Purification and Growth of PbI_2 Crystals: Dependence of the Radiation Response on the PbI_2 Crystal Purity

I. B. Oliveira, F. E. Costa, M. J. Armelin, L. P. Cardoso, and M. M. Hamada

***Abstract*—Lead iodide starting materials have been purified by a multipass zone refining process. The effectiveness of the purification method on the material purity was determined by neutron activation analysis after three different purification passes numbers. A significant decrease of the impurities concentration was observed in function of the passes number. The purest material of the zone refined ingots, middle section, was used for crystal growth by Bridgman method. The results of the dark leakage current, the resistivity, and the response of the alpha and gamma radiations were strongly dependent on the purity of the crystal.**

***Index Terms*—Crystal growth, lead iodide crystal, semiconductor radiation detector, zone refine.**

I. Introduction

LEAD iodide (PbI_2) is a very promising material with large technological applicability as X-Ray and γ-ray room temperature detectors [1]–[4]. PbI_2 is a wide bandgap energy (2.3–2.6 eV) semiconductor composed of high atomic number elements ($Z_{\rm Pb} = 82$, $Z_{\rm I} = 53$), with high resistivity (10^{13} Ωcm) and density of 6.2 g/cm^3 [2], [3], [5]–[11]. The wide bandgap enables low noise operation of the PbI_2 detectors at room temperature and above [7], [9], [12], [13]. One of the apparent disadvantages of PbI_2 is the low mobility of its charge carriers, 8 cm^2/Vs for electrons and 2 cm^2/Vs for holes [6], [7], [10]. Therefore, in order to enhance the electrical properties, the trapping time (τ) characteristics and the mobilities (μ) should be improved [6], [10].

The role of the crystal impurities on the electrical properties of PbI_2 is crucial, then improvements on the chemical purification should be achieved [2], [6], [7], [10]. The PbI_2 melts congruently at 408 °C and it does not undergo a transition phase between its melting point and room temperature, which allows the purification and growth of crystals from the melt [2], [8], [10], [11]. It is well known that the PbI_2 crystal is dominated by structural defects which, when eliminated, provide an improvement of the electrical properties, revealing its actual potential [6], [10].

The primary difference between recently developed PbI_2 detectors and those earlier fabricated appears to be the degree of crystal purity [2], [14], [15]. Purity, crystallinity, and orientation are critical to determine the detector performance [7]. Several studies [2], [5]–[10], [13]–[15] have been carried out about the preparation of the PbI_2 semiconductor detector and progresses have been made by the improvement of the techniques of purification, growth, and characterization of the crystal. In this work, the commercial PbI_2 powders, used as starting materials, were purified by zone refining method and grown by Bridgman method. The efficiency of removing the impurities after 200, 300, and 500 purification passes was evaluated by measurements of the impurities concentrations in the PbI_2 ingot using neutron activation analysis. The dependence of the radiation response on the PbI_2 crystal purity was studied.

II. Experimental

The commercially available PbI_2 powders with nominal purity of 99.0%, 99.999% (Aldrich) and 99.9999% (Strem Chemical) were used as starting materials for growing crystals for detector applications. To reduce impurities, this material was purified by the multipass zone refining (ZR) technique. This method is well described in the literature [2], [6], [7], [10], [11], and one important parameter that should be considered is the segregation coefficient: the ratio of the solubility of the impurity in the solid to the solubility in the melt [6], [7].

Prior to the purification, chemical etching was made in the quartz tubes by their immersion in 10% HF solution for 20 min. After that, the tubes were treated thermally evacuating them at 550 °C, in order to avoid the adherence of the crystals in the tubes walls used in the melt. Subsequently, the PbI_2 powder was introduced into a treated 30-cm-long quartz tube of 10 or 20 mm diameter, evacuated to 10^{-5} mmHg and sealed off. The ampoule was mounted into the horizontal zone refining furnace and the heaters moved along the length of the ingot. Several runs with various temperatures and heater moving speeds were used resulting in a cracking at the end of the zone refined tubes. A heater moving speed of 10 cm/h and a furnace temperature of 550 °C allowed to accomplish 500 passes of purifications without tube cracking. These parameters are very similar to those found by Chen *et al.* [3]. The zone refining (ZR) process was repeated multiple times up to 500 passes in order to investigate the purification effectiveness as a function of the passes number.

The purification efficiency was evaluated by impurities analysis in the ZR ingot, after 200, 300, and 500 purification passes using the neutron activation analysis (NAA) technique [16]. The bottom, middle, and upper section samples from purified ingots after 200, 300, and 500 passes and the PbI_2 starting material were irradiated in a Nuclear Reactor IEA-R1 at IPEN. For short life elements, the samples were irradiated about 6 min under 1×10^{12} n.cm^{-2}.s^{-1} flux, while for identification

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I. B. Oliveira, F. E. Costa, M. J. Armelin, and M. M. Hamada are with the IPEN/CNEN-SP, Cidade Universitária, 05508-900 São Paulo, Brazil (e-mail: ibolivei@net.ipen.br; armelin@net.ipen.br; mmhamada@net.ipen.br).

L. P. Cardoso is with the IFGW, UNICAMP, 13083-970 Campinas-SP, Brazil.

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TABLE I
IMPURITIES CONCENTRATIONS OF THE LEAD IODIDE POWDERS BY NEUTRON ACTIVATION ANALYSIS

Impurities	**Concentration (ppm)**		
	99.0%	**99.999%**	**99.9999%**
Br	15.41 ± 0.03	4.10 ± 0.40	2.05 ± 0.01
Co	0.29 ± 0.007	0.02 ± 0.001	0.03 ± 0.003
Na	7.58 ± 0.25	4.18 ± 0.13	3.52 ± 0.11
K	4038.00 ± 65.00	2454.00 ± 39.26	980.00 ± 15.68
W	1.05 ± 0.10	0.19 ± 0.01	0.01 ± 0.0015
Au	0.40 ± 0.04	0.06 ± 0.006	0.008 ± 0.0001
Ag	4.02 ± 0.04	7.10 ± 0.70	1.28 ± 0.10
Mn	**1.20 ± 0.01**	**0.54 ± 0.05**	**0.06 ± 0.009**

of long life elements were irradiated about 8 h under 2.4×10^{12} n.cm^2.s^{-1} flux. To quantify the trace elements, standard samples with well-known mass were irradiated simultaneously, under the same conditions.

The purest materials of the ZR ingots were used for crystal growth by Bridgman method, after 200, 300, and 500 purification passes, which were denominated ZR200, ZR300, and ZR500 crystals, respectively. The crystals were grown with a rate of 1 mm/h at 550 °C into the tube of quartz in a vertical Bridgman furnace. The obtained crystals (approximately 20 mm length and 10 mm diameter) were annealed at 150 °C for 20 h.

The crystalline quality was analyzed by X-ray diffraction (XRD). An X-ray Phillips powder diffractometer Model PW 1710 using Cu Kα radiation with a secondary graphite monochromator (40 kV, 35 mA in the 2θ range from 0 to 60°) was used for structural characterization of the PbI_2 crystal.

In order to be prepared as a radiation detector, the grown crystals were cleaved perpendicularly to direction (001) using a diamond saw in the dimensions of 10 mm^2 and thickness of 500 μm. In order to reduce heat and mechanical damage, the diamond wheel was set to low speed and it was continuously lubricated with deionized water [6]. Each side of the diamond-cut slice was later removed by chemical polishing, immersing the slices in a 10% NaI solution for 5 min. After the etching, the surface quality was evaluated by scanning electron microscopy and it was suitable to apply the electrical contact. This was applied with conductive graphite painting on both sides of the wafers. This low-resistance contact was used to minimize the noise [12].

The dark leakage currents were measured as a function of the applied voltage, at room temperature, using a Keithley electrometer (Model 619) and an EG&G Ortec (model 556) dc high-voltage power supply. The radiation response of the detectors was studied using the conventional electronic setup including the voltage power supply, charge sensitive preamplifier, a linear amplifier, and an oscilloscope. The pulse-height spectra were analyzed using an EG&G Ortec model 918A multichannel analyzer, using ^{241}Am, ^{57}Co and ^{133}Ba gamma radiation sources and an ^{241}Am alpha radiation source.

III. RESULTS AND DISCUSSION

PbI_2 decomposition, vapor iodine and black residues were observed in the lead iodide powders 99.999% and 99.9999% used in our experiment, when they melted at 10^{-5} mmHg, during the zone refining purification, making impossible to carry out the studies with these materials. Fornaro *et al.* [13] found similar occurrence, which they believe to be a consequence of the high vapor pressure of lead iodide, which first vaporizes and then decomposes, giving lead and iodide. This was not observed in the PbI_2 99.0% used in this work. So, all results presented in this work are related to those obtained for PbI_2 99.0%. Despite the lower level of its purity the use of PbI_2 99.0% did not invalidate the purpose of this work. The decrease of the impurity concentration as a function of the pass number and the dependence of the radiation response on the crystal purity could be clearly shown.

Table I summarizes the result of the impurities concentration analysis of the PbI_2 powders used as starting material by NAA technique. The sensitivity of NAA for the identified elements W, Au, and Mn is ~0.01 ppb; for Br, Co, Na, and Ag is ~1 ppb and for K is 10 ppb [16].

In previous literature, PbI_2 purity has been analyzed by atomic absorption [10] or plasma-optical emission spectroscopy [6], [7], [13]. As far as we know, the PbI_2 impurity determined by neutron activation analysis (NAA) has not been previously reported. NAA is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor, and trace elements in samples from almost every conceivable field of scientific or technical interest. For many elements and applications, NAA offers sensitivities that are superior to those attainable by other methods on the order of parts per billion or better. In addition, because of its accuracy and reliability, NAA is generally recognized as the "referee method" of choice when new procedures are being developed or when other methods yield results that do not agree [16]. Some impurities as Ca, Fe, Zn Al, Cu, Mg, and Cr reported in the literature [6], [7], [10], [13] were not found in the present work, in spite of the high sensitivity of NAA for these elements (~0.01 ppb for Mn, Au, W; 1 ppb for Cu, Al, Cr, Zn, Ag, Br, Co, Na, and 10 ppb for Ca, Mg, Fe, K) [16]. Besides this, in this work many assays were carried out to confirm these results. In addition, elements such as Ca, Zn, Al, and Cr were not reported in the suppliers analysis certificates of the PbI_2 powder used in our experiment.

The ZR PbI_2 ingot showed distinguished different colors. The upper section showed the darkest color, followed by bright and slightly dark colors for the middle and bottom sections, respectively. Fig. 1 shows the impurities identified, as well as, the concentration profiles for impurities found in the bottom, middle,

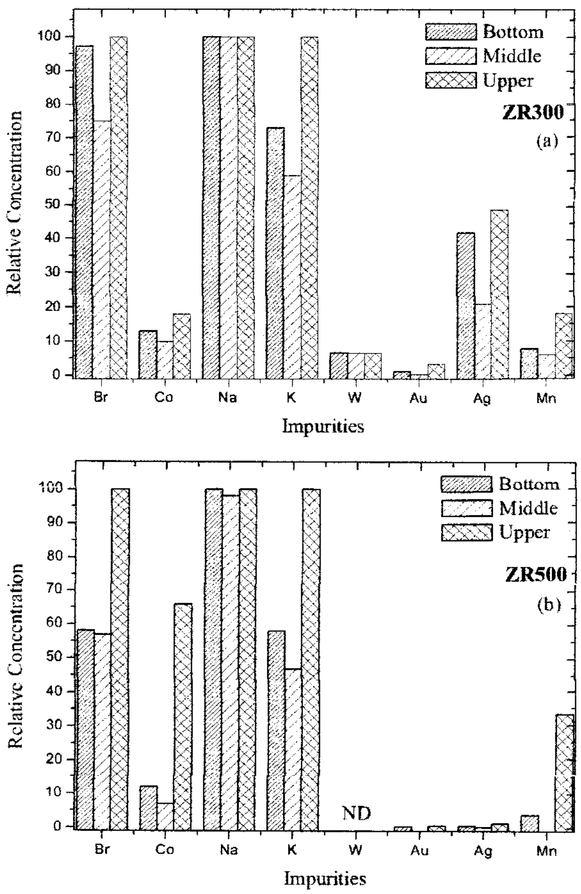

Fig. 1. Impurity concentrations in the bottom, middle and upper sections of purified PbI_2 ingots with (a) 300 and (b) 500 zone refining passes. ND = no detected. Impurity level: ppm.

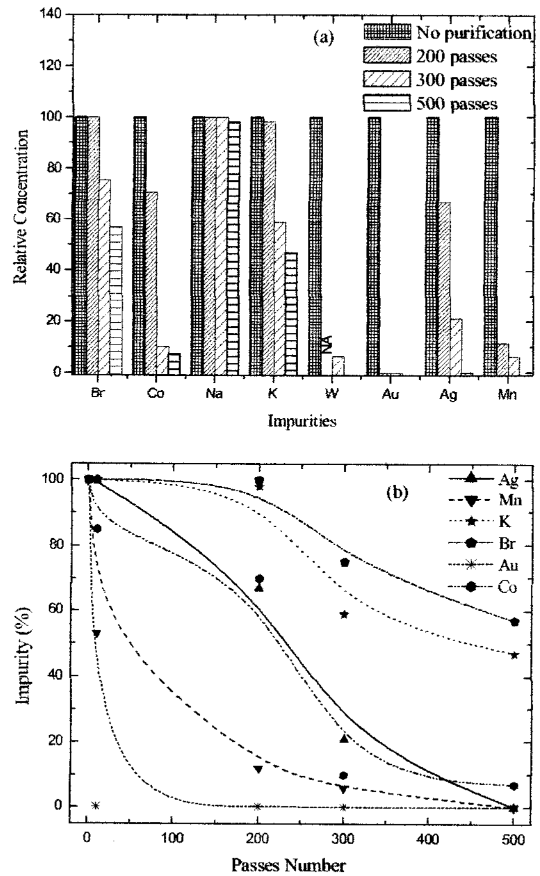

Fig. 2. (a) Impurity reduction and (b) tendency of the concentration decrease in function of the purification passes number. NA = no analyzed.

and upper sections of the crystal evaluated by neutron activation analysis.

It was observed a trend for impurities to segregate to the upper part of the ingot (last to freeze), as a consequence of the ZR. It also appears that the total impurity concentration is smaller toward the middle of the ingot, indicating that for some elements the segregation coefficient is below or above unity. So, these impurities segregate to the first or last parts of the ingot to freeze. Same behavior was observed for others authors [6], [7].

Fig. 2 shows the tendency of the impurity concentration decrease in function of the purification passes number. As it can be observed, there was a significant reduction of the impurities according to the purification passes numbers. However, the decrease depends on each element since they have different segregation coefficients. For a segregation coefficient different from a unity, the ZR process is more efficiently to remove the impurities to one of the ingot ends.

The apparent low purification effectiveness compared to [6] and [7] is due to the low purity of the starting material and the high speed of the RZ furnace moving, requiring more passes to have an effective purification.

The crystals grown by Bridgman method were transparent and bright yellow. Fig. 3 presents the X-ray diffraction characterization for the ZR300 and ZR500 crystals. The results show that both crystals have a similar structure with the hexagonal crystalline pattern of the PbI_2 crystal. The diffractograms indicate that the samples are preferentially oriented in the (001) direction. Nevertheless, a small polycrystalline characteristic contribution is observed by the presence of other (110) and (113) reflections in both diffractograms although, they appear stronger in the ZR500 sample. It should be pointed out that the ZR300 sample is crystallographically better than ZR500, confirmed by its (001) peak more intense than that of ZR500 sample and also, by the ratio among the relative intensities of the ZR300 peaks (001, 003, 004) closer to the expected ratios in the Joint Committee on Powder Diffraction Standards [17]. However, a background intensity contribution, which appears at lower angles, probably due to some impurity, is still present in the ZR 300 result. Finally, it is worthwhile to observe that there was no other crystalline phase in the grown samples since, all detected peaks were identified as belonging to the PbI_2 sample oriented in the (001) direction.

The grown crystals were cleaved perpendicularly to direction (001), using a diamond wheel saw. According to the studies evaluated by Hermon *et al.* [6] and Schlesinger [7], the chemical etching can be used to controllably remove the damage in the near surface region that results from the diamond sawing of lead iodide. Fig. 4 shows the micrographs by scanning electron microscopy (SEM) before and after the chemical etching. As can be observed, after the etching, the polish residues were removed from the surface revealing a "flaky nature," which is a characteristic of the PbI_2 crystal [2].

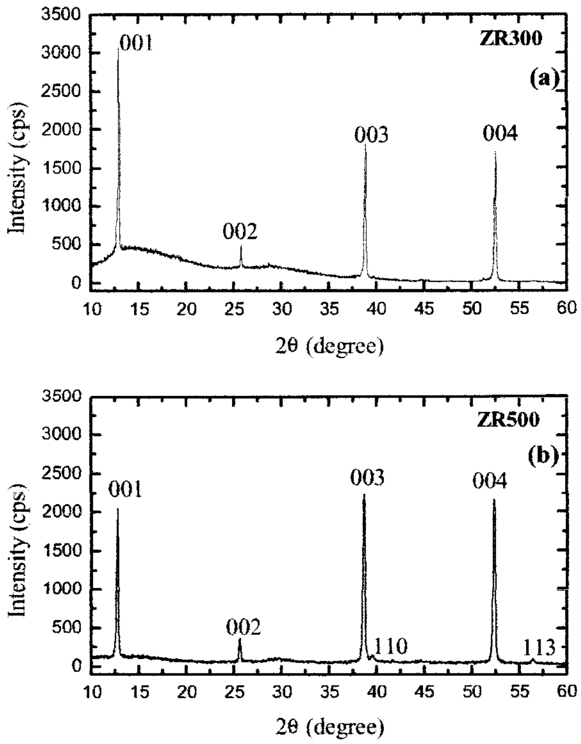

Fig. 3. X-ray diffraction of PbI_2 crystals: (a) ZR300 and (b) ZR500.

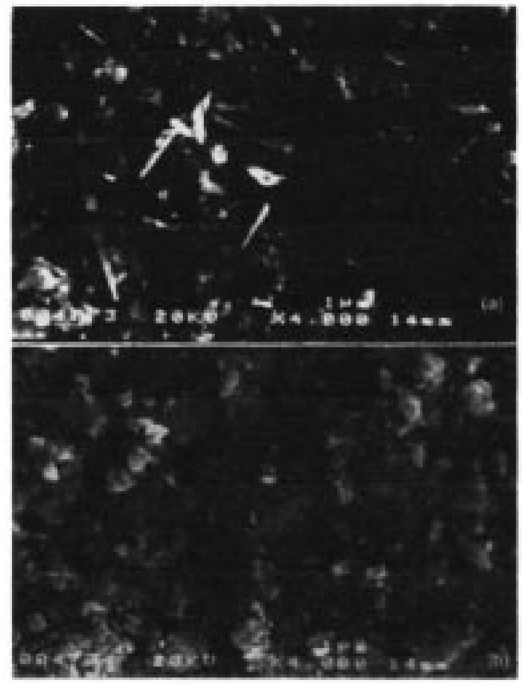

Fig. 4. SEM micrographs of PbI_2 crystal (X4000) (a) after and (b) before chemical etching.

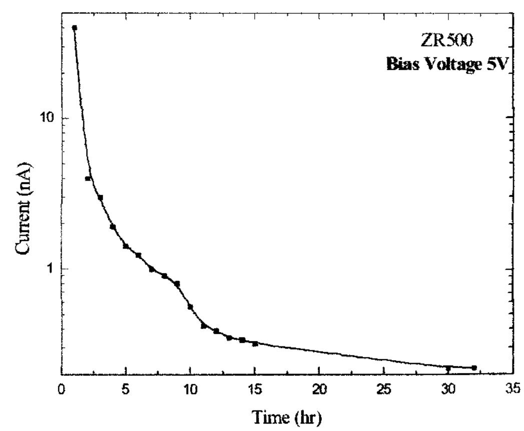

Fig. 5. Current–time curve for the PbI_2 detector.

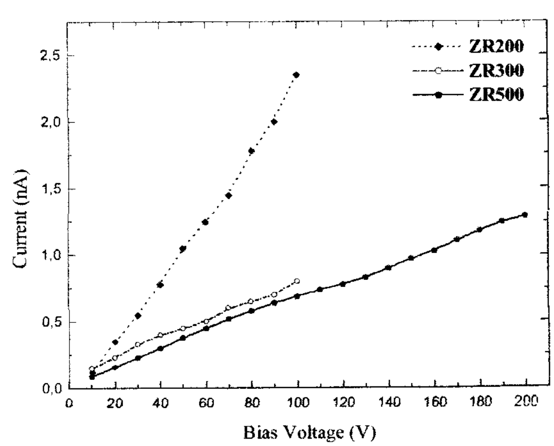

Fig. 6. Current–voltage curves of PbI_2 detectors.

Subsequently after the detector preparation, a bias voltage of 5 V for 30 h was necessary to be applied in order to stabilize the dark current. Fig. 5 shows the leakage current stabilization measurements as a function of the time, with the decrease of the leakage current clearly observed. In further experiments, the stabilization time of 30 h was not necessary.

Fig. 6 shows the results of the leakage current as a function of the applied bias voltage. As can be observed, the leakage current values decrease with the impurity reduction. This difference can be attributed to the various levels of the impurity concentration that act as charge carriers traps, causing an increase in the leakage current. For ZR200 and ZR300 crystals, the measurements were possible to be carried out up to 100 V—above this value some spikes occurred. For the ZR500 crystal, a bias voltage up to 200 V could be applied. For ZR200 crystal, the resistivity value was 6.6×10^{10} Ωcm, while for ZR300 and ZR500 crystals the resistivity was similar, around 1.7×10^{11} Ωcm, close to the value reported in the literature [3], [6], [8], [10], [18].

The importance of the PbI_2 crystal purity for its application as a radiation detector, described in the literature [2], [3], [6], [9]–[15], [18] was confirmed by the results found in the spectrometric measurements for alpha and gamma radiations. For ZR200 crystal, no radiation response was observed, probably due to the interference of the high leakage current in the eventual radiation signal detection.

Fig. 7 shows the results of the relative radiation response, in current mode, for ZR300 crystal. For this crystal, it was possible to observe the radiation response only in the current mode. The detection in the pulse mode was not observed due to a low radiation response and a high noise signal.

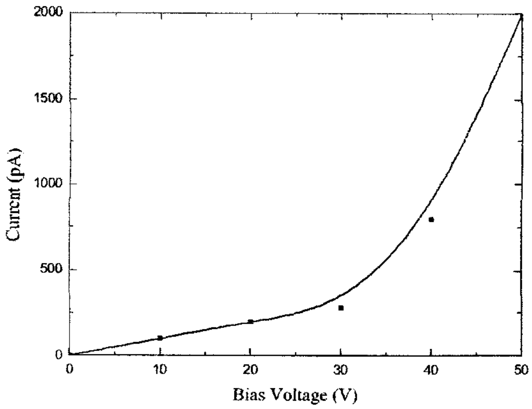

Fig. 7. Relative results of the response in current mode of the ZR300 detector under a ^{137}Cs gamma-ray excitation.

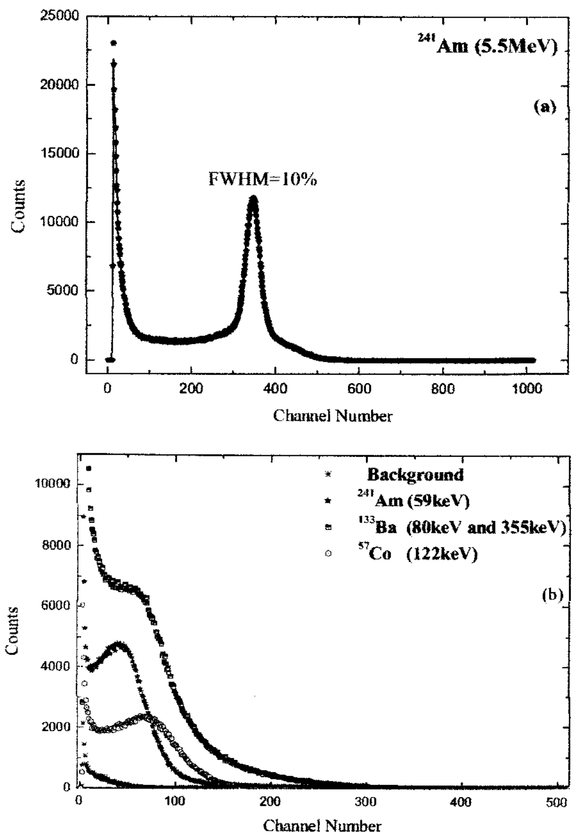

Fig. 8. Pulse height spectra for (a) alpha particle and (b) gamma excitations.

For ZR500 crystal, a better radiation response was observed compared to those of ZR200 and ZR300 crystals. Fig. 8 presents the pulse-height spectra of the ZR500 crystal under ^{241}Am alpha particle excitation and under ^{241}Am, ^{57}Co, and ^{133}Ba gamma radiations excitations. The better radiation response of ZR500 crystal, despite its worse crystalline quality may be attributed to its better purity, which permits to apply a higher bias voltage to the detector; so the charge carriers produced by radiation excitation can be collected more easily, obtaining a detector with better efficiency. Thus, further studies should be carried out in order to have the accurate information on the contribution of each of these parameters, i.e., purity and cristallinity, in the detector performance.

A resolution of 10% was obtained for 5.5-MeV alpha particles from ^{241}Am, what seems to be similar to that obtained in [14]. The ZR500 crystal presented pulse heights with recognizable features under gamma-ray excitation, although the resolution was poor. The 80-keV peak was not well defined for ^{133}Ba due to the overlap of the Compton scattering generated by 355-keV photon from ^{133}Ba. These results were also observed by Shoji *et al.* [14]. The resolution can be improved by: 1) using a charge sensitive pre-amplifier with lower noise; 2) using an amplifier with longer shaping time; and 3) obtaining purer crystals. Shah *et al.* [9] have developed a low noise electronic device to improve the PbI_2 detectors and obtained good resolutions.

With the appropriate processing techniques, it has been found that detectors fabricated from high purity crystal exhibit significant improvement in performance compared to those produced from low purity crystals. However, problems still exist in lead iodide due to the low charge carrier collection efficiency, which is probably caused by additional impurities or defects incorporated during crystal growth and detector fabrication processes. In addition, pulse-processing techniques should be investigated to improve gamma energy resolution.

IV. Conclusion

Concluding, we could show that the zone refining is effective to reduce the concentration of many impurities in lead iodide. The neutron activation analysis (NAA) showed to be a special technique to identify and quantify the impurities in the PbI_2 crystals and to evaluate the reduction of the impurities, after the purification.

A significative improvement in the characteristics of the detector crystal was achieved when the starting materials became purer.

The resistivity (Ω.cm) and the energy resolution (FWHM) were sensitive parameters to evaluate the detector quality in function of the purity degree.

In the present work, the purer starting materials could not be used to crystal growth. Further studies using PbI_2 purer (above 99.99%) from different suppliers should be carried out in order to obtain better quality detectors.

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