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Trace impurities analysis determined by neutron activation in the PbI_2 crystal semiconductor

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Abstract

In this work, a methodology for impurity analysis of PbI_2 was studied to investigate the effectiveness of the purification. Commercial salts were purified by the multi passes zone refining and grown by the Bridgman method. To evaluate the purification efficiency, samples from the bottom, middle and upper sections of the ZR ingot were analyzed after 200, 300 and 500 purification passes, by measurements of the impurity concentrations, using the neutron activation analysis (NAA) technique. There was a significant reduction of the impurities according to the purification numbers. The reduction efficiency was different for each element, namely: Au > Mn > Co ~ Ag > K ~ Br. The impurity concentration of the crystals grown after 200, 300 and 500 passes and the PbI_2 starting material were analyzed by NAA and plasma optical emission spectroscopy.

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1. Introduction

A great interest has being focused on the development of the room temperature radiation detector, using semiconductor materials that have high atomic number and wide band gap. This type of detector has a large applicability as X-ray and γ-ray spectrometer, operating at room temperature [1–3]. Layered semiconductor materials have a number of properties that make them attractive for such application. However, the role of the crystal impurities on the detector performance is crucial, then improvements on the chemical purification and the impurity reduction analysis should be achieved [2,3].

PbI_2 is a layered semiconductor material with a wide band gap energy ($E_g = 2.58$ eV), high resistivity ($10^{13}\,\Omega$ cm) and because of its high density (6.2 g/cm^3) and high atomic number elements ($Z_{Pb} = 82$, $Z_I = 53$), it is well suited for use as X-ray and γ-ray spectrometers at room temperature [1,2]. Successful growth of high optical and electrical quality of the PbI_2 crystal detector is largely dependent on the purity of the material used [2,3]. In this work, the commercial PbI_2 powders, used as starting materials, were purified by zone-refining method and grown by Bridgman

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method. In order to evaluate the efficiency of the purification, the measurements of the impurity concentrations in the PbI_2 ingot after the different purification passes were carried out using neutron activation analysis (NAA) [4]. In the previous literature PbI_2 purity has been analyzed by plasma-optical emission spectroscopy. In this work, the impurity concentration of the PbI_2 starting material and the crystal grown after 200, 300 and 500 purification passes were also analyzed by NAA and compared to that evaluated by plasma emission spectroscopy (ICP-MS).

2. Materials and method

The commercially available PbI_2 powder is unsuitable as starting material for growing crystals for detector applications. To obtain suitable pure material, the commercially available powder with nominal purity of 99.0% was purified using the multiple pass zone-refining technique [2,3]. Horizontal zone refining is carried out in high-purity quartz tubes on an apparatus specifically designed for this purpose. Zone refining was conducted in 300-mm-long quartz tube of 20 mm inside diameter. The 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. Samples from the bottom, middle and upper sections of the ingots purified after 200, 300 and 500 passes and the PbI_2 and starting material were analyzed by the NAA technique [4] and the concentration of the impurities was determined. All samples were irradiated in a Nuclear Reactor IEA-R1 at IPEN. For short life elements, the samples were irradiated for about 5 min under $1 \times 10^{12}\,n\,cm^{-2}\,s^{-1}$, while for identification of long life elements they were irradiated for about 8 h under $2.4 \times 10^{12}\,n\,cm^{2}\,s^{-1}$. To quantify the trace elements, standard samples with well-known mass were irradiated simultaneously, under the same conditions.

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

The impurity concentrations of the PbI_2 starting material, ZR200, ZR300 and ZR500 grown crystals were evaluated by NAA. The impurity concentrations of the same samples were determined by plasma emission spectroscopy, in order to compare the results of both techniques.

3. Results and discussion

The PbI_2 ingot obtained by the ZR purification, showed well-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 the impurities found in the bottom, middle and upper sections of the crystal evaluated by NAA. It was observed that the impurities tended 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 minor 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 [2,3]. The segregation of most of the total impurities to the ends of the ingot indicates that the zone-refining method is very effective.

Fig. 2 shows the tendency of the impurity concentration to 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 numbers. However, the decrease depends on each element, since they have different segregation coefficients. For a segregation coefficient very different from a unity, the ZR process is more efficient to remove the impurities to one of the tube ends.

In the previous literature, PbI_2 purity has been analyzed by atomic absorption or plasma emission

spectroscopy [2]. As far as we know, the PbI_2 impurity determined by 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 of 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, in the order of parts per billion or greater. 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 [4]. In order to compare the NAA technique, the concentration of the impurity in the PbI_2 powder, used as starting material, was determined by inductively coupled plasma–mass spectroscopy (ICP-MS). Table 1 and Fig. 3 show the results of the impurity concentration analysis by NAA and ICP-MS techniques. Both NAA and ICP-MS presented similar results for almost all impurities. However, the sensitivity for some elements is greater in one method compared to the other as

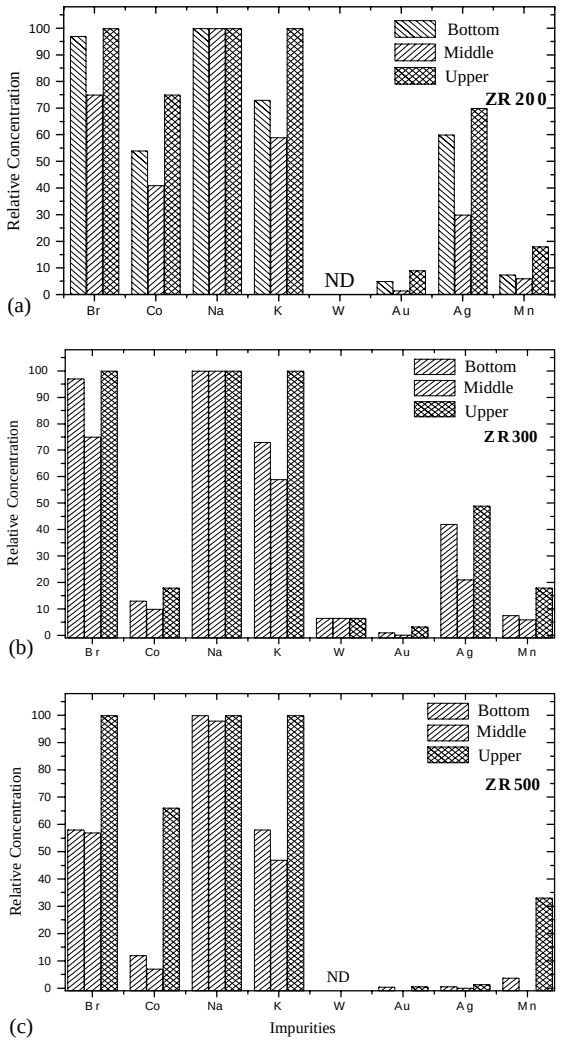

Fig. 1. Impurity concentrations in the bottom, middle and upper sections of purified PbI_2 lingots with 200 (a), 300 (b) and 500 (c) zone refining passes. ND = no detected.

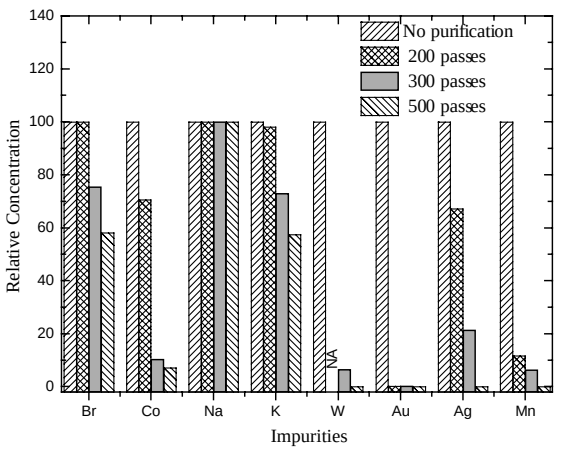

Fig. 2. Impurity reduction of the concentration in function of the ZR purification passes number. NA = no analyzed.

Table 1
Impurities concentrations of the lead iodide powder by NAA and ICP analysis

	Br	Ag	Na	K (ppm)	Mn	Co	Fe	W (ppb)	Au (ppb)
NAA	16.4	9.0	7.6	4038	1.20	0.29	ND	1.05	0.40
ICP	17.6	9.8	8.0	3630	0.05	0.32	0.4	ND	ND

*ND—no detected, **standard error: 10%.

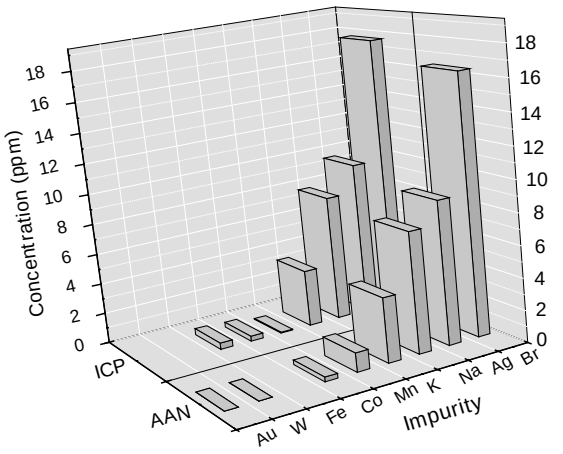

Fig. 3. NAA and ICP analysis elemental of PbI_2 powder. The value of the K concentration was divided by 1000, for a better visualization.

Table 2
Impurity concentration of ZR200, ZR300 and ZR500 crystals, by NAA and ICP-MS techniques

[*C*] ppm	RZ 200	RZ 300	RZ 500	ICP 200	ICP 300	ICP 500
Br	2.12	1.84	1.5	1.4	0	0
Ag	1.51	0.6	0.26	1.51	0	0
Na	2.93	0.93	0.37	2.83	0.69	0.30
K	3457	2698	475	3149	2941	127
Mn	0.36	0.08	0.04	0.05	0	0
Co	0.05	0.04	0.04	0	0	0
Fe	ND	ND	ND	0.38	0	0
[*C*] ppb						
W	0.5.2	0.27	0.06	ND	ND	ND
Au	0.18	0.12	0.10	ND	ND	ND

shown in Table 1 and Fig. 3. The discrepancy observed for Mn determination between NAA and ICP and W and Au detected only by NAA are probability due to high sensitivity of NAA to these elements, which are presented in the proportion of ppb in the ingot.

The sensitivity of NAA to the identified elements, W, Au and Mn is $\cong 0.01$ ppb, for Br, Co, Na and Ag is $\cong 1$ ppb and for *K* is $\cong 10$ ppb. On the other hand, Fe measured by ICP was not detected by NAA. Some impurities as Ca, Fe, Zn Al, Cu, Mg and Cr reported in the literature [4] were not found in the present work, in spite of the high sensitivity of NAA for these elements, (~ 1 ppb for Cu, Al, Cr, Zn; and ~ 10 ppb for Ca, Mg and Fe). In addition, in this work many assays were carried out to confirm these results. Furthermore, elements such as Ca, Zn, Al and Cr were not reported in the manufacture analysis certificates in the PbI_2 powder used.

The crystals grown were transparent and bright yellow. The impurity concentrations were smaller for the crystal grown with PbI_2 submitted to greater purification passes number, as shown in Table 2. Both NAA and ICP-MS techniques presented comparable results.

Concluding, the NAA showed to be a special technique to identify and quantify the impurities in the PbI_2 crystal, evaluating the reduction of the impurities after the purification and growth. The results of the impurity concentrations obtained by NAA were similar to those of the inductively coupled plasma–mass spectroscopy (ICP-MS).

The importance of the PbI_2 crystal purity for its application as a radiation detector was confirmed by the results found in the spectrometric measurements for α and γ radiations, described in our previous paper [3].

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