PL bands play a major role determining the detector performance [8,9]. Good crystallinity is testified by a relatively strong and narrow band-1, and is therefore advisable for high quality detectors. The correlation of band-2 to detector performance is still not clear [9], but certainly the presence of this band is related to iodine deficiency and therefore must be kept as low as possible to avoid stoichiometric defects. The third band, which is induced by contamination impurities, must be avoided for high quality detector preparation.

## 3. Examples of HgI<sub>2</sub> samples analyzed

In order to explain better the correlation between various purification steps and the PL results we are reproducing some of the published results [10] (produced by one of the co-authors A. Zuck for his M.Sc Thesis Hebrew University of Jerusalem). The PL studies were performed at 10 K on various polycrystalline-starting materials of  $HgI_2$  and compared with a high quality single crystal from which spectrometric grade nuclear radiation detectors were prepared. The materials investigated were: 1. Commercial purchased powder of  $HgI_2$  which has a poor purity and which cannot be used to produce nuclear radiation detectors, 2. Aqueous synthesized materials from HgCl2 and KI, 3. Same as #2 synthesized powders but using a different stirring rate, 4. Conventional HgI<sub>2</sub> 4XMSI purification method, which means, four repeated open tube sublimations (4X), melting (M) and followed by an additional close tube sublimation (S) in presence of iodine (I) [1,11]. 5. Re-crystallized by Physical Vapor Deposition from 4XMSI source material. 6. Re-crystallized material from commercial  $HgI_2$  precursor in presence of polyethylene. In this case the source material is mixed with 2% in weight of polyethylene powder and then heated to 250 °C. The HgI<sub>2</sub> condenses at the cold end of the ampoule. This purification method is called PE treatment [1,10,11] and is known in the literature as platelet growth 7. Same preparation procedure as for #6, but where the polyethylene is in form of a sheet. 8. Same preparation as #7 followed by another PE treatment (2xPE). 9. Single crystal grown from starting materials as #4, from which good detectors were prepared, and which was milled and then re-crystallized as #6. The samples were characterized by low temperature (10 K) photoluminescence. The spectra were obtained using the 488 nm line of an Ar<sup>+</sup> laser, with 0.1  $\text{Wcm}^{-2}$  power density and 1 mm laser spot diameter. The spectral resolution was 3.

#### 4. Results and discussion

The PL spectra of the nine samples are reported in Fig. 2. The PL spectrum of the commercial powder is the most structured one. On one side it is characterized by a very sharp and intense excitonic band and a relatively low band-2, meaning that the powder grains have good stoichiometry and crystalline

perfection, on the other side a strong impurity band-3 appears at 620 nm. This confirms the importance of purifying the commercial powder before using it as a starting material for HgI<sub>2</sub> crystal growth. Better results can be obtained by controlled aqueous solution synthesis. Here, while maintaining a good stoichoimetry, the impurity content is much less (shown by a reduction of a factor five of the band-3 intensity) than in the commercial powder and the inclusion seems to be influenced by stirring speed (see differences between samples 2 and 3). As expected, the standard 4XMS procedure [1] depletes the iodine content of the powder (see the strong reduction of band-1 respect to band-2). On the other side the impurity band is completely disappeared, in agreement with previous studies [8]. Re-crystallization of 4XMSI powders (sample 5), worsens the stoichiometry ratio of precursors, while leaving the impurity band-3 fairly low. Much better results can be obtained by PE treatment of the commercial Baker HgI<sub>2</sub> powders (samples #6-#8). Here, as in the 4XMSI sample before re-crystallization (sample 4) we have a strong predominance of stoichiometry defect related band-2 and no impurity related band-3. The same considerations may be done for sample 7 and 8, where in the latter, however, we do not observe any improvement repeating two times the PE treatment. Impurity related band reappears in the control sample 9, probably due to the additional processing steps as milling, etc. Even in this sample the iodine deficiency related band -2 is strongly predominant.



Fig. 2. Photoluminescence spectra of different  $HgI_2$  precursor samples. The scale intensity scale is the same for each spectra. The sample number is reported in each panel.

In the search of highly purified  $HgI_2$  precursors with the correct stoichiometry, the same approach was used to determine the detector performance by PL measurement. This assures a precursor quality as near as possible to the need for high quality detector fabrication.

A strict relation of band-3 intensity and the detector quality is reported in the literature [9]. Fig. 3 shows the relative intensity of the impurity related band in our samples. We recorded several spectra for each sample to overcome possible in-homogeneities in these powder samples. Obviously, preparing the HgI<sub>2</sub> precursors in a controlled environment and choosing the correct stirring speed can obtain a strong reduction of the impurity band. The best aqueous solution sample shows an impurity content that is only slightly higher than the standard 4XMSI treated samples (#4, #5 and #9). A strong improvement in reduction of the impurity content is achieved via PE treatment of the precursors. PE treatment reduces the band-3 relative intensity more than one order of magnitude. The change of polyethylene form from powder to foil is not affecting its purifying ability. Second PE treatment does not improve the impurity reduction. As a matter of fact, all the PE treated samples have impurity content less than the detector grade HgI<sub>2</sub> crystal (sample #9).



Fig. 3. Relative intensity of band-3, normalised to the total spectrum integrated intensity.

No KI-etching was applied to the powder samples before PL measurements. Our spectra are therefore affected by aging effect. As shown by Bao et al. [15,16], it mainly affects the relative importance of the excitonic lines inside band-1. However, the detector grade is influenced by the ratio between band-2 and a specific line in band-1 (line P2) which is unaffected by aging and dominates the band-1 of an aged sample [9]. We therefore simply reported in Fig. 4 the ratio between band-2 and band-1 integrated intensities. As previously observed [8], the sublimation treatments depletes the iodine content of HgI<sub>2</sub>, which gives a band-2 to band-1 ratio of treated powders at least 1 order of magnitude higher than in aqueous solution grown precursors. However, the sample which has undergone to standard PE treatment (poly-ethylene in form of powder), shows a strong reduction of the ratio, which is only a factor three higher than in the aqueous solution samples, therefore displaying a relatively good stoichiometry.



Fig. 4. Band-2 to band-1 ratio of the PL spectrum of HgI2 ay 10k shown in Fig. 2.

#### **5.** Conclusions

The PL characterization of  $HgI_2$  precursors presented in this work suggests the PE treatment as the optimum both for the impurity content and for the relatively good stoichiometry of the resulting powders. Over the standard 4XMSI has the advantage of a lower iodine deficiency that makes it preferable for detector quality fabrication. The mechanism involved in this purification treatment is still under study. It was speculated that polyethylene influences the vapor transport and the mechanism of  $HgI_2$  formation by reacting with impurities or mercuric iodide at the crystal growth surface [11]. We have also demonstrated the ability of PL to provide that analytical method for measuring impurities in this material so important for a real optimization of the growth process.

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