

A COMPARATIVE STUDY ON SURFACE MORPHOLOGY FROM THE HgI₂ SEMICONDUCTORS PREPARED BY DIFFERENT TECHNIQUES

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ABSTRACT

The impurity effect in the surface morphology quality of HgI₂ crystals was evaluated, aiming a future application of these crystals as room temperature radiation semiconductor detector. The crystals were purified and grown by two techniques: (1) physical vapor transport (PVT) and (2) saturated solution from dimethylsulfoxide (DMSO) complexes. Systematic measurements were carried out for determining the stoichiometry, structure orientation, surface morphology and impurity of the crystal. The best quality of surface morphology was found for the crystals purified and grown by the PVT technique. Significant decrease in the impurity concentration was found, purifying the crystal by means of two successive growths by the PVT technique, while a Si contamination in the HgI₂ crystal was observed, during its growth by the DMSO method. Thus, for DMSO technique was not possible to identify the peaks of the other trace elements present as impurities in the PVT crystal, due to the high intensity of the Si peak in the DMSO crystal. It was demonstrated the impurities affect significantly the surface morphology quality from the HgI₂ crystal.

Key Words: Semiconductor crystal, Radiation Detector, Mercury Iodide crystal, surface morphology

1. INTRODUCTION

HgI₂ is a layered semiconductor material with a wide band gap energy ($E_g = 2,13$ eV), high resistivity ($>10^{14}$ Ωcm), high density (7.5 g/cm³) and high atomic number elements ($Z_{Hg}=80$ and $Z_I=53$) [1]. These characteristics became the mercury iodide (HgI₂) a very promising material with large technological applicability as a room temperature radiation detector. However, problems still exist and to grow HgI₂ crystals with suitable purity and surface morphology to be used as a room temperature radiation detector is a technological challenge.

Most of semiconductor crystals are purified and grown by the fusion technique. However, the HgI₂ undergoes structural phase transition below its melting point (259 ° C), what makes its growth by fusion technique more difficult compared to PbI₂ (405 ° C) and TlBr (468 ° C) [2]. HgI₂ can present three solid phases, being differentiated by structural features. One of the phases is known as α -HgI₂, of red color, and it is obtained below the transition temperature, around 127 ° C. Its structure is tetragonal and is the most stable of all phases of HgI₂ [3]. Another phase is the β -HgI₂ of yellow color with orthorhombic structure and it can be obtained in different ways, generating two different types of characteristic polymorphisms.

One way of obtaining it is above the transition temperature, i.e. above 127 ° C: this is known as yellow^{HT} (HT - High Temperature), it is in a complete HgI₂ transition phase, but not totally stable. Another form is metastable, known as yellow^M (M - metastable), and it is obtained by a rapid evaporation of a solvent, which can be below the transition temperature. The third phase of this material is known as orange HgI₂, only having differences in the positions of the mercury atoms between the atoms of iodine. Thus, the fusion technique is not recommended for the growth of HgI₂, other techniques, such as "Physical Vapor Transport" (PVT) [4] or "Saturated Solution" [3] are more adequate for HgI₂ growth.

The performance of radiation detectors is controlled by both intrinsic and extrinsic factors. Carrier lifetime, mobility and the atomic number of the material used for radiation detectors represent intrinsic parameters, while extrinsic factors such as crystallographic perfection, surface morphology and impurity levels can also play a major role in the performance of radiation detectors [5].

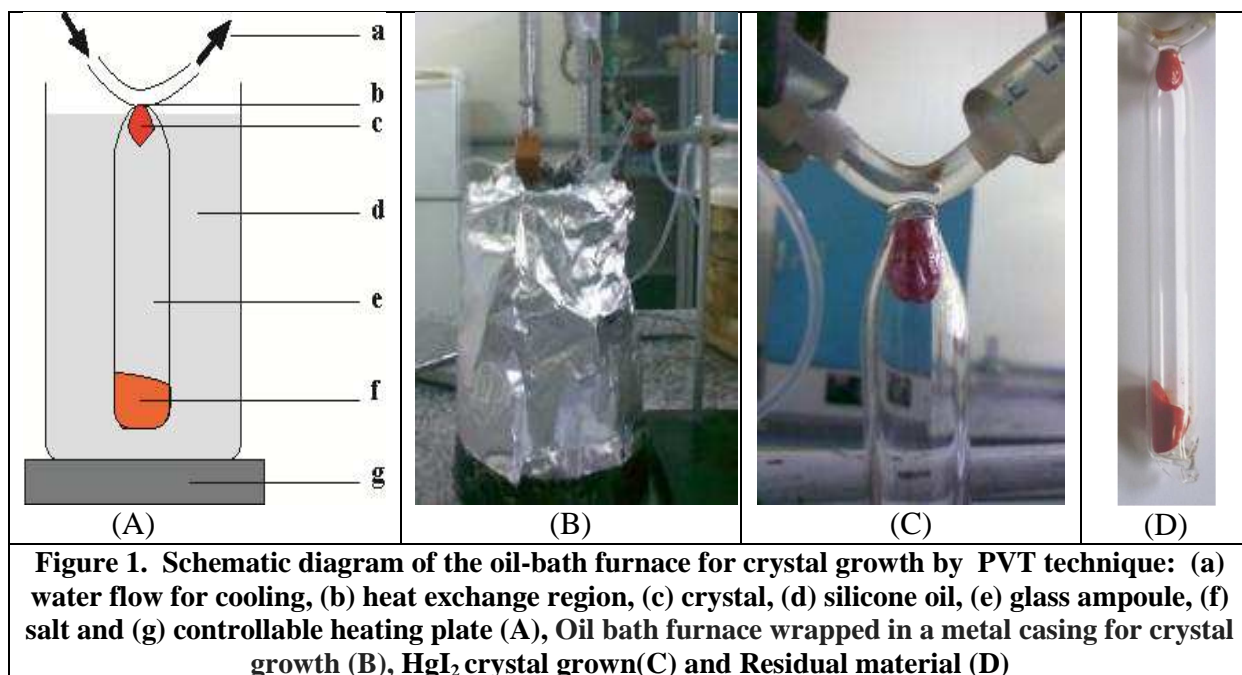
The impurities can influence the charge carrier lifetime and the surface morphology, affecting the detector efficiency. There is agreement in the literature on the difficulty in growing crystals with high crystallographic perfection, high chemical purity and good stoichiometry and surface morphology, suitable to be used as room temperature semiconductor detectors [6,7]. The role of the crystal impurities on the electrical properties and surface morphology of HgI₂ is crucial, and the performance of these detectors has been limited by the crystals quality.

Studies have been carried out to establish a correlation between roughness, surface morphology, and the resulting values of the detector leakage currents with the smoothest surface producing the lowest noise in detectors [8,9]. However, as far as we know, studies related to the impurity effect of the HgI₂ crystal on surface morphology quality have not been previously reported. In this work, the surface morphology of the crystals grown with two different methods, physical vapor transport (PVT) and saturated solution from dimethylsulfoxide (DMSO) complexes were evaluated.

EXPERIMENTAL PROCEDURE

The commercially available HgI₂ powders (Alpha Aesar), with nominal purity of 99.9%, was used as the starting material for growing crystals. The crystals were grown by PVT and DMSO complexes Saturated Solution techniques.

The schematic diagram of the oil-bath furnace, used for HgI₂ crystal growth from PVT is shown in Fig. 1A. For growth, the borosilicate glass ampoules were filled with 5 g of HgI₂ salt, evacuated at 90 °C for 15 min and subsequently sealed, aiming the salt dehumidification, the HgI₂ vapor loss prevention and the addition of contaminants. Next, that the ampoule containing HgI₂ salt at the bottom is placed in the bath of silicone oil and wrapped in a metal casing. The heated HgI₂ salt sublimates to the upper region of the ampoule, being deposited in the heat exchange region, where the crystalline structure is formed. The raw material residual remained at the ampoule bottom. Following the same procedure, the crystal obtained at the upper region was grown twice, aiming to obtain purer crystal.



For the DMSO complexes saturated solution technique, 25 g of the HgI₂ salt was added to 250 ml of DMSO solution under constant agitation and a colorless solution was formed. After that, this solution was left to stand covered with filter paper. Evaporation of the solvent should be quite slow, what is of fundamental importance for the formation of good crystal lattices. As the solvent evaporates, the HgI₂ salt is assembled at the bottom of the glass due to its lower solubility and, consequently, the HgI₂ solubilized forms crystals (Fig. 1B). The crystals grown in the DMSO solution were selected in terms of their appearance and dimension, as shown in Fig. 1B. The selected crystals were re-grown in order to obtain purer crystals, since impurities are expected at each growth.

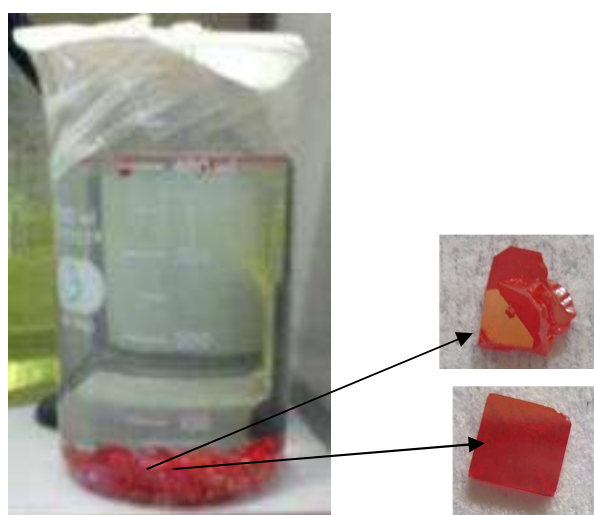


Figure 2. DMSO solution containing HgI₂ crystals and some sampling of the selected crystals from the DMSO saturated solution.

The impurity concentration, the surface morphology and the stoichiometry of the HgI_2 crystal were analyzed by the scanning electron microscopy with back-scattered electrons (SEM-BSE) technique, using the scanning electron microscopy (SEM-BSE), LX 30 Philips model. The crystalline quality and structural characterization of the HgI_2 crystal were analyzed by X-ray diffraction (XRD). X-ray diffraction patterns were obtained in a Siemens (D5005) Diffractometer, using $\text{CuK}\alpha$ radiation (2θ ranging from 10° to 100°).

RESULTS AND DISCUSSION

A brilliant dark red color crystal with 15 mm maximum diameter and 20 mm thickness obtained from two successive growths by PVT method and a crystal wafer after cleavage with a deep red color are shown in Fig. 3 (a) and (b), respectively. The HgI_2 crystals obtained by the PVT technique were re-grown twice in order to be purified, since the reduction of impurities is expected at each growth. Figs 3 (c) and (d) present the crystal re-grown by DMSO solution and cleavaged, respectively. Crystals of 1 cm^2 superficial area and 0.5 cm thickness with regular angulations plus uniform and transparent surface were obtained, as it may be observed in the figure.



HgI_2 grown by PVT

(a)



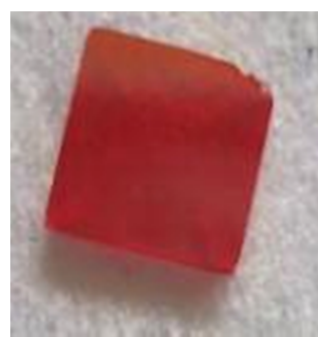
Crystal cleaved by PVT

(b)



HgI_2 grown by DMSO

(d)



Crystal cleaved by DMSO

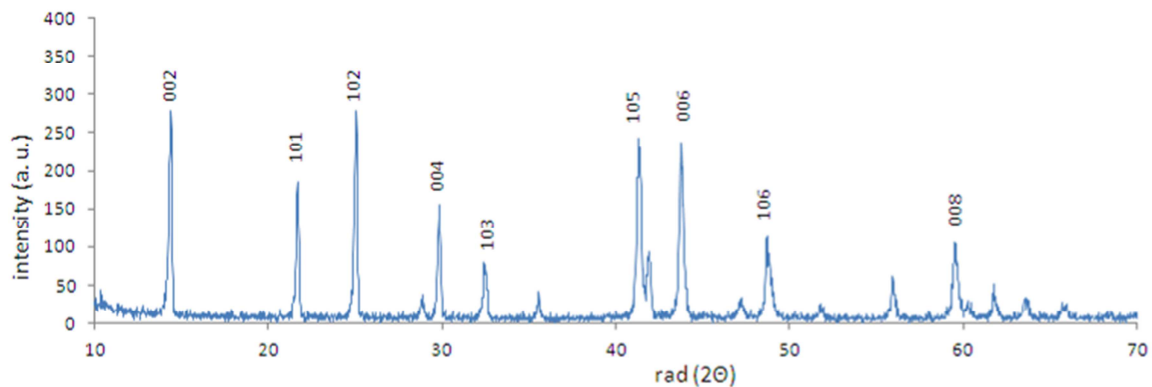
(e)

Figure 3. Crystal original form re-grown by PVT (a) after the cleavage (b) and magnified 50X with optical microscope (c). HgI_2 crystal original form re-grown by DMSO complex (d) after the cleavage (e) and magnified 50X with optical microscope (f).

The typical X-ray diffraction patterns of the cleavage surface from HgI_2 crystals grown by PVT and DMSO techniques are shown in Fig. 4. No significant difference was observed in

the diffraction pattern between the crystals grown by both techniques. The results show that the crystals have a similar structure to the tetragonal crystalline pattern of the HgI_2 . The X-ray diffraction pattern indicates that both crystals are, preferentially, oriented in the (001) and (101) directions. Similar results were found by Ariesanti et al [10]. The lower intensities observed on the diffraction pattern from DMSO crystal (Fig. 4b) could be attributed to the misorientations, absorption related with defects or impurities in the crystal. However, these imperfections seem not have affected the crystal structure, as presented in Fig. 4. Thus, this lower intensity found in DMSO crystals may possibly be due to the superficial defects in the crystal surface.

(a)



(b)

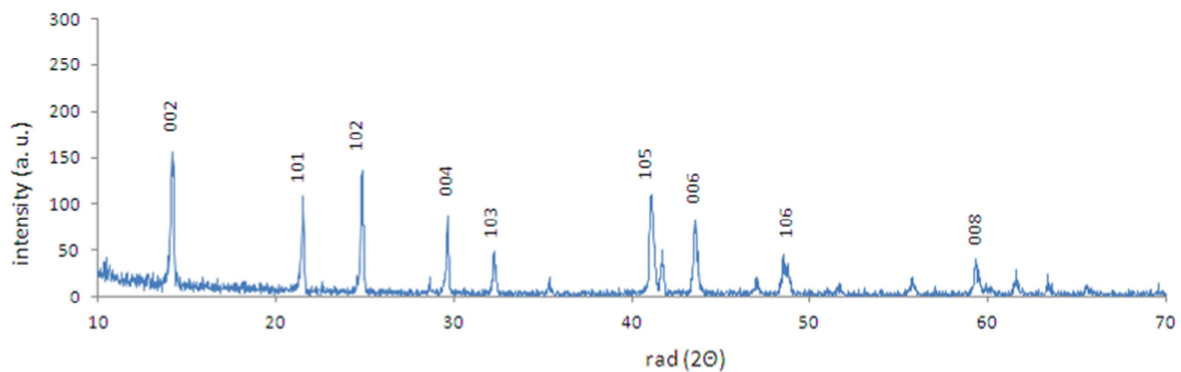


Figure 4. X-ray diffraction pattern of HgI_2 grown by PVT (a) and DMSO (b) techniques.

The HgI_2 crystal grown by PVT technique is illustrated in Fig 5(a), while its elemental composition and stoichiometry determined by SEM-BSE method are shown in Fig. 6 and Table 1, As it can be seen from these figure and table, an proper stoichiometry was found. For example, the Hg atomic percentage was 28.53 while for I_2 was 55.52, corroborating a good stoichiometry for HgI_2 crystal. Other elements, like O, Al, Si, K, were observed in the trace form, acting as impurities in the crystal. These results demonstrate the PVT efficiency

as a purification method and SEM-BSE for determining the impurity concentration and stoichiometry.

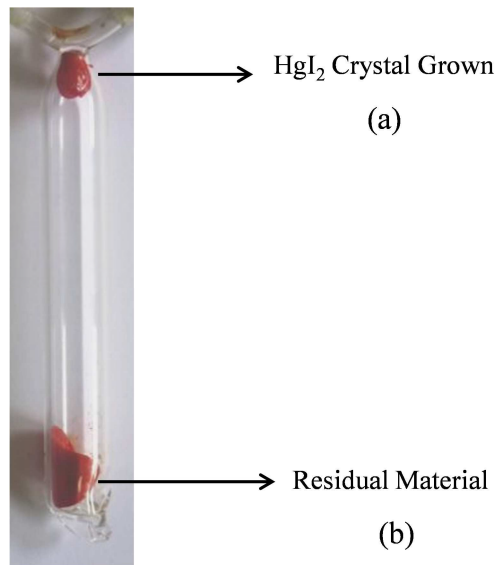


Figure 5. Picture of HgI₂ crystal inside its growth ampoule.

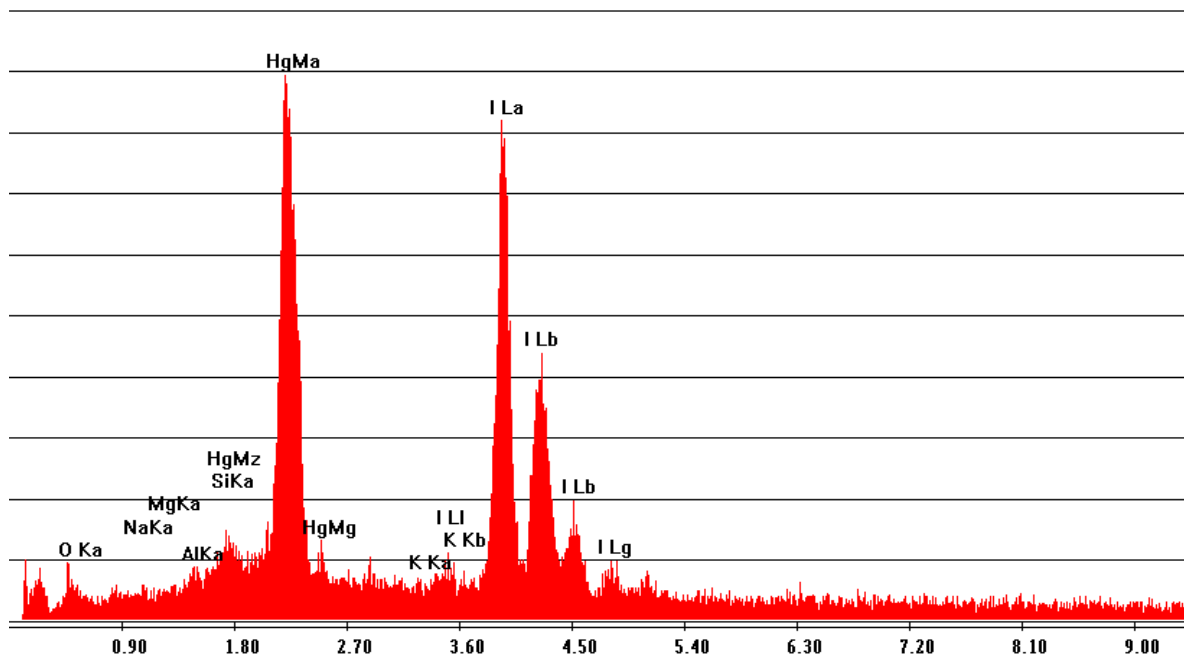


Figure 5 – Spectrum of the micrograph of the HgI₂ crystal grown by PVT technique.

Table 1- Elemental composition of the HgI₂ crystal surface grown by PVT technique.

Element	Weight (%)	% atomic	Errors (%)
O	1,72	13,99	11,10
Al	0,09	0,48	99,98
Si	0,28	1,29	46,99
Hg	43,66	28,53	1,65
K	0,26	0,86	42,04
I	54,09	55,52	1,57

Figure 6 shows the micrographs of the scanning electronic microscopy with secondary electrons (MEV-SE) carried out in the HgI₂ cleavage wafer from the crystals grown twice by PVT technique, in order to evaluate the quality of the HgI₂ cleavage wafer surface. As can be seen in this figure, the crystal magnified 200 times presented smooth surface (Fig. 5a). Extending 650 times a structure with uniform layers can be observed (Fig. 6b), indicating a good orientation in the crystal structure.

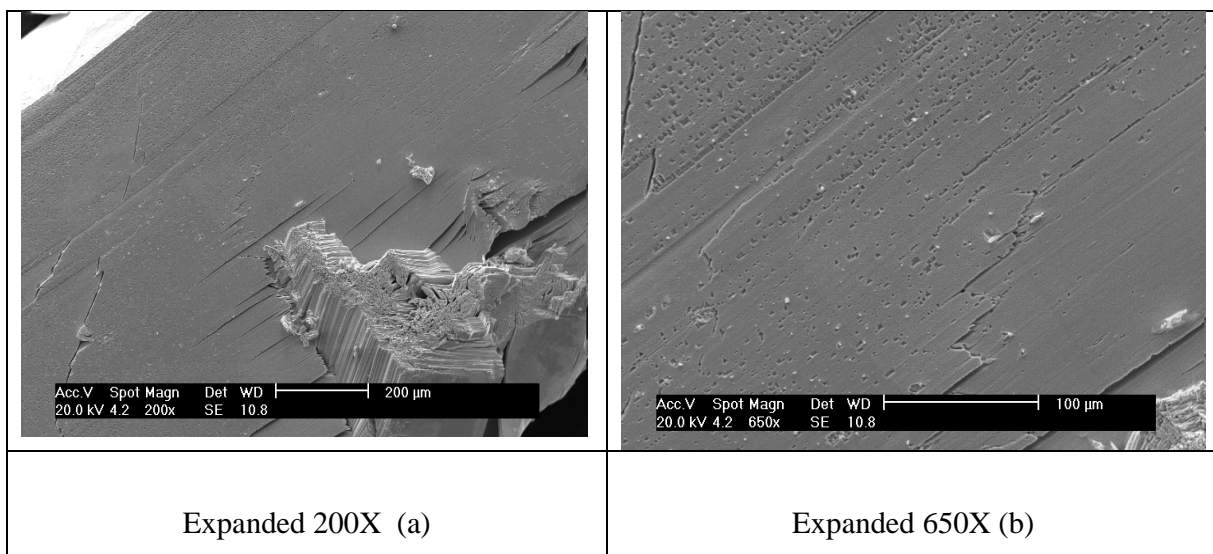


Figure 6 – MEV-SE micrographs of the HgI₂ crystal surface grown by PVT

In addition, the micrographs of the scanning electron microscopy with back-scattered electrons (SEM-BSE) carried out in the HgI₂ cleavage wafer from the crystals grown twice by PVT is showed in Fig. 7. A structure with uniform layers may be also observed, even magnifying the image 5000 times (Fig. 7), confirming a good orientation in structure of this crystal.

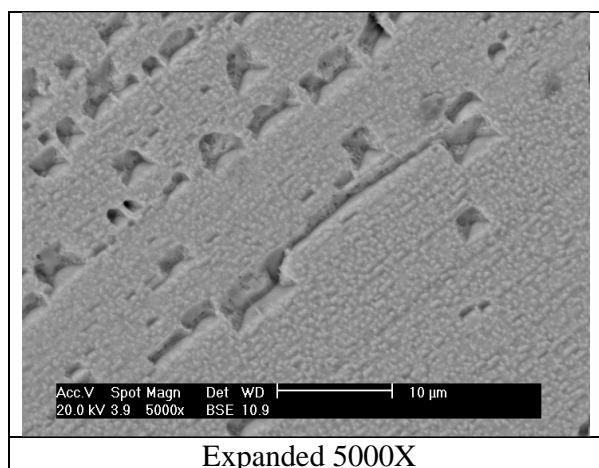


Figure 7 – SEM-BSE micrographs of the HgI₂ crystal surface grown by PVT (expanded 5000X).

The elemental composition determination from the residual salt after the crystal growth (Fig. 5.b) by PVT was performed to evaluate the efficiency of HgI₂ purification by the PVT technique. Samples from the residual HgI₂ salt were evaluated by the SEM-BSE technique (Fig. 8 and Table 2) and compared with those obtained for the HgI₂ crystal grown twice by PVT (Table 1). The presence of significant amounts of impurities can be observed, namely, O, Na, Mg, Al, Si, K, mainly potassium, K, (21.41%) and oxygen, O, (53.28%), which were higher than those of Hg (4.35%) and I (4.54%). The stoichiometry of HgI₂ was not followed in this sample, contrary to that found in the HgI₂ crystal grown. This result demonstrates again the efficacy of the PVT technique to purify the starting material and SEM-BSE to determine the impurity concentration.

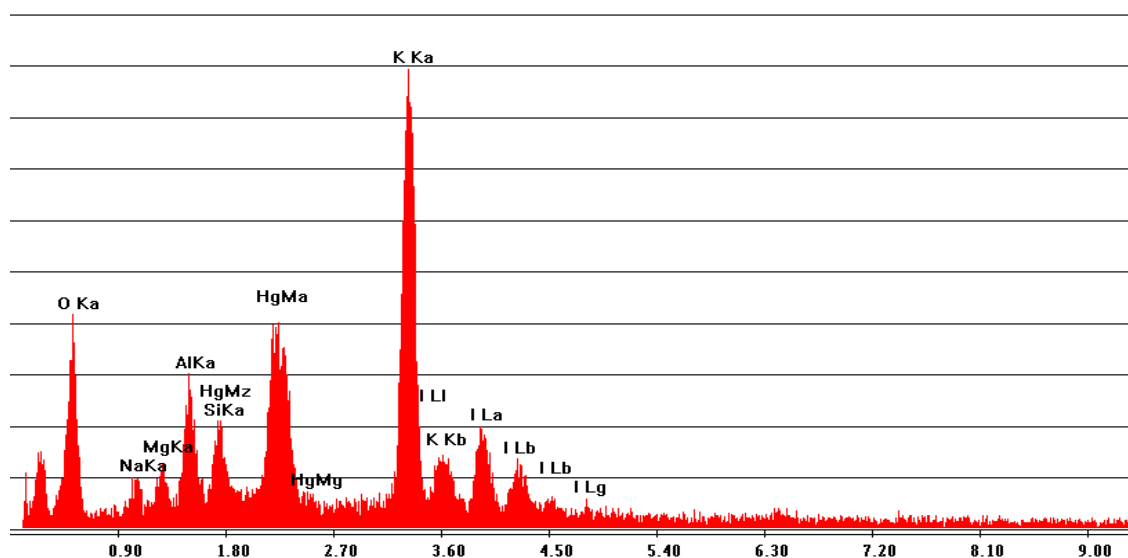


Figure 8 – Spectrum of elemental composition of the HgI₂ crystal grown by PVT techniques.

Table 3 - Elemental composition from the HgI₂ residual salt after the crystal growth by PVT method.

Element	Weight (%)	% atomic	Error (%)
O	23.92	53.28	16.61
Na	2.11	3.27	1.44
Mg	1.94	2.84	1.52
Al	5.18	6.84	3.84
Si	2.73	3.47	2.02
Hg	24.46	4.35	6.54
K	23.49	21.41	19.99
I	16,17	4,54	3,65

Fig. 9 shows the residual salt surface layer from the bottom ampoule after the growth obtained by SEM-BSE technique. As it can be seen from this figure, the image showed an amorphous structure, as expected, since the crystal must be formed at the upper extremity of the ampoule.

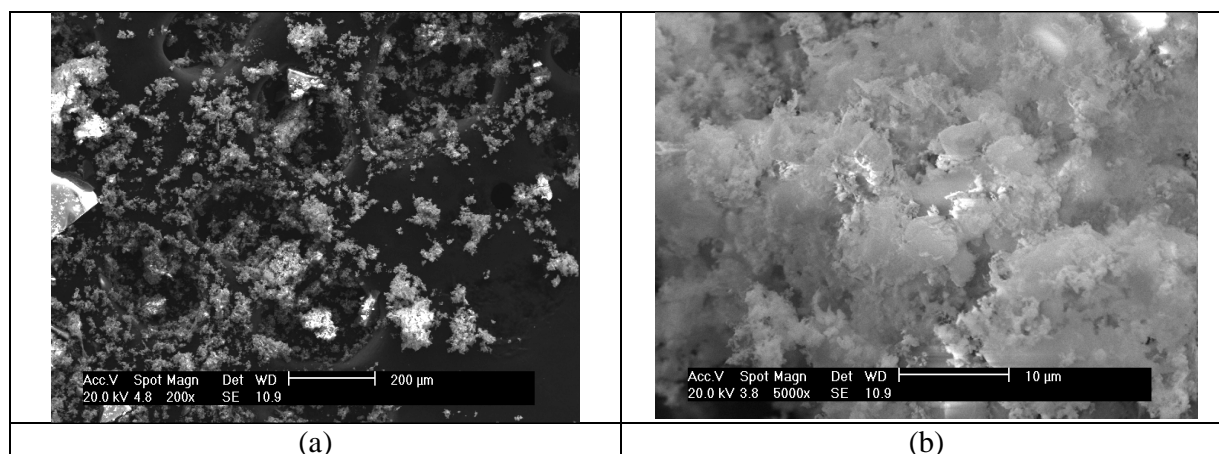


Figure 9 – SEM-BSE micrographs of the HgI₂ residual salt after the crystal growth by PVT, expanded 200 X and 5000 X.

In Fig. 10 and Table 1 the elemental composition of the HgI₂ crystal grown by DMSO complexes, twice, are summarized. Although the suitable stoichiometry of HgI₂ (atomic% Hg = 28.46, I₂ = 54.45) was found, a significant amount of Si was identified (Table 3). The contents of 21.52% Si in the crystal was not expected, taking into account the trace amount of Si found in the HgI₂ salt used for growth, as well as, that Si values estimated for crystal grown by PVT (Table 1) and its material residual. (Table 2). This suggests a Si contamination in the HgI₂ crystal from the silicone oil used as heating bath for crystal growth, since in the DMSO technique, the HgI₂ salt é immersed in DMSO complex inside an open glass recipient (Fig. 1). Silicone oil is any polymerized siloxanes with organic side chains and they are formed of alternating silicon-oxygen atoms (...Si-O-Si-O-Si...). Thus, although silicone oil has temperature-stability and good heat-transfer characteristics, it can have

volatilized and contaminated the surface of the HgI_2 crystal during the growth [11]. From the results of diffraction pattern, showed in Fig. 3, it can be realized that no modification in structure and orientation of the crystal was presented, suggesting the contamination occur only in the crystal surface. However, a further study should be carried out to understand these results. Furthermore, due to the high intensity of the Si peak in the DMSO crystal, it was not possible to identify the peaks of the other trace elements present as impurities in the PVT crystal (Table 1).

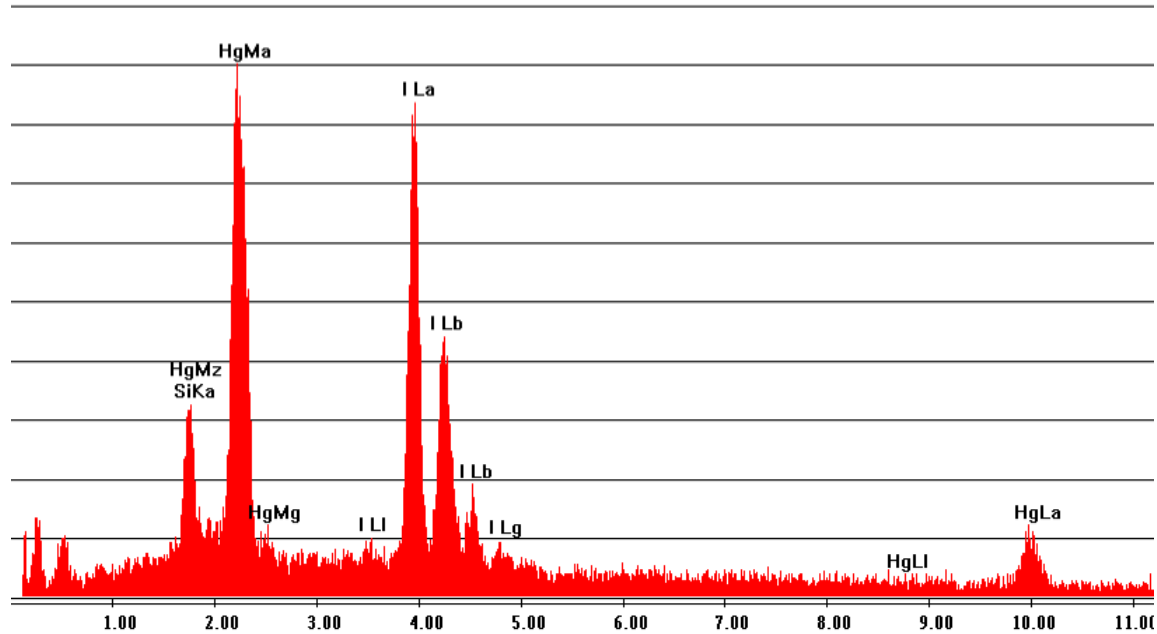


Figure 10 – Spectrum of the micrograph of the HgI_2 crystal grown by DMSO technique.

Table 3- Elemental composition of the HgI_2 crystal surface grown by DMSO technique

Element	Weight (%)	Atomic %	Error (%)
Si	21.52	59.76	1.43
Hg	35.43	13.78	2.09
I	43.06	26.46	1.88

Fig. 11 illustrates the micrographs of the of the scanning electronic microscopy with secondary electrons (MEV-SE) carried out in the HgI_2 cleavage wafer from the crystals grown twice by DMSO technique. As can be observed in this figure, the crystal expanded 65 times (Fig. 11.a) shown roughness in the surface, which can be due to the impurities and defects in the crystal

surface. Expanding the image 350 times (Fig. 11 b), overlapping layers can be seen on the crystal surface. The granules observed on its surface can be attributed to the impurities from the waste solvent.

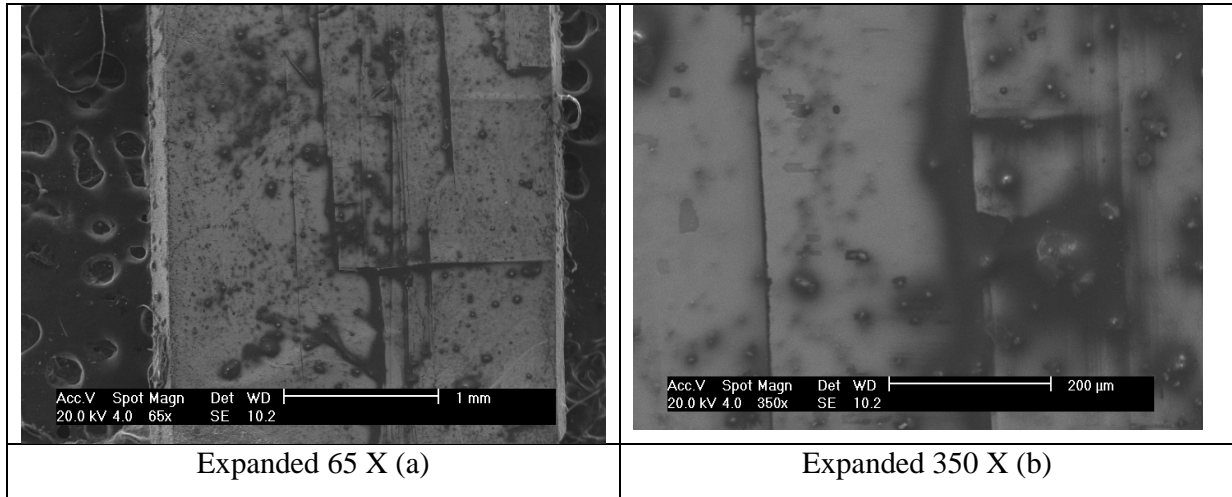


Figure 11– MEV-SE micrographs of the HgI_2 crystal surface grown by DMSO complexes.

Besides, Fig. 12 shows the micrographs of the scanning electron microscopy with back-scattered electrons (SEM-BSE) carried out in the HgI_2 cleavage wafer from the crystals grown twice by DMSO complexes method. A structure with non-uniform layers may be observed in the crystal surface. Also, the roughness and the incrustations of the distinct elements may already be detected, clearly, magnifying the image only 120 times.

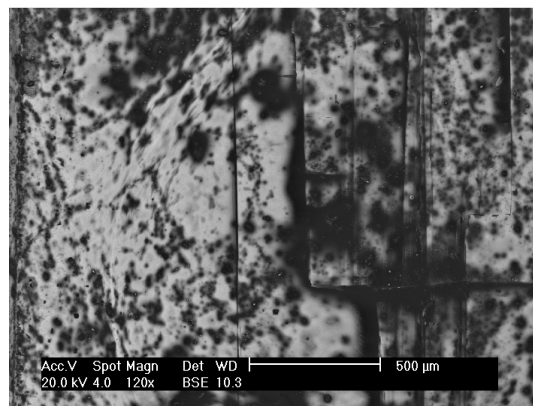


Figure 13 – SEM-BSE micrographs of the HgI_2 crystal surface grown by PVT (expanded 120 X).

CONCLUSIONS

The HgI₂ crystals grown by PVT method were effective to reduce the concentration of HgI₂ impurities compared to the DMSO solution. The HgI₂ crystals grown by PVT method presented better surface morphology quality compared to that grown by DMSO solution. For crystal grown by DMSO, the roughness and the incrustations of the distinct elements may be detected, clearly, while for crystal grown by PVT, a structure with uniform layers may be observed, indicating a good orientation in structure of this crystal. It was demonstrated that impurities affect strongly the crystal surface morphology quality.

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