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

Icimone B. Oliveira, Fabio E. Costa, Maria J. Armelin and Margarida M. Hamada
Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP, Brazil

Abstract - **This article describes the methodology for the purification of the PbI_2 salt by technique of multipass zone refining and the growth by Bridgman method. A significant decrease of the impurities concentration was observed in function of the purification passes number. The results of the dark leakage current, the resistivity and the response of the alpha and gamma radiations were strongly dependent of the purity of the crystal.**

I. Introduction

The lead iodide (PbI_2) is a very promising material with large technological applicability as room temperature radiation detectors [1]-[3]. PbI_2 is a yellowish semiconductor with high resistivity ($10^{13}\Omega$cm) and density of 6.2 g/cm^3. The bandgap energy of the order of 2.58 eV and the high atomic number (Z_{Pb}=82 and Z_I=53) are important factors to be used as compact detectors and a low thickness is necessary for the detection of X-rays and γ-rays [4]-[6]. The relatively large bandgap energy indicates that devices should operate with low leakage currents and low polarization at elevated temperatures. Their disadvantages are low mobility (μ) of 8 cm^2/Vs and 2cm^2/Vs for electrons and holes respectively. Therefore, in order to enhance the electrical properties, the trapping time (τ) characteristics and the mobilities (μ) should be improved. The role of the crystal impurities on the electrical properties of PbI_2 is crucial, then improvements on the chemical purification should be achieved [7]-[9]. The melting point of PbI_2 is 408°C and it melts congruently. PbI_2 does not undergo a transition phase between its melting point and room temperature, which allows the purification and growth of crystals from the melting. It is well known that PbI_2 crystal is dominated by structural defects, when eliminated, the eletrical properties should improve, revealing their actual potential [8],[10],[11]. Recently, PbI_2 crystal has also been mentioned as a promising material to be used as a photodetector due to its physical, chemical and electronic properties[10].

The primary difference between recently demonstrated PbI_2 detectors and those fabricated earlier appears to be the degree of crystal purity [3],[8]. Purity, crystallinity and orientation are most likely critical in determining detector performance. Several studies [10],[12]-[17] 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. However, the performance of these detectors has been limited by the crystals quality. In this work, a methodology for purification and growth of the PbI_2 crystal and for its characterization as a room temperature radiation detector was developed. The dependence of the radiation response on the PbI_2 crystal purity was also studied.

II. Detector Fabrication

The commercially available PbI_2 powder with nominal purity of 99.0% was used as the starting material for growing crystals for detector applications. To reduce impurities, this material was purified by the many pass zone refining technique. This method is well described in the literature [7],[8], and it is based on the differential solubility of the impurities in the melted and the solid portions of the material.

Preliminarily, all the tubes were submitted to a rigorous chemical treatment and subsequent thermal treatment to avoid the adherence of the crystals in the tubes walls used in the melting. Subsequently, the PbI_2 powder was introduced into a treated 30cm long quartz tube of 10 or 20mm diameter, evacuated to 10^{-6}Torr

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I.B. Oliveira, F.E. Costa, M.J. Armelin and M.M. Hamada are with the IPEN/CNEN-SP, Travessa R, 400, 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 Institute of Physics – UNICAMP, Cidade Universitária "Zeferino Vaz", Barão Geraldo, Campinas-SP .

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and sealed off. The ampoule was mounted into the zone refining furnace and the heaters moved at a speed of 10cm/hr across the length of the ingot and upon reaching the end, quickly moved back to the starting point to prevent melting of the ingot during the reverse motion. The furnace temperature was set to approximately 500°C, above the melting point of 408°C. This process was repeated multiple times (200, 300 and 500 passes) in order to increase the purification efficiency to semiconductor standards. For segregation coefficient very different from the unity, there is a better efficiency for removing to one of the ends. It is shown that detectors fabricated from the section containing the purest material resulted in a best detector performance.

The crystals were grown by Bridgman method, after 200, 300 and 500 purification passes, which we denominated ZR200, ZR300 and ZR500 crystals, respectively. The purest section of the zone refined (ZR) ingot was introduced into the tube of quartz and melted in a Bridgman vertical furnace at temperature of 550°C and moved at a speed of about 1mm/hr. The obtained crystals (approximately 20mm length and 10mm diameter) were submitted to a thermal treatment during 20h at 150°C.

Samples from the bottom, middle and upper section of the ZR ingot were analysed after 200, 300 and 500 purification passes. The efficiency of the purification was evaluated, by measurements of the impurities concentrations, using the neutron activation analysis technique [18].

The crystalline quality was analyzed by X-ray diffraction. A Phillips Model DR 714020 X-ray diffractometer with Cu Kα radiation (40kV, 35mA in the 2θ range from 0 to 60°) was used for structural characterization of the PbI_2 crystal grown with different impurities.

In order to be prepared as a radiation detector, the grown crystals were cleaved perpendicularly to direction (001), using the diamond saw, in the dimensions of 4 to 10 mm^2 and thickness of 400 to 800μm. The wafer surfaces were then treated with a NaI (10%) solution to remove damage by the crystal cleavage. After the treatment, the surface quality was evaluated by scanning electron microscopy and it was suitable to apply the electric contact. This was applied with conductive graphite painting on both sides of the wafers. These low resistance contacts were used to minimize the noise[17].

The dark leakage currents were evaluated, applying different tensions. At first, the decrease of the leakage current, as time passed, was clearly studied, subsequently after the radiation.

The nuclear response of the detectors was studied using the conventional eletronic setup including the voltage power supply, charge sensitive preamplifier, a linear amplifier and a oscilloscope. The pulse height spectra were analysed using an ORTEC model 918A multichannel analyser, using a ^{241}Am, ^{57}Co and ^{133}Ba gamma radiation sources and a ^{241}Am alpha radiation source.

III. Results and Discussion

Figure 1 shows the concentration profiles for impurities found in the bottom, middle and upper sections of the crystal. It was observed a trend for impurities to segregate to the upper part of the ingot (last to freeze), as a consequence of the zone refining. It also appears that the total impurity concentration is a minimum towards 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.

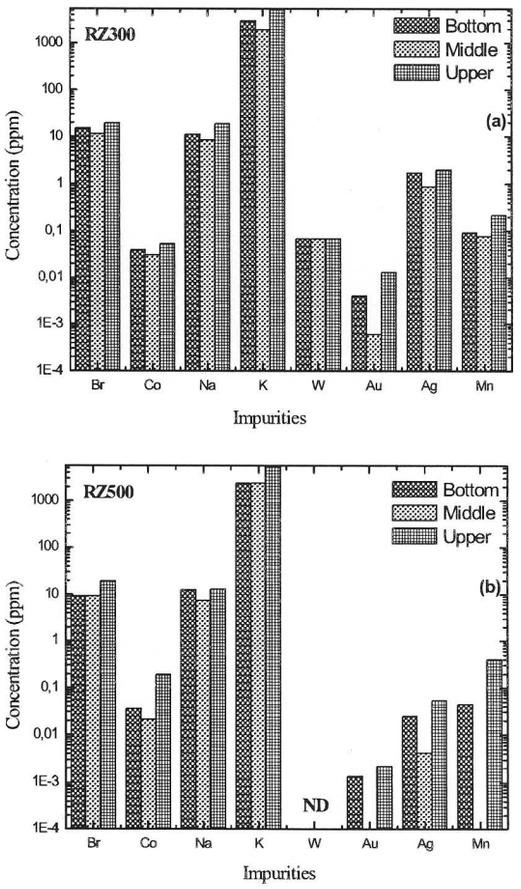

Fig. 1. Impurity concentrations in the bottom, middle and upper sections of purified PbI_2 lingots with 300 (a) and 500 (b) zone refining passes. ND = no detected. Impurity level: ppm

Figure 2 shows the tendency of the impurity concentration decrease in function of the purification passes number. As we can observe in this figure, there was a significant reduction of the impurities with the purification numbers. However the decrease depends on each element, since they have different segregation coefficients.

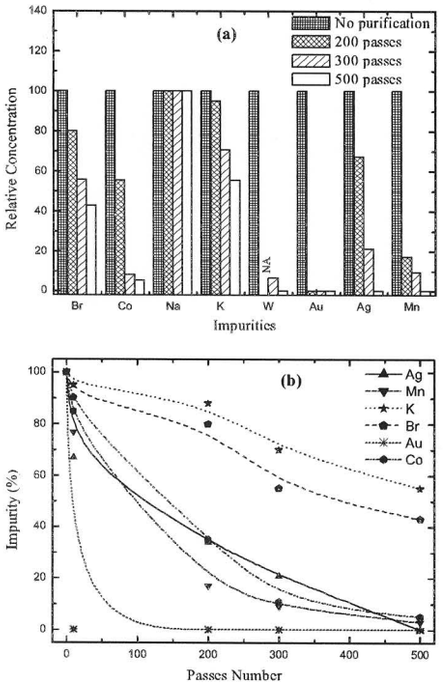

Fig. 2. Impurity reduction (a) and tendency of the concentration decrease (b) in function of the purification passes number. NA = no analysed.

Figure 3 presents the X-ray diffraction obtained for ZR300 and ZR500 crystals grown by Bridgman method. 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 crystals are preferentially oriented in the direction (001). In the ZR500 crystal it was observed the presence of reflection with low intensities peaks (110) and (113), which can to be due to the crystal position in the diffractometer. The crystal ZR300 was crystallographically better than ZR500, confirmed by the ZR300 peak (001) more intense than that of ZR500 crystal and the rate among the relative intensities of the ZR300 peaks (001, 003, 004) are closer to the archives Us Joint Committee on Powder Diffraction[19]. However, it could be observed that there was no other crystalline phase in the grown crystals, which can be confirmed by comparison with the diffraction pattern of the PbI_2 oriented in the direction (001).

The grown crystals were cleaved perpendicularly to direction (001), and prepared suitably with the electric contact to be used as a radiation detector. At first, the dark leakage current of the prepared detector was stabilized, applying a bias voltage of 5 V for 30 hr, subsequently after the preparation. Figure 4 shows the leakage current measurements as a function of the time. The decrease of the leakage current, as time passed, was clearly observed, as shown in Fig. 4. For further experiments, the stabilization time of 30 hr was not necessary.

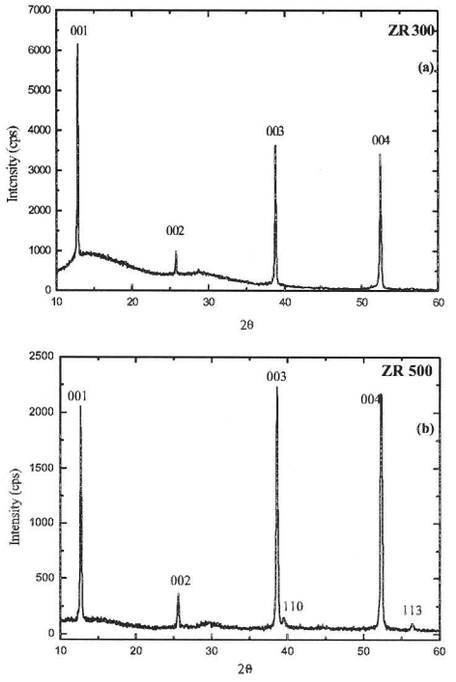

Fig. 3. X-ray diffraction of PbI_2 crystals: ZR300 (a) and ZR500 (b).

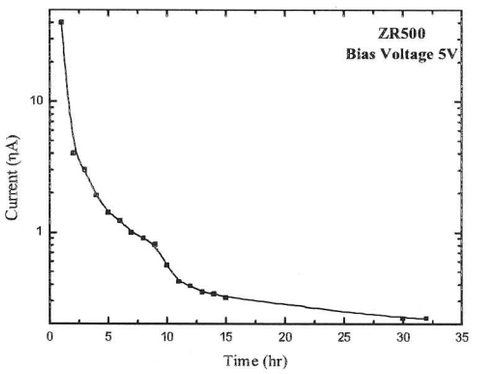

Fig. 4. Current-time curve for the PbI_2 detector.

Figure 5 shows the results of the leakage current as a function of the applied bias voltage. As it can be observed, for ZR200 and ZR300, the measurements were possible to be carried out in the range 0 to 100 V, while for the ZR500 crystal it could be applied up to 200 V. From these results the resistivity values were $10^{10}\Omega$cm for ZR200 and $10^{11}\Omega$cm for ZR300 and ZR500 crystals. The ZR300 and ZR500 crystals had the same order of resistivity values, however, in the ZR500 crystal the leakage currents were lower, due to the depletion region that produces an electrostatical potential, which decreases the leakage current, indicating the better characteristics of the ZR500 crystal as a semiconductor. The decrease of the leakage current due to the impurity reduction observed

in this work was in agreement with the literature [7], [12]. The differences can be attributed to the various levels of the impurity concentration that act as charge carriers traps, causing an increase in the leakage current.

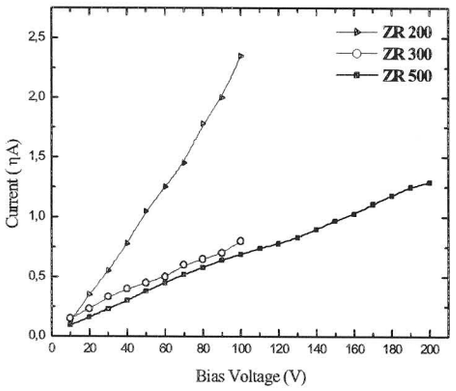

Fig. 5. Intensity X Bias Voltage curves of the PbI_2 detectors.

The importance of the PbI_2 crystal purity for its application as a radiation detector, described in the literature[2], [7], [11], [14], [15] 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. For ZR300 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. Figure 6 shows the results of the relative radiation response, in current mode, for ZR300 crystal.

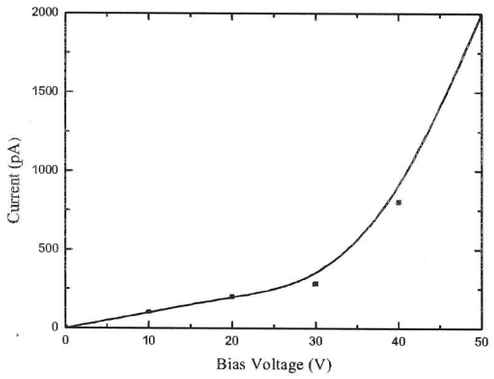

Fig. 6. Relative results of the response, in current mode, of the ZR300 detector, under a ^{137}Cs gamma ray excitation.

For ZR500 crystal, a good radiation response was observed. Figure 7 presents the pulse height spectra of the ZR500 crystal under ^{241}Am alpha particle excitation (a) and under ^{214}Am, ^{57}Co and ^{133}Ba gamma radiations excitations (b). The better radiation response of ZR500, despite its worse crystalline quality compared that of ZR200 and ZR300 crystals, 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, leading to obtain a detector with better efficiency. However, further studies should be carried out in order to know the accurate information on the contribution of each of these parameters, i.e., purity and cristallinity, in the detector performance.

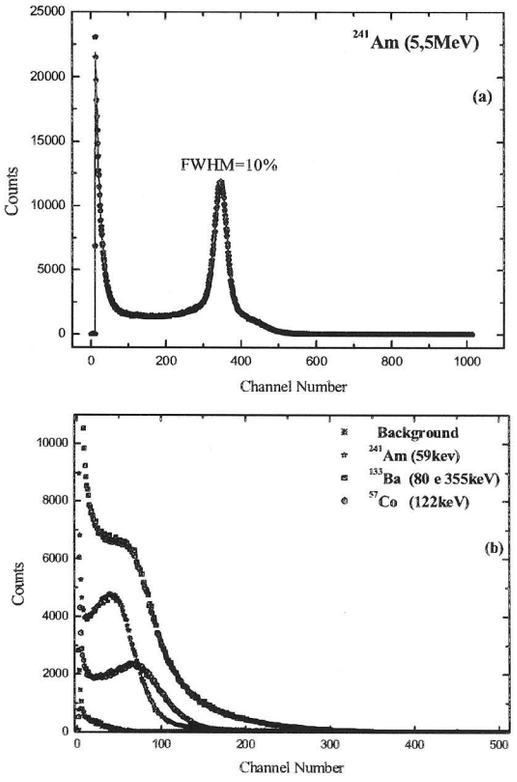

Fig.7. Pulse height spectra for alpha particle (a) and gamma (b) excitations.

For 5.5 MeV alpha particles from ^{241}Am, a resolution of 10% was obtained, which is in agreement with the literature [12]. For gamma ray excitation, a good response was observed for gamma radiation, however, the resolution was poor. The 80 keV peak not was well defined for ^{133}Ba due to the interference of the Compton scattering, generated by emitted 355 keV from ^{133}Ba. Shoji et al.[14] found similar results and they suggested that the resolution can be improved by: (a) using a charge sensitive pre-amplifier with lower noise, (b) using an amplifier with shaping time longer and (c) obtaining purer crystals. Lund et al. [13] have developed an electronic of low noise to improve the PbI_2 detectors and obtained good resolutions.

IV. Conclusion

Concluding, we have shown that the zone refining is effective to reduce the concentration of many impurities in lead iodide. 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.

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