THE PHYSICAL VAPOR TRANSPORT AS A TECHNIQUE FOR PURIFICATION AND GROWTH OF THE HgI₂ CRYSTAL

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ABSTRACT

In this work, the establishment of a technique for HgI₂ purification and crystal growth is described, aiming a future application of this crystal as a room temperature radiation semiconductor detector. Repeated Physical Vapor Transport (PVT) technique was studied for purification and growth of the crystal. In order to evaluate the obtained crystals, systematic measurements were carried out for determining the stoichiometry, structure, orientation, surface morphology and impurity of the crystal. The X-ray diffractograms indicated that the crystals were, preferentially, oriented in the (001) e (101) directions with tetragonal structure for all crystals and uniformity on the surface layer of the crystal was found. Significant improvement in the HgI₂ radiation detector performance was achieved for purer crystals, growing the crystal twice by the PVT technique.

1. INTRODUCTION

A semiconductor material with wide energy band gap (above 1.35 eV) presents low leakage current, making its use possible as a detector at room temperature [1]. The main physical semiconductor properties required for fabrication of room temperature semiconductor detectors are: (1) high atomic number [Z]; (2) high density; (3) high absorption coefficient; (4) a band gap large enough to keep leakage currents low, at room temperature, and (5) large electron and hole mobility-lifetime products [$\mu\tau$], for an efficient charge collection [2.3].

Among the promising materials for use as semiconductor radiation detectors to operate at room temperature, the HgI2 has emerged as a material particularly interesting due to its large band gap value (twice than the Si value) and high atomic number of its constituent atoms. It has characteristics comparable to or higher than other semiconductors, showing potential for application as a radiation detector. HgI₂ has large band gap (2.13 eV), large density (6,2 g/cm³), high atomic number elements (Z_{Hg}=80 and Z_I=53) and high resistivity (>10^{14} Ωcm) [4]. These are important factors in applications where compact and small thickness detectors are necessary for X- and gamma ray measurements [5].

There is agreement in the literature on the difficulty in growing crystals, with high crystallographic perfection, high chemical purity and good stoichiometry, suitable to be used as room temperature semiconductor detectors. These basic requirements must be met at various stages in the manufacture of the detector. The procedures for obtaining the radiation semiconductor detector comprise: (a) purification of the starting material, (b) crystal growth, (c) crystal surface preparation, (d) ohmic contacts preparation, (e) mounting on a rigid substrate and (f) detector encapsulation. Each of these stages can affect the crystalline quality and introduce defects and imperfections, deteriorating the radiation detector response [6,3,7].

Several studies [8-12] have been carried out about the preparation of the HgI_2 semiconductor detector and progresses have been made by the improvement of the techniques of purification, growth and characterization of the crystal. However, problems still exist and to grow HgI_2 crystals with suitable purity to be used as a room temperature radiation detector is a technological challenge. The impurities that act as charge carriers traps influence the charge carrier lifetime, affecting the detector efficiency [1].

Most semiconductor crystals are grown by the fusion technique. However, the HgI_2 undergoes structural phase transition below its melting point (259 ° C), what makes its growth by fusion technique [13,14] more difficult compared to PbI2 (405 ° C) and TlBr (468 ° C). Thus, other techniques, such as "Physical Vapor Transport" (PVT) [15,16] or "Saturated Solution" [17] are more recommended for the growth of HgI_2.

In this work, the HgI_2 crystals were purified and grown by the PVT technique. The physical vapor transport technique for HgI_2 crystal growth validates one of its properties, which is the sublimation. The HgI_2 undergoes the vapor phase, when heated, even below its boiling or fusion temperatures. This property allows the use of the PVT technique for crystal growth, without requiring either high temperature or pressure. In this technique, a homogeneous heat source warms the salt until it becomes vapor and can solidify in another region with lower temperature.

EXPERIMENTAL PROCEDURE

The commercially available HgI2 powder (Fluka Chemika), with nominal purity of 99.9%, was used as the starting material for growing crystal, aiming their application as a radiation detector. The purification and growth were carried out using the PVT technique.

The schematic diagram of the oil-bath furnace, used for HgI_2 crystal growth from PVT is shown in Fig. 1. The system consists of a lard oil bath, controlled by a controllable heating plate that transfers heat to the salt contained within the bottom tube. The heat is transmitted from a resistive plate through a bath of silicone oil, wrapped in a metal enclosure in order to reduce heat loss. For growth, the ampoule containing salt HgI_2 must be sealed to prevent HgI_2 vapor loss and contaminants.
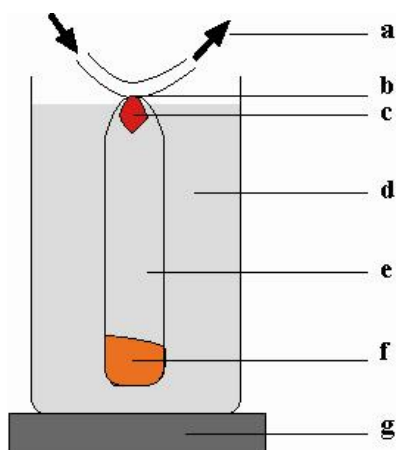
Figure 1 – Schematic diagram of the oil-bath furnace for crystal growth by PVT technique: (a) water flow for cooling, (b) heat exchange region, (c) crystal, (d) silicone oil, (e) glass ampoule, (f) salt and (g) controllable heating plate.

In this work, the borosilicate glass ampoules were filled with 5 g of HgI_2 salt, evacuated at 90 ° C for 15 min and, subsequently, sealed. Hence, the salt is dehumidified, but also prevented to be re-hydrated. This ampoule filled with HgI_2 salt at the bottom is placed in the bath of silicone oil, wrapped in a metal casing (Fig. 2a) for growth. The HgI_2 salt heated sublimes crystal being deposited in the heat exchange region (FIG 2b). Fig 3 shows a sealed ampoule containing HgI_2 crystal, grown at the upper region of the ampoule, and the raw material at the bottom.

(a)   (b)

Figure 2 – Oil bath furnace wrapped in a metal casing (a) and HgI2 crystal grown (b).

Figure 3 – Sealed ampoule with an HgI$_2$ grown (seed) in one of the extremities (A) and the HgI$_2$ in another extremity (B)

Following the same procedure, the crystals were grown twice for purification. The impurity concentration in the HgI$_2$ crystal was measured by inductively coupled plasma mass spectroscopy (ICP-MS) technique, in order to evaluate the purification efficiency by PVT technique. The impurities of the salt remaining in the bottom of the ampoule were, also, determined.

The crystalline quality and structural characterization of the TlBr crystal were analyzed by X-ray diffraction (XRD). X-ray diffraction patterns were obtained in a Siemens (D5005) Diffactrometer, using CuKα radiation (2θ ranging from 20° to 60º).

The surface morphology and the stoichiometry of the HgI$_2$ crystal were analyzed by using the scanning electron microscopy (SEM-BSE), model LX 30 Philips.

RESULTS AND DISCUSSION

Fig. 4 shows the HgI2 crystals grown once by PVT technique. As it can be observed in this figure, the crystal grown presented a brilliant dark red color, being more accentuated in the upper section.

Figure 4 –HgI$_2$ crystal grown by PVT technique

The crystals obtained by the PVT technique were selected for a re-growth in order to purify the crystals, since the reduction of impurities at each growth is expected. In Fig. 5 the purified crystal, for two successive growths by the PVT method is shown, as it follows: the crystal grown with 1.5 cm diameter and 2.0 cm thick (FIG 5a), after cleavage (FIG 5b) and enlarged 50 times with an optical microscope (FIG 5c), where a deep red color and glossy surface can be observed.
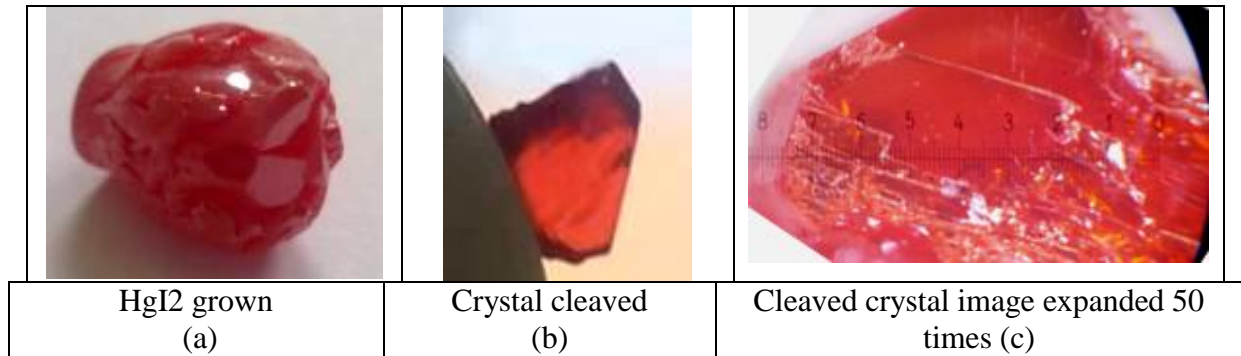

| HgI2 grown (a) | Crystal cleaved (b) | Cleaved crystal image expanded 50 times (c) |

Figure 5 - HgI$_2$ crystal original form grown by PVT (a) after the cleavage (b) and expanded 50X with optical microscope (c)

Fig. 6 shows the typical X-ray diffraction pattern of the cleavage surface from HgI$_2$ crystals grown. No significant difference was observed in the diffractograms between the crystals grown from both growths. The results show that the crystals have a similar structure to the tetragonal   crystalline pattern of the HgI$_2$. The diffractogram indicates that the crystal is, preferentially, oriented in the (001) and (101) directions. Similar results were found by Ariesanti e col [18].
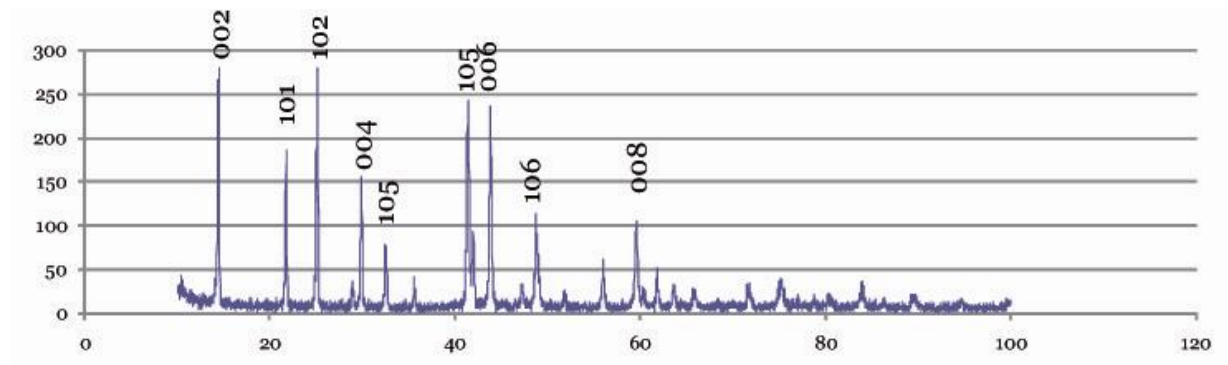

Figure 6 - X-ray diffractogram of HgI$_2$ grown

Fig. 7 shows the micrographs of the scanning electron microscopy with back-scattered electrons (SEM-BSE) carried out in the HgI$_2$ cleavage wafer from the crystal grown twice by the PVT technique, in order to evaluate the quality of the HgI$_2$ cleavage wafer surface. Expanding the image 5000 times, a structure with uniform layers can be observed, indicating a good orientation in the crystal structure.
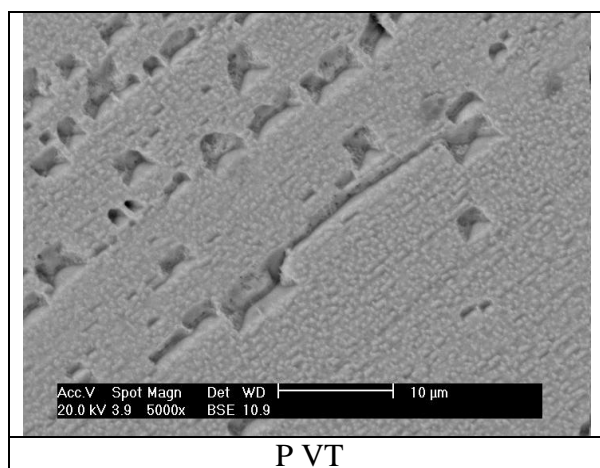
P VT

Figure 7 – Micrographs of the HgI2 crystal surface grown by PVT (expanded 5000X)

Additionally, SEM-BSE technique provides a semi quantitative scanning of the elements present on the surface of the crystal, as well as the stoichiometry of HgI_2. The elemental composition of the crystal surface obtained is shown in Fig. 8 and Table 1. As it can be seen from these figure and table, an appropriate stoichiometry was found. For example, the Hg atomic percentage was 29.51 while for I_2 was 55.68, corroborating a good stoichiometry for HgI_2 crystal.   Other elements were observed in the trace form, acting as impurities in the crystal.
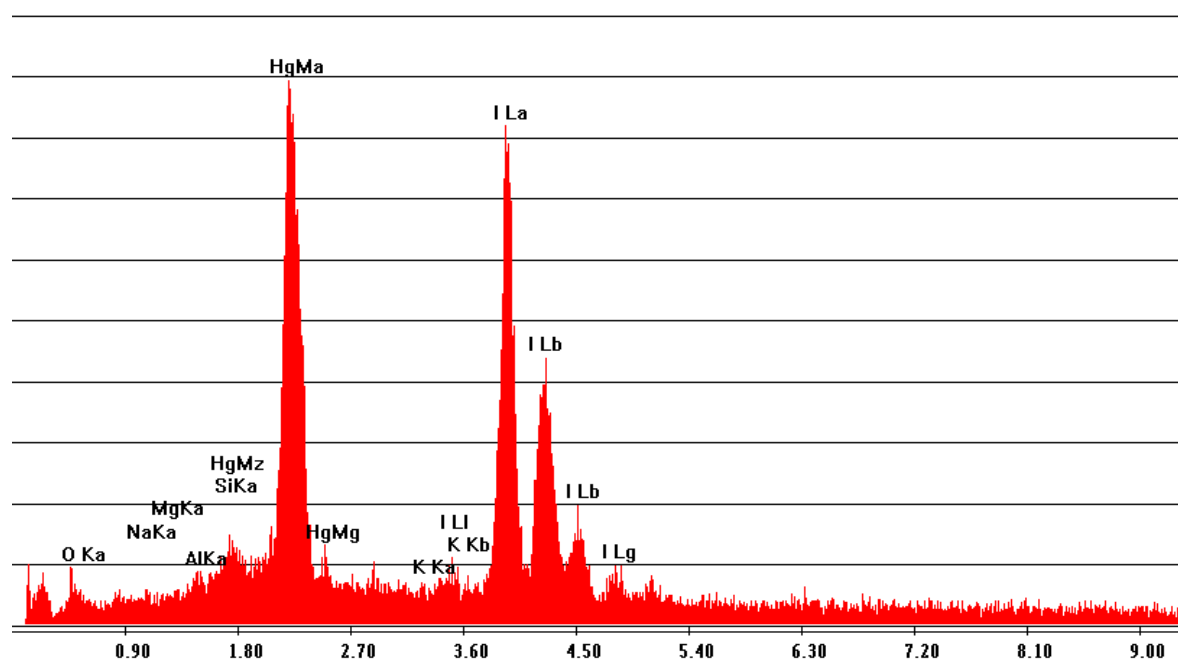

Figure 8 – Spectrum of elemental composition of the HgI₂ crystal surface

Table 1- Elemental composition of the HgI2 crystal surface

Element	Weight (%)	% atomic	Errors (%)
O	1.50	12.47	11.90
Al	0.10	0.49	141.02
Si	0.26	1.22	48.97
Hg	44.65	29.51	1.63
K	0.18	0.62	58.85
I	53.30	55.68	1.59

In Fig. 9 and Tab. 2 the elemental composition results from the residual salt after the crystal growth by PVT, are presented. This analysis was performed to evaluate the efficiency of HgI_2 purification by the PVT technique. Samples from the residual HgI_2 salt were evaluated by the SEM-BSE technique and compared with those obtained for the HgI_2 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%), plus I (4.54%). The stoichiometry of HgI2 was not followed in this sample, contrary to that found in the HgI_2 crystal grown. This result demonstrates the efficacy of the PVT technique to purify the starting material.
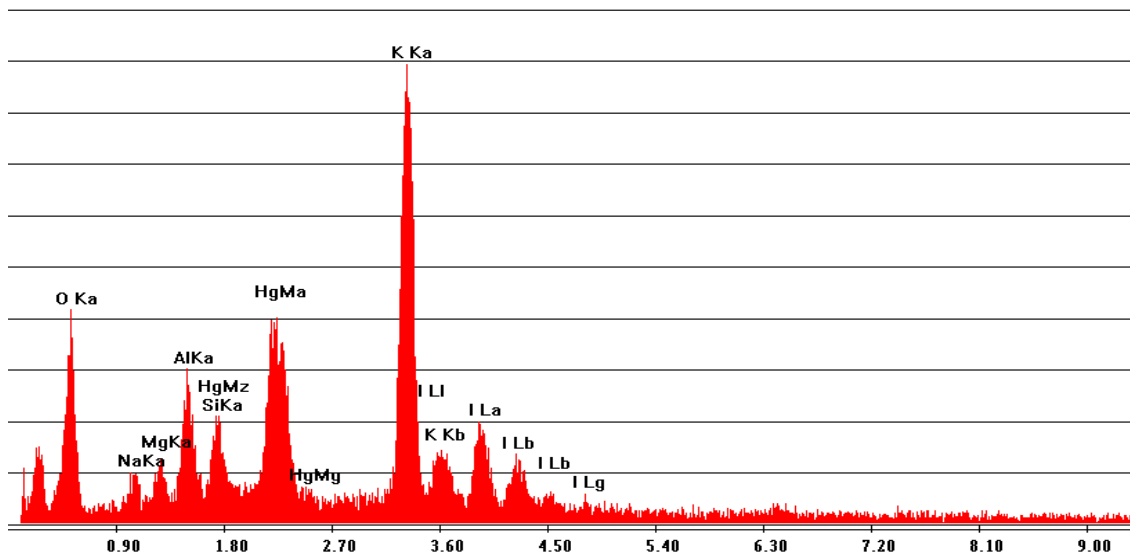

Figure 9 - Elemental composition from the HgI$_2$ residual salt after the crystal growth by PVT

Table 2 - Elemental composition from the HgI$_2$ residual salt after the crystal growth by PVT

Element	Weight (%)	% atomic	Erros (%)
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. 10 shows the residual salt surface layer from the bottom ampoule after the growth. 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.
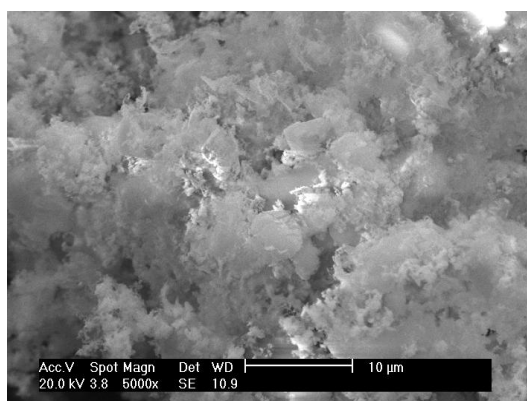

Figure 10 – Micrographs of the HgI$_2$ residual salt after the crystal growth by PVT (expanded 5000X)

Fig. 11 presents the analysis results of the impurities in the HgI$_2$ salt used as a starting material, by inductively coupled plasma mass spectroscopy (ICP-MS) technique. This technique is ideal for the elemental concentration analysis lower than $\mu g \cdot g^{-1}$ [1] due to its low detection limit (around $ng \cdot kg^{-1}$ - or less). It should be emphasized that there is scarce literature describing the impurities present in the starting material (salt) for HgI$_2$ crystal growth and, even among these few references, there is no consensus as to the elements found[19-22].
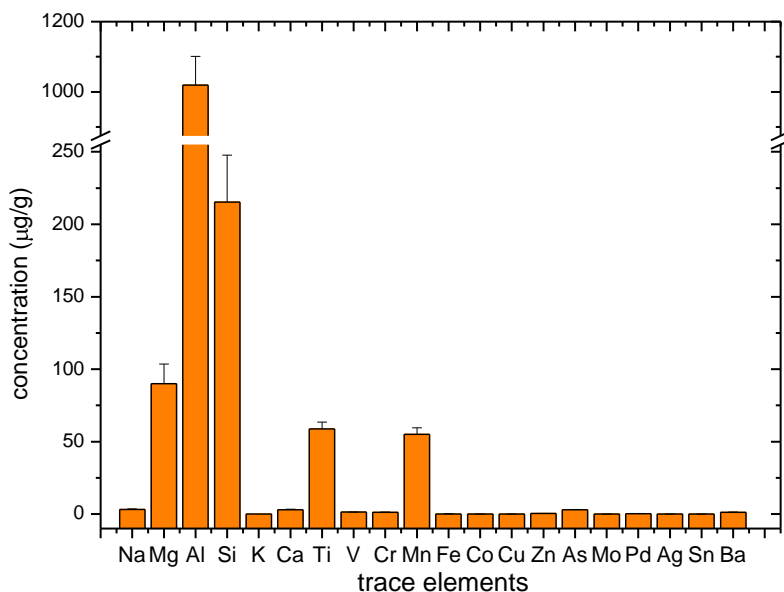
Figure 11- Impurities found in the starting material sample and their concentration expressed in mg /g.

Fig. 12 shows the impurities identified, as well as, the concentration profiles for impurities found in the raw material (HgI_2 salt), HgI_2 crystal grown once, twice and the residual impurities from the remaining salt in the ampoule bottom evaluated by the ICP-MS technique. As it can be observed from this figure, there was a significant reduction of the impurities after the first growth compared to that of the raw material. Also, a decrease in most impurities was noticed after the second growth compared to the first growth, indicating the effectiveness of the PVT purification technique. The purification process by PVT should be performed repeatedly, in order to determine the repetition number required to reduce the impurity concentration, at the maximum.
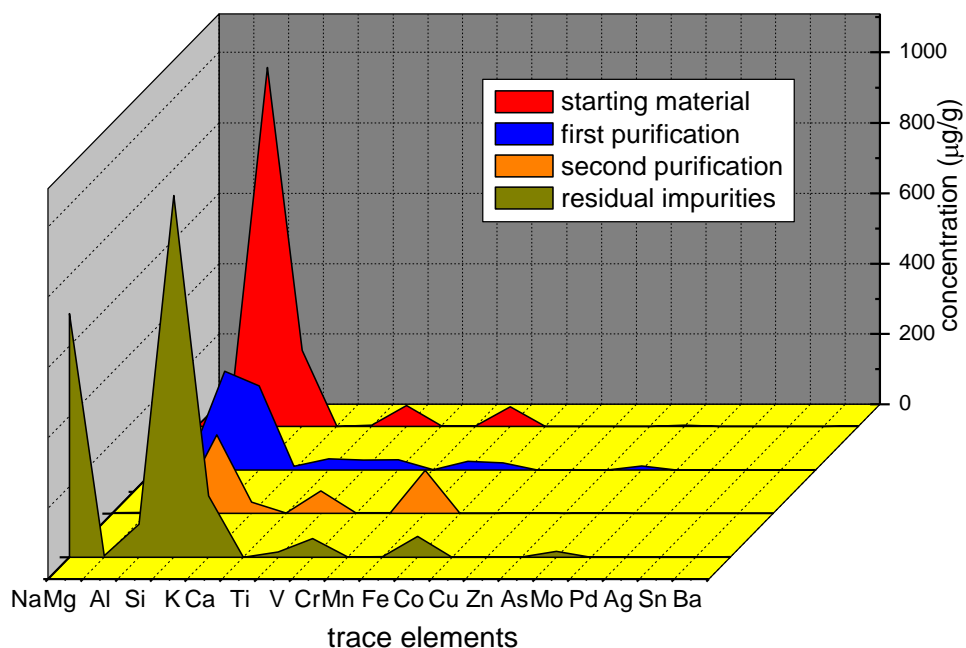
Figure 12 – Trace elements found in the samples from the starting material, the crystal grown once, twice and the residual impurities from the growth. The concentration of trace elements is expressed in μg/g.

Validation of the PVT technique as a purification process of the HgI_2, as well as the establishment of a method for determining the number of purification repetitions for obtaining a crystal with an adequate purity are important for future works. This information allows the reduction in the concentration of these elements to be accompanied, after each purification process. In addition, it makes possible to study the influence of impurities on the performance of HgI_2 crystal as a radiation detector, since the main application of the crystal is to be used as an HgI_2 radiation detector.

3. CONCLUSIONS

The PVT technique was effective to reduce the concentration of HgI_2 impurities. The ICP-MS analysis showed to be a special technique to identify and quantify the impurities in the HgI_2 crystal and to evaluate the reduction of the impurities, after the purification. The PVT technique, also, demonstrated to be a useful technique to grow HgI_2 crystals. Similar structures to the tetragonal model of the crystal HgI_2 were found in the crystals developed. A good uniformity in the surface morphology of HgI_2 layers was found, indicating a good orientation in the crystal grown structure. An appropriate stoichiometry of the HgI2 crystals developed was confirmed by the SEM-BSE analysis

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