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MERCURIC IODIDE SEMICONDUCTOR DETECTORS ENCAPSULATED IN POLYMERIC RESIN

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ABSTRACT

The development of new semiconductor radiation detectors always finds many setback factors, such as: high concentration of impurities in the start materials, poor long term stability, the surface oxidation and other difficulties discussed extensively in the literature, that limit their use. In this work was studied, the application of a coating resin on HgI_2 detectors, in order to protect the semiconductor crystal reactions from atmospheric gases and to isolate electrically the surface of the crystals. Four polymeric resins were analyzed: Resin 1: 50% - 100%Heptane, 10% - 25% methylcyclehexane, <1% cyclohexane; Resin 2: 25% - 50% ethanol, 25% - 50% acetone, <2,5% ethylacetate; Resin 3: 50% - 100% methylacetate, 5% - 10% n-butylacetate; Resin 4: 50% - 100% ethyl-2-cyanacrylat. The influence of the polymeric resin type used on the spectroscopic performance of the HgI_2 semiconductor detector is, clearly, demonstrated. The better result was found for the detector encapsulated with Resin 3. An increase of up to 26 times at the stability time was observed for the detectors encapsulated compared to that non-encapsulated detector.

1. INTRODUCTION

The HgI_2 presents the advantage of high mobility charge carriers, , 100 cm^2/Vs for electrons and 6 cm^2/Vs for holes for example the PbI_2 has (8cm^2/Vs for electrons and 2cm^2/Vs for holes) or TlBr (6 cm^2/Vs for electrons and 2cm^2/Vs for holes). However, HgI_2 has the disadvantage of undergoing structural phase transition below its melting point(259°C), which makes their growth by the fusion technique more difficult[1] compared to that of PbI_2 (405°C) or TlBr (468°C), technique which is commonly used for the growth of the overwhelming majority of radiation detectors crystals[2].

In Radiation Technology Center at Nuclear and Energy Research Institute has traditionally been used growing technique by melt called Bridgman for scintillators crystals CsI(Tl) and semiconductors which operate at room temperature, such as, PbI_2 and TlBr.

However, due to HgI_2 property to undergo structural phase transition below its melting point[4] makes their growth by the Bridgman technique unsuitable. Therefore the most efficient technique for crystal growth HgI_2, which meets the characteristics required for their application as radiation detectors is the PVT technique [1].

2. EXPERIMENTAL PROCEDURE

The proposed work consists of four distinct experimental steps which are:
1. Purification of starting material.
2. Growth of crystals.
3. Preparation of surfaces.
4. Manufacture of the detectors.

2.1. Purification of starting material by the Physical Vapor Transport (PVT)

When heated HgI_2 passes into the vapor phase, the contaminants have different sublimation temperature that the salt, therefore the salt may be purified by this method
The heat is provided by a resistive wire which covers the bottom of the tube, heat exchange is performed by flowing water, the system plus a metallic shell to reduce heat loss to the room, whose scheme is shown in Figure 1.

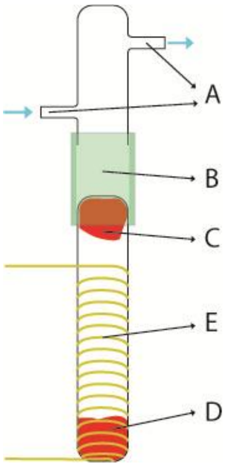


Figure 1: schematic of the salt purification system, a) cooler water flow b) heat exchange region c) purified salt d) salt and e) resistive wire.

The borosilicate ampoules were filled with approximately 5g of HgI_2 salt and subsequently evacuated under 90 ° C for 15 minutes and sealed. Thus it the salt hydration is avoided, which eventually compromise purification

2.2. Crystal Growth by Physical Vapor Transport (PVT)

The HgI_2 crystals growth was also performed by PVT technique. Growth theory is quite similar to the purification, differs up by the parameters of temperature and time, also the furnace and ampoule used.
The heat is transmitted from a sealed resistance contained within the furnace (figure 2), which has outer stainless steel walls in order to reduce the loss of heat to the room and provide structural resistance. For growth, the ampoule containing the purified solid HgI_2

should be hermetic in order to prevent loss of vapor HgI_2, and reduce the possibility of contamination or loss of stoichiometry in the grown crystals.

Figure 2: Furnace designed for HgI_2 crystals growth

The time and temperature parameters was found by equation (1) where the Q_{max} value is the quantity of the purified solid HgI_2 placed in the ampoule, T is the temperature in the hottest region of furnace and k a proportionality constant.

$$\frac{dT}{dQ} = e^{-kQ}(Q_{\max} - Q) \qquad (1)$$

2.3. Preparation of surfaces

The preparation of the surfaces can be broken down into two distinct steps, namely: the cleavage of the crystals and the contacts deposition

2.3.1. Cleavage of the crystals

Applying a force or knock, minerals may break with certain particularities, sometimes reflecting the crystal structure.

The HgI_2 crystal has a cleavage plane along its axis <100>, due to lower bond energy between atoms and greater interatomic spacing. Among iodine atoms there is 151kJ/mol of bond energy and between iodine atoms and mercury atoms that energy is 291kJ/mol this lower energy is resulting interactions enters atoms less intense, leading to greater crosslink spacing, this can best be understood in Fig 3.

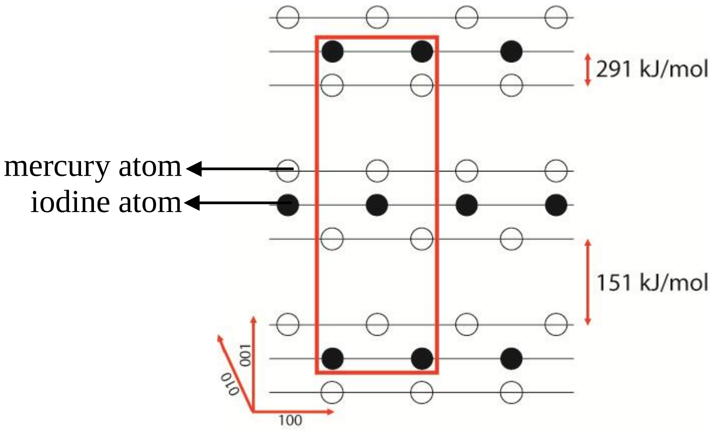


Figure 3: Crystalline planes of tetragonal HgI_2 crystal

The crystals were cleaved using a thin ceramic blade, such material has been used due to the high reactivity of metals with HgI_2, knowing the morphology of the crystals was necessary just a low pressure along its axis to cleaving the crystals.

2.3.2. Contacts deposition

The conductive ink contacts and copper wire were applied on the faces of the recently cleaved crystal as fast as possible in order to minimize the reactions between the exposed surfaces and the atmospheric gases. After approximately two minutes (necessary for drying the conductive ink) the crystals were coated with a polymeric resin which insulates of atmospheric gases. They were used four kinds of commercial polymeric resins to evaluate the influence of encapsulation on the performance of crystals as a radiation detector. The compositions of commercial resins used are summarized in Table 1:

Table 1. Composition of resins

Resin 1:	50% - 100% Heptane 10% - 25% Methylcyclohexane < 1% Cyclohexane	Resin 3:	50% - 100% Methylacetate 5% - 10% n-butylacetate
Resin 2:	50% - 100% Heptane 10% - 25% Methylcyclohexane < 1% Cyclohexane	Resin 4:	50% - 100% ethyl-2-cyanacrylate

3. RESULTS AND DISCUSSIONS

3.1. Purification evaluation

Impurities present in HgI2 salts and the stoichiometry of the crystals were measured by Scanning electron microscope using Back-scattered electrons (SEM-BSE). This technique provides semi-quantitative scanning of the elements present in the crystal surface also the stoichiometry of the HgI_2.

3.1.1. Impurities identification

The results presented here are from three representative samples of purified material. The elemental compositions of the surface of the crystals are shown in FIG 4, 5 and 6 and Table 2, 3 and 4. Due to the microscopy small spot beam, samples for analysis were taken from three different points on the surface of the crystals.

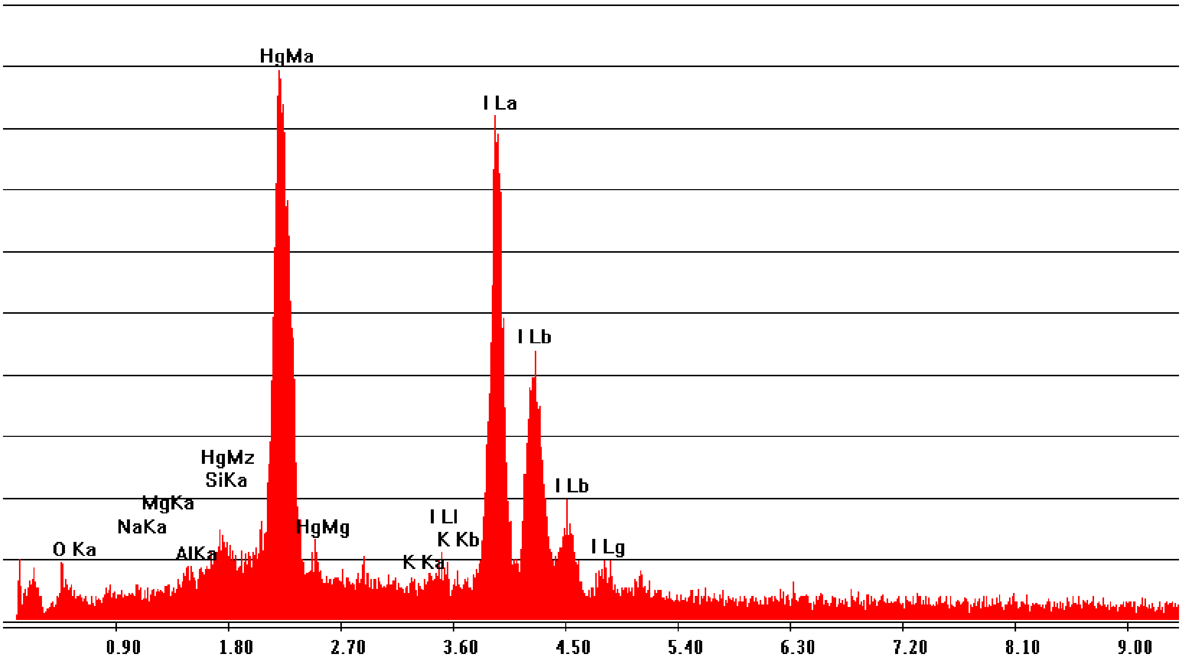


FIGURE 4 - Spectrum of the surface composition of the crystals

TABLE 2 elemental composition of the surface of the crystals

Element	% de mass	% atomic	Error %
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

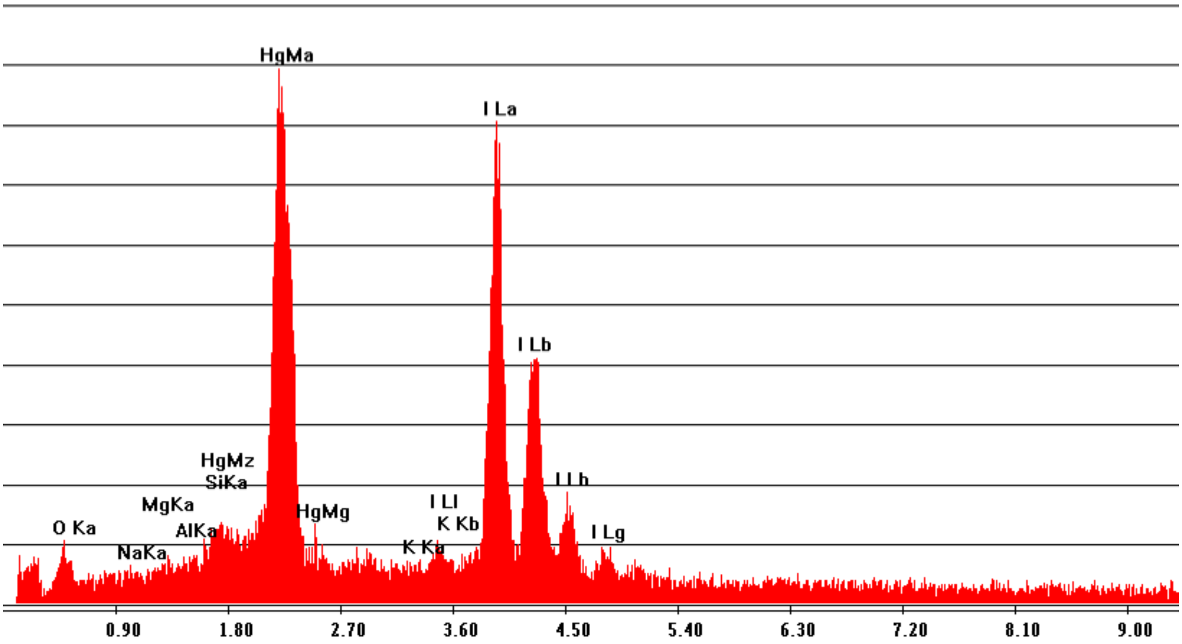


FIGURE 5 - Spectrum of the surface composition of the crystals

TABLE 3 elemental composition of the surface of the crystals

Element	% de mass	% atomic	Error %
O	2.20	17.34	8.75
Al	0.00	0.00	0.00
Si	0.29	1.32	40.60
Hg	44.83	28.17	1.53
K	0.39	1.27	25.91
I	52.28	51.91	1.53

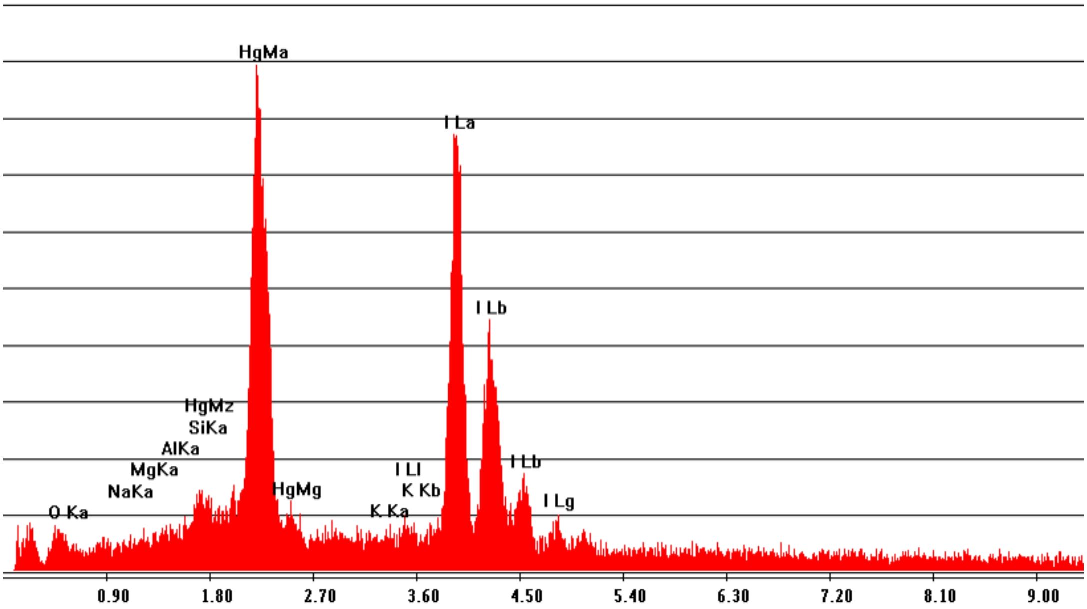


FIGURE 6 - Spectrum of the surface composition of the crystals

TABLE 4: Elemental composition of the surface of the crystals

Element	% de mass	% atomic	Error %
O	1.72	13.99	11.10
Al	0.00	0.00	0.00
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

For example, in the table 2 it can be inferred that the atomic percentage of Hg was 29.51 and I_2 was 55.68, which describes a good stoichiometry because the amount of iodine is almost double of mercury. The atomic percentage of O_2 14.60 ± 2.49 found can be attributed to atmospheric exposure of the surface. It relevant that proper stoichiometry has been found in three points extracted in three crystals, indicating uniformity across the surface of the crystals.

With the intent of proving the effectiveness of the purification technique, the residual material has also been measured using the same method. The results are presented at Fig. 7 and Table 5.

It´s possible to infer from the comparison of Table 5 and Table 2,3 and 4 that the purification method is more effective to elements such as O, Na, Mg, Al, Si, K, specially K (21,41%), that were present with higher concentrations.

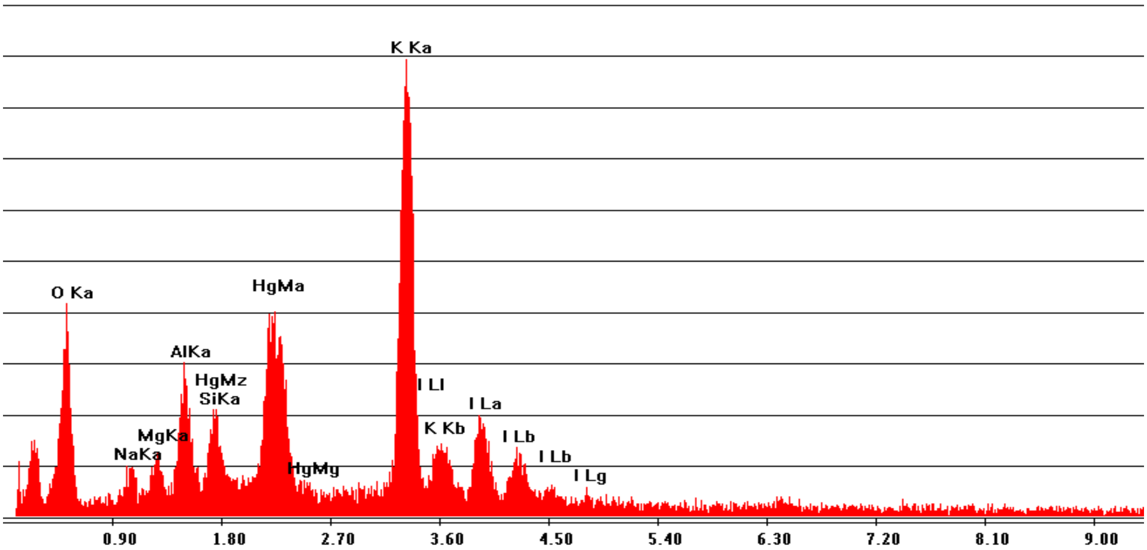


FIGURE 8 – Elements composition of the reminiscent residue from the HgI_2 salt used.

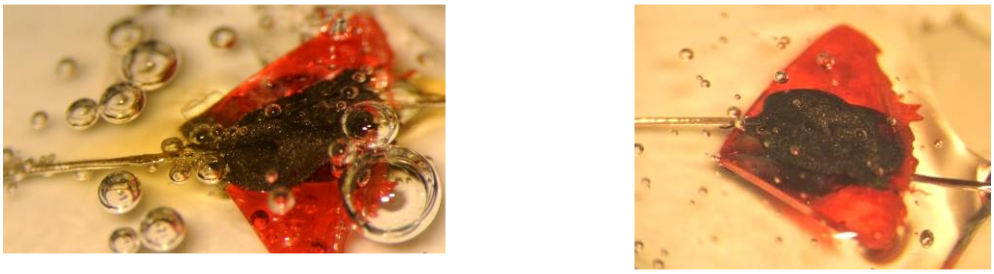
TABLE 6: Elements composition of the reminiscent residue from the HgI_2 salt used.

Element	Mass %	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

3.2. Encapsulation

Amongst the four studied resins, in the samples number 2, 3 and 4 it couldn´t be observed reactions with the electric contact components, however with the sample number 1 (hepitane, methylcyclohexane and cyclohexane) it has been observed during the polymerization process reactions between the crystal and the cupper conductive wire components, which can be associated to the formation of free radicals. This reaction can be observed within a few minutes after the polymerization, with the formation of bubbles and alteration of the resin color, as shown in the Fig. 9.

In comparison, there are no evidences of chemical reactions during the polymerization of resin number 3 (methyl-acetate e n-butyl-acetate) as well as of resin number 2 (ethanol, acetone e ethyl-acetate) and 4 (ethyl-2-cianoacrilate)



Detector encapsulated with resin number 1 Detector encapsulated with resin number 3

Figure 9: Detector encapsulated with resin number 1 and 3

As far as known, all of the work found in literature aiming to study the effect of stability of the HgI2 detectors are focused on the study of purity and defects of crystals or morphologic quality of their surfaces. For the first time it has been purposed in this work alongside the Albert-Ludiwg University the encapsulation of the detector prepared to avoid the oxidation of the surface with the intent of increasing the stability of the HgI2 detector, what is still subject of study.

At this study it was observed that the detector performance depends on the resin composition. The resin that better performances was number 3, that´s composed by 50% - 100% of methyl-acetate and 5% - 10% of n-butyl-acetate.

In previous studies in this group without the encapsulation and also in works realized by other groups the stability found in HgI2 detectors lasts for a few hours, while in encapsulated detectors in this work the stability lasted till 78 hours.

3.3. Electronic coupling

The crystal coupled using resin 3 presented the best resullts in the spectrometry (Fig. 10), in which the photopics were more clearly observed. The obtained spectra from crystals encapsulated with resins 2 and 4, although sensitive to radiation do not have energetic resolution to form the photopic. A possible explanation can be the formation of ionic free radicals, that can conduce electric corrent, however more detailed studies can be done. It was not possible to test the crystal encapsulated with resin 1 due to chemical reaction with the electric contacts.

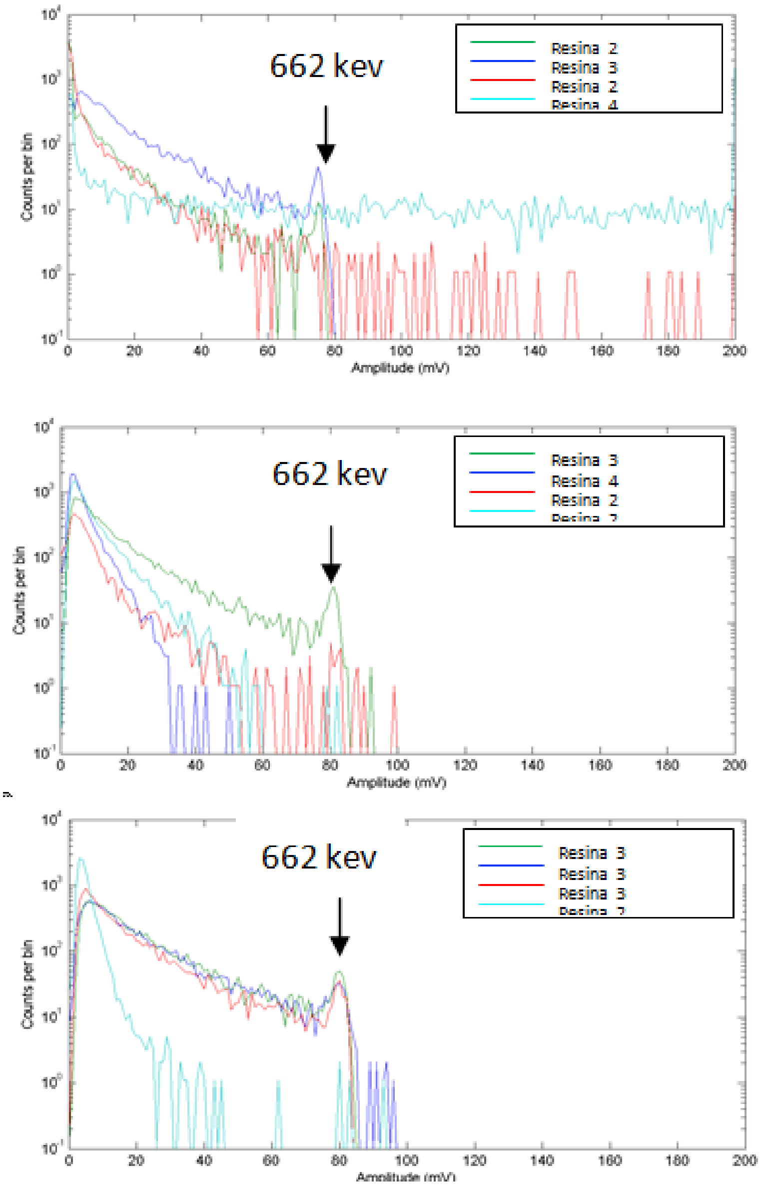


Figure 10: Spectra detected with the detectors.

4. CONCLUSIONS

The grown crystals have good crystaline orientation and stoichiometry. The identifyed impurities are coherent with the ones pointed by literature.

The encapsulation made in order to offer protection from the atmosphere is a point of relevance of this work, specially for being about an inedit study in literature.

The results presented undoubtly point to an improvement of the purification techniques and HgI2 crystals growth.

The crystals encapsulated in resin were fully capable of detecting gama radiation.

ACKNOWLEDGMENTS

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REFERENCES

1. OLIVEIRA, I.B. **Desenvolvimentodo cristal semicondutor de brometo de tálio para aplicações como detector de radiação e fotodetector.** São Paulo: 2005. 110p. Tese (Doutoramento) - Instituto de Pesquisas Energéticas e Nucleares, USP.
2. UGUCIONI, J.C.; NETTO, T. Ghilardi; MULATO, M. **Mercuric iodide crystals obtained by solvent evaporation using ethanol**. Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment, Volume 615, Issue 3, 11 April 2010, Pages 259-266
3. NICOLAU, Y.F.; ROLLAND, G. ***Deviation from stoichiometry in*** α-HgI_2 Materials Research Bulletin, Volume 16, Issue 6, June 1981, *Pages 759-770*