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PURIFICATION OF BISMUTH(III) IODIDE FOR APPLICATION AS RADIATION SEMICONDUCTOR DETECTOR

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ABSTRACT

This work describes the experimental procedure of a purification method of BiI_3 powder, aiming a future application of these semiconductor crystals as room temperature radiation detector. The Repeated Vertical Bridgman Technique applied to the purification, based on the melting and nucleation phenomena. An ampoule filled with a maximum of 25% by volume of BiI_3 powder mounted into the Bridgman furnace and vertically moved at a speed of 2 millimeters per hour, inside the furnace with programmed thermal gradient and temperature profile, at a maximum temperature of 530ºC. The reduction of the impurities in the BiI, after each purification procedure, analyzed by the Instrumental Neutron Activation Analysis (IINAA), in order to evaluate the efficiency of the purification technique established in this work, to trace metal impurities. It demonstrated that the Repeated Bridgman is effective to reduce the concentration of many impurities in BiI_3, such as Ag, As, Br, Cr, K, Mo, Na and Sb. The crystalline structure of the BiI_3 crystal purified twice and three times was similar to the BiI_3 pattern. However, for BiI_3 powder and purified once, an intensity contribution of BiOI observed in the diffractograms.

1. INTRODUCTION

A great interest has been focusing on the development of a room temperature radiation detector, using semiconductor materials that have a high atomic number and a wide band gap. This type of detector has a large applicability as X ray and gamma ray spectrometers, operating at room temperature [1,2]. Layered semiconductor materials have a number of properties that make them attractive for such applications. However, the common factors among the semiconductor materials to operate as room temperature semiconductor radiation detectors are their difficulty to grow crystals with high crystallographic perfection, high purity and good chemical stoichiometry. The performance of a radiation detector depends on several factors, such as, the carrier lifetime, the mobility, the crystallographic imperfections and the impurity concentrations of the detector. These factors may have an important role in the final performance of radiation semiconductor detectors [2,3].

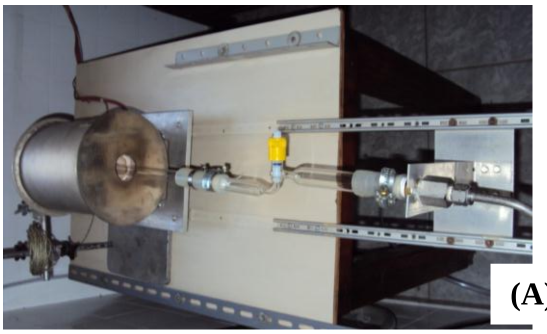
The main physical semiconductor properties required for fabrication of room temperature semiconductor detectors are: (1) high atomic number and density for high stopping power; (2) a band gap large enough to keep leakage currents low at room temperature and (3) large electron-hole mobility-lifetime products for efficient charge collection. High-Z compound semiconductors such as CdTe, Cd1-xZnxTe (CZT), HgI_2, PbI_2 and TlBr have been investigated as materials for nuclear radiation detectors that can operate at room temperature, since the early 1980s [2,3,4,5]. Recently, BiI_3 emerged as a particularly interesting material in view of its wide band gap (1.7eV), large density (5.7g/cm^3), high atomic number elements (Z=68) and high resistivity (>10^{9}Ωcm) [6,7]

Even though several studies on the preparation of room temperature semiconductor detectors and improvements in the methodology of purification, growth and characterization of the crystals have been carried out [2-8], problems found in the room temperature semiconductor detectors are not yet completely resolved. Among them, the low collection efficiency of charge carriers and the stability, which are probably caused by impurities or defects created during the crystal growth. [2-8]. The semiconductor crystal purity is a crucial factor for its optimal performance as a radiation detector [2-6]. Nevertheless, as far as is known, few studies on impurities reduction methodology in the BiI_3 semiconductor crystal have been found in the literature.

The experimental procedure for the BiI_3 purification by Repeated Bridgman methodology [8,9] established, aiming a future application of these semiconductor crystals as room temperature radiation detectors. The efficiency of this methodology for removing impurities was evaluate by the measurements of the impurity concentrations in the BiI_3 powder and crystals after the different purification numbers, using the neutron activation analysis (INAA) technique [4].

2. EXPERIMENTAL PROCEDURE

Two commercially available BiI_3 powders, with nominal purity of 99.99%, used as the starting material for the purification intended for growing semiconductor crystals. The Repeated Bridgman method applied to the purification of these BiI_3 powders. Prior the purification, the 14.4 mm diameter x 150 mm long borosilicate glass tubes, used as crucible, submitted to chemical etching and thermal treatment. The tubes were deep in a cleaning solution (Extram MA 02, 1% Neutral) for removal of dust particles and possible plump. After this procedure, the tubes were wash, repeatedly, with distilled water. Subsequently, they underwent chemical treatment (with 30% NH_3 solution) in order to remove impurities and/or any detergent adsorbed on the walls. Thereafter, traces of acid were removed by successive rinses with deionized water, and the crucibles placed in a furnace for drying. In the sequence, the tubes were treat thermally, evacuating them for a period of 2 hours at 400ºC at 10^{-5} Torr, in order to avoid the adherence of the crystals in the walls of the tubes used in the melting. Subsequently, 15 g of BiI_3 powder introduced into the tube, evacuated to 10^{-5} Torr and sealed off (Figure1).



(A)

(B)

Figure 1: Furnace used for thermal treatment (A) and tube sealing after thermal treatment at 10^{-5} Torr (B)

For purification, the tube containing BiI_3 powder was mount into the vertical Bridgman furnace (Fig. 2) and the BiI_3 melted at a temperature of 408°C; afterwards, the tube with BiI_3 moved vertically down with a rate of 2 mm/hr at 530ºC into the furnace.

Figure 2: Vertical Bridgman Furnace used for BiI_3 purification (A) and Tube with BiI_3 (B)

Crystal around 2.0 mm diameter x 40 mm long obtained after the first purification. Following the same procedure, the crystals are grown repeatedly (three times) for purification, since the impurities tend to migrate to the extremities of the crystal, during the growth, due to the impurities segregation along the crystal. Thus, it is expected that the best purity is found in the middle region. For each re-growth, the PYREX tube was open and three little sliced samples were taken from the crystals. The first sample (Sample T) corresponds to the upper crystal extremity (top), the second sample (Sample M) was taken from the middle region of the crystal, and the third sample reserved from the lower crystal extremity (bottom). A small amount of about 50 mg of sample was taken from each slice (samples T, M and B) to identify and determine the concentration of impurities. The impurity concentrations of the samples, taken from slices after each growth and BiI_3 powder were analyzed by the Instrumental Neutron Activation Analysis (INAA) technique [4]. All samples were irradiated in a Nuclear Reactor IEA-R1 at IPEN.

The crystalline quality was analyzed by X-ray diffraction (DRX). An X-ray diffractometer Phillips Model DR 714020, with Cu Kα radiation target (40kV, 35mA in the 2θ range from 0 to 60º), used for structural characterization of the BiI_3 crystal grown with different levels of impurities.

3. RESULTS AND DISCUSSION

Figure 3 shows the characteristic curve of the furnace temperature profile obtained for BiI_3 crystal growth, by Bridgman method. This procedure was necessary to verify the symmetry of the temperature gradient before and after the maximum furnace temperature region.

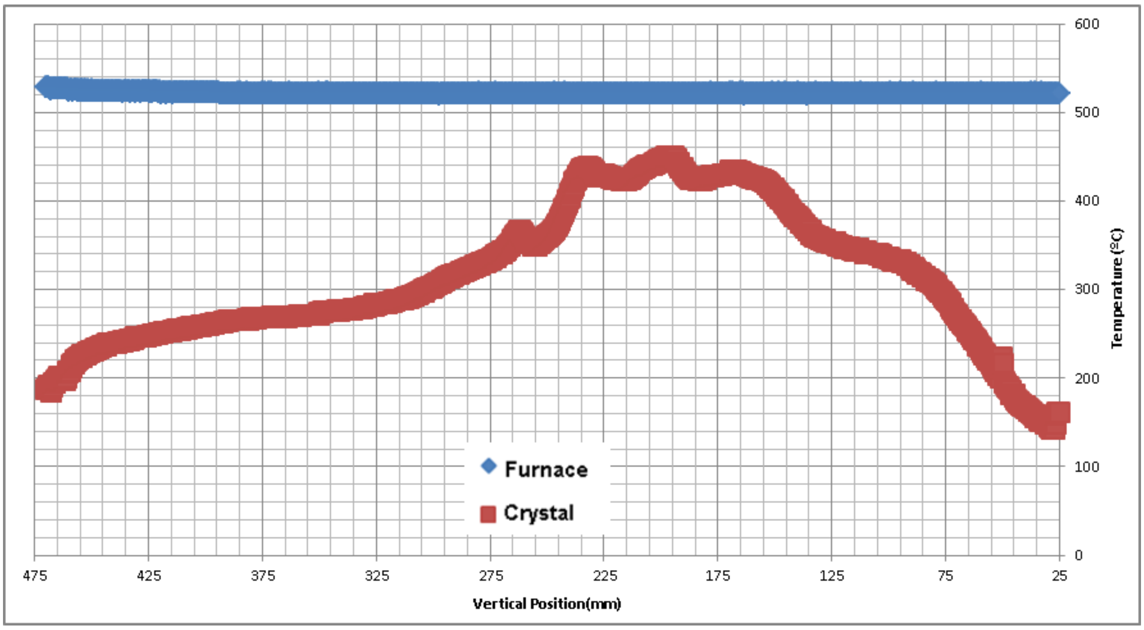
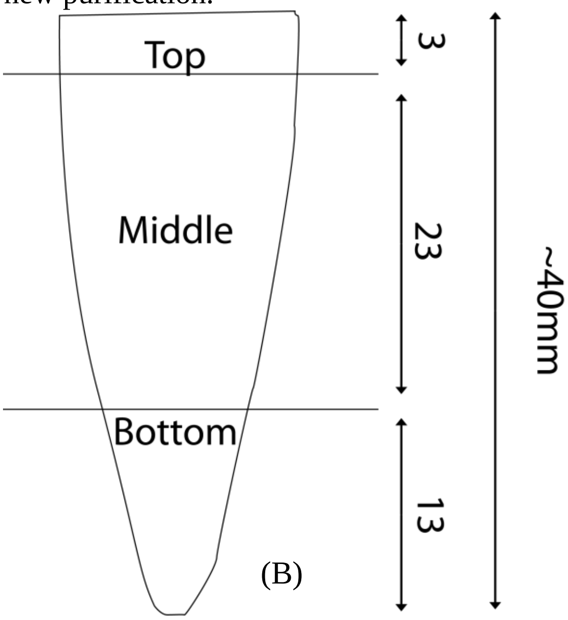


Figure 3: Typical curve of furnace temperature: redline, crystal growth temperature and blue line, furnace temperature

BiI_3 crystals of ~40mm long, obtained by the Repeated Bridgman Purification, cleaved, after each purification, in the following dimensions: the "*TOP*" sample (upper region) with ~3mm thickness, the "*MIDDLE*" sample with ~23mm thickness and the "*BOTTOM*" with ~13mm thickness, as shown in Fig.4. Samples from each of the crystal regions were taken for performing the physical-chemical characterizations, after each purification step. After taking a small piece from the *MIDDLE* region, it used for new purification.

(A)

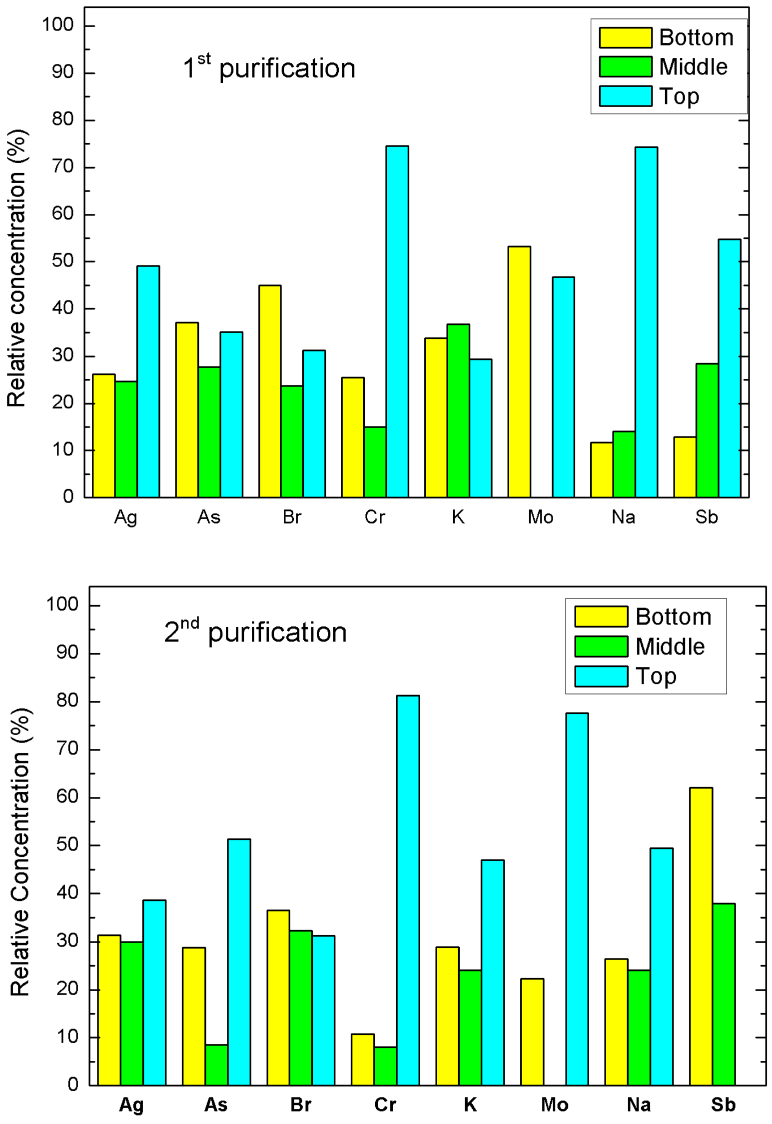


(B)

Figure 4- A) Crystal obtained by Repeated Bridgman purification; B) Crystal dimensions and cleavage proportions.

To assess the effectiveness of the Repeated Bridgman methodology as a means of purification, the INAA technique employed to investigate the presence and concentrations of some impurities in three different regions (top, middle and bottom) of the crystal and in the commercial BiI_3 powder. The following impurities were identified: Ag, As, Br, Cr, K, Mo, Na and Sb. It is important to stand out that the reduction of the impurities present in the BiI_3 after purification by the Repeated Bridgman technique is being reported firstly in this work.

Fig. 5 shows the impurities identified, as well as the concentration profiles, for the impurities found in the bottom, middle and upper regions of the crystal evaluated by the neutron activation analysis. As observed that the impurities tended to segregate to the upper part of the crystal (the last one to freeze), as a consequence of the Bridgman Growth. It, also, appears that the total impurity concentration is minor towards the middle of the ingot, indicating that the segregation coefficient is below or above unity, for some elements. Therefore, these impurities segregate in the first or last parts of the ingot to freeze [2,3]. The segregation of the most total of impurities to the ends of the crystal indicates that the purification method established in this work was effective. As it can be observed in Figure 5, most impurities moved to the top region of the crystal, suggesting that the segregation coefficient (k) of this element is k > 1.



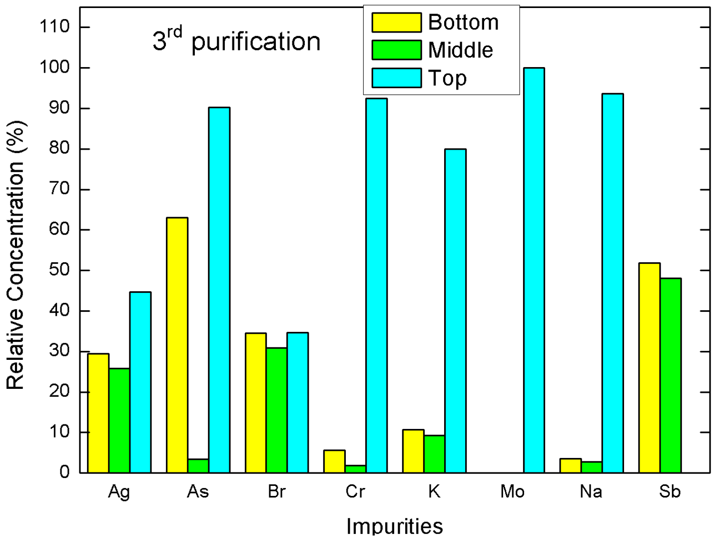


Figure 5- Impurity concentrations in the bottom, middle and upper sections of purified BiI_3 crystals with 1 (a), 2 (b) and 3 (c) purification numbers.

Fig. 6 shows the tendency of the impurity concentration to decrease in function of the number of purification processes. As it can be observed, there was a significant reduction of most impurities according to the number of purification procedures, excepting for Br. The decrease depends on each element, since they have different segregation coefficients. For a segregation coefficient very different from a unity, the Bridgman process was more efficient to remove the impurities to one of the tube ends. The Mo was removed fully at the first purification, while, As, Cr and Sb impurities decreased significantly after a third purification. Almost all impurities decreased, excepting the Br, whose quantity, differently, increased after each purification step. Probably, the segregation coefficient is less than 1 or some contamination may have occurred during the experiments. Further studies should be carried out to elucidate this result.

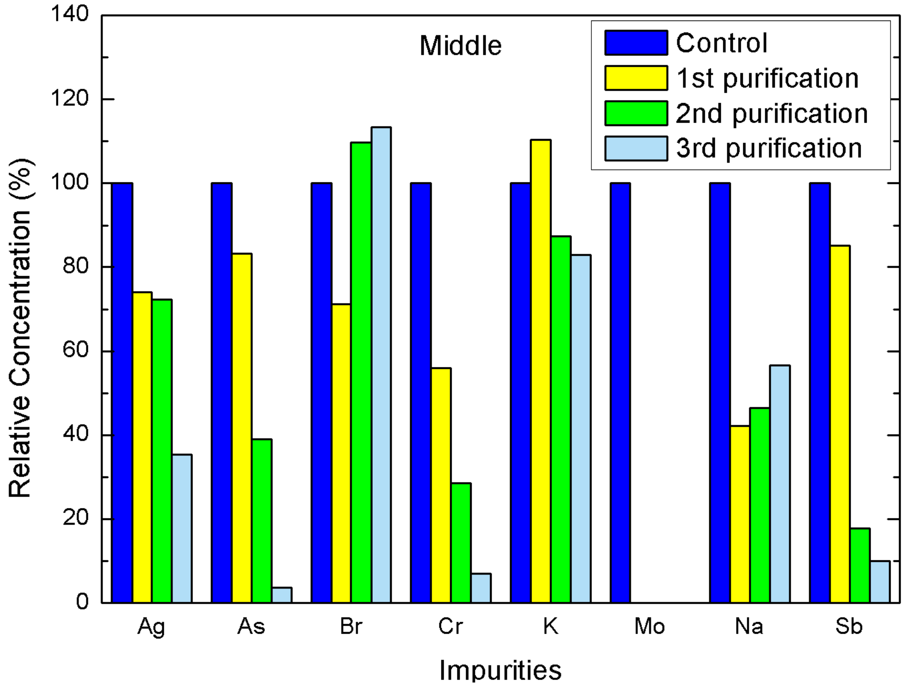


Figure 6 - Impurity reduction of the concentration in function of the Bridgman purification number.

Fig. 7 and 8 present the X-ray diffraction characterization of samples from the bottom, middle and top regions of the crystal purified twice and three times, respectively. As it can be observed from Fig. 7 and 8, crystals purified twice and three times present a similar structure with the rhombhoedric crystalline pattern to the BiI3 crystal [6,7]. On the other hand, the diffractograms of BiI_3 powder and the samples from crystal purified only once presented not only the peaks belonging to the BiI_3 crystals, but also, an intensity contribution from Bismuth Oxide Iodide (BiOI) appears in the angles, as it can be observed in Fig. 9. [10]. A background intensity contribution, which appears in the angles, probably due to some trace impurities still present in the crystal. However, the trace impurities did not affect, significantly, the crystalline structure, suggesting that they did not enter the crystal structure during the growth. Finally, it is worthwhile to observe that there was no other crystalline phase in the grown samples after the two purification procedures, since all detected peaks were identified as belonging to BiI_3.

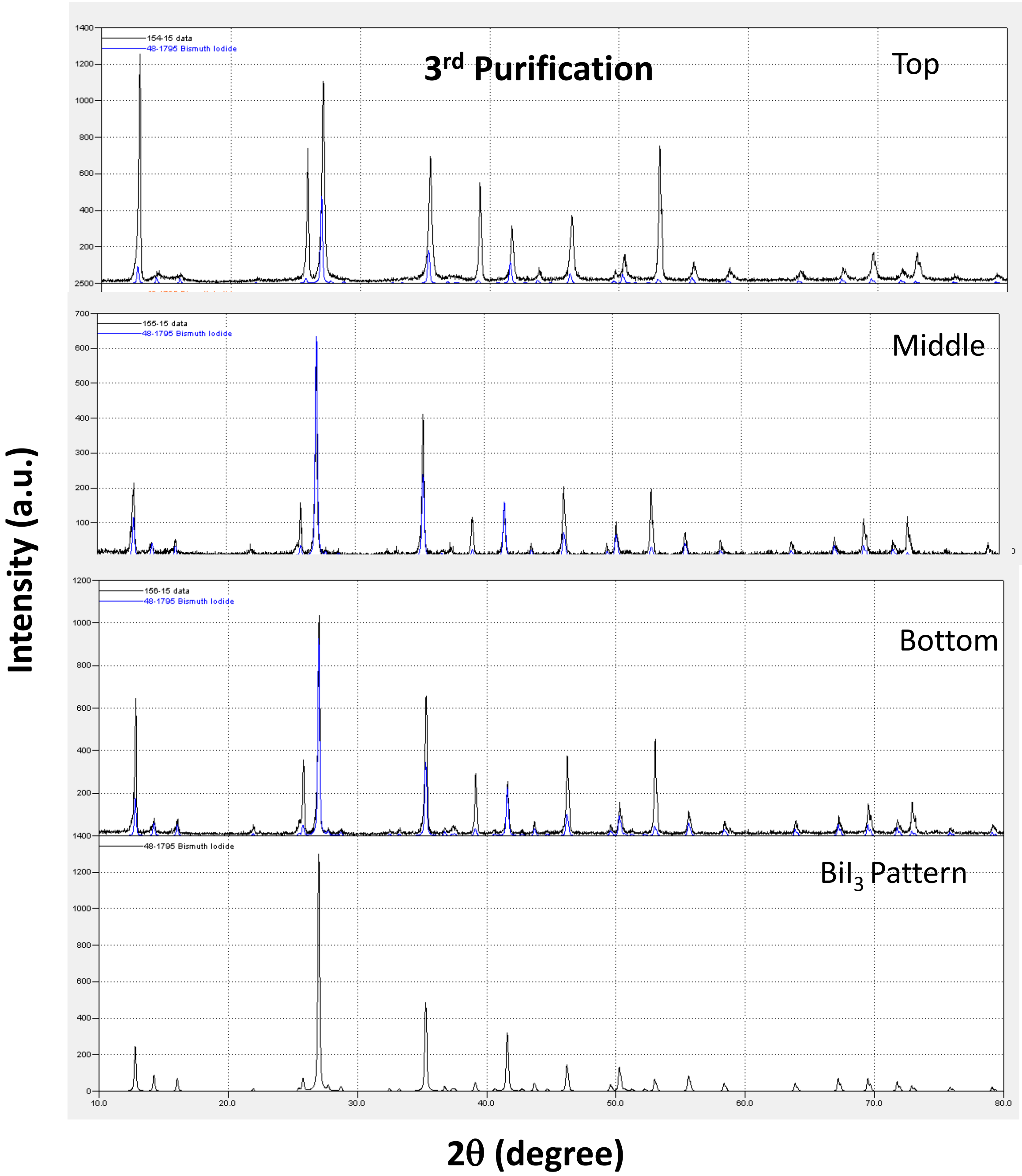


Figure 7. X-ray diffraction of the Top, Middle and Bottom samples from BiI_3 crystal purified three times. X-ray diffraction pattern of BiI_3 (Card Information PDF Number: 48-1795) [11]

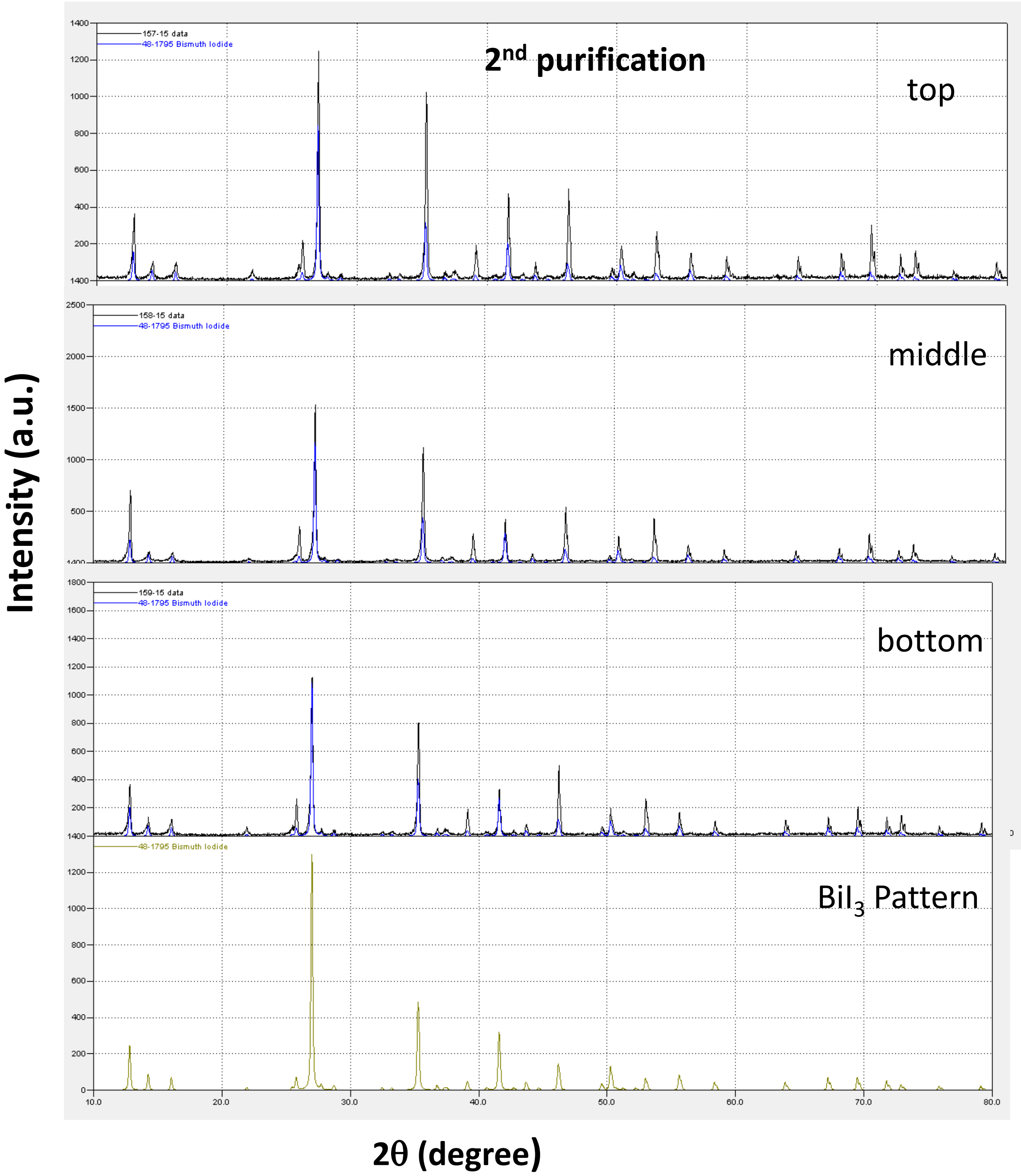


Figure 8. X-ray diffraction of the Top, Middle and Bottom samples from BiI_3 crystal purified twice. X-ray diffraction pattern of BiI_3 (Card Information PDF Number: 48-1795) [11]

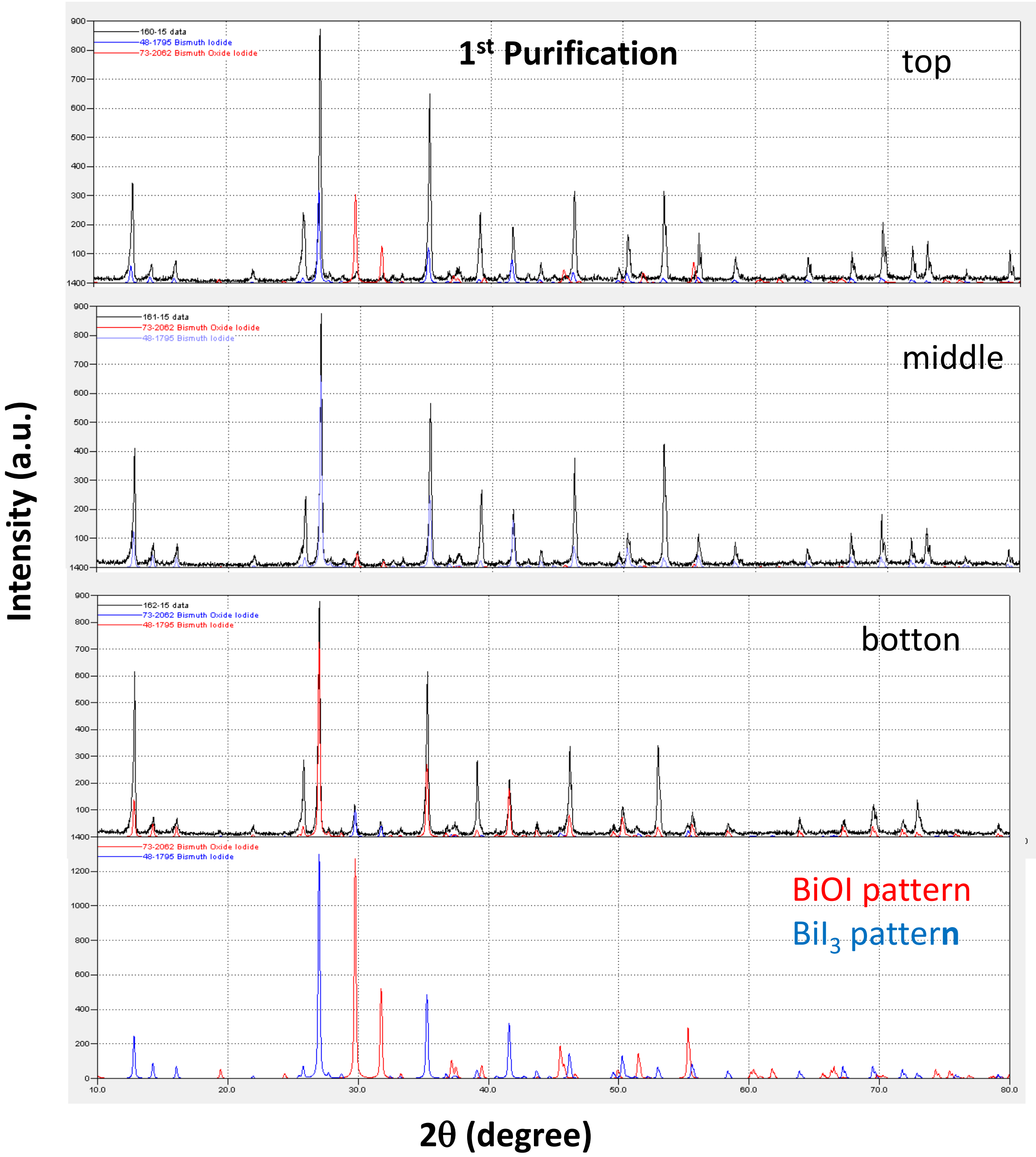


Figure 9. X-ray diffraction of the Top, Middle and Bottom samples from BiI_3 crystal purified once. X-ray diffraction pattern of BiI_3 and BiOI (Card Information PDF Number: 48-1795) [11]

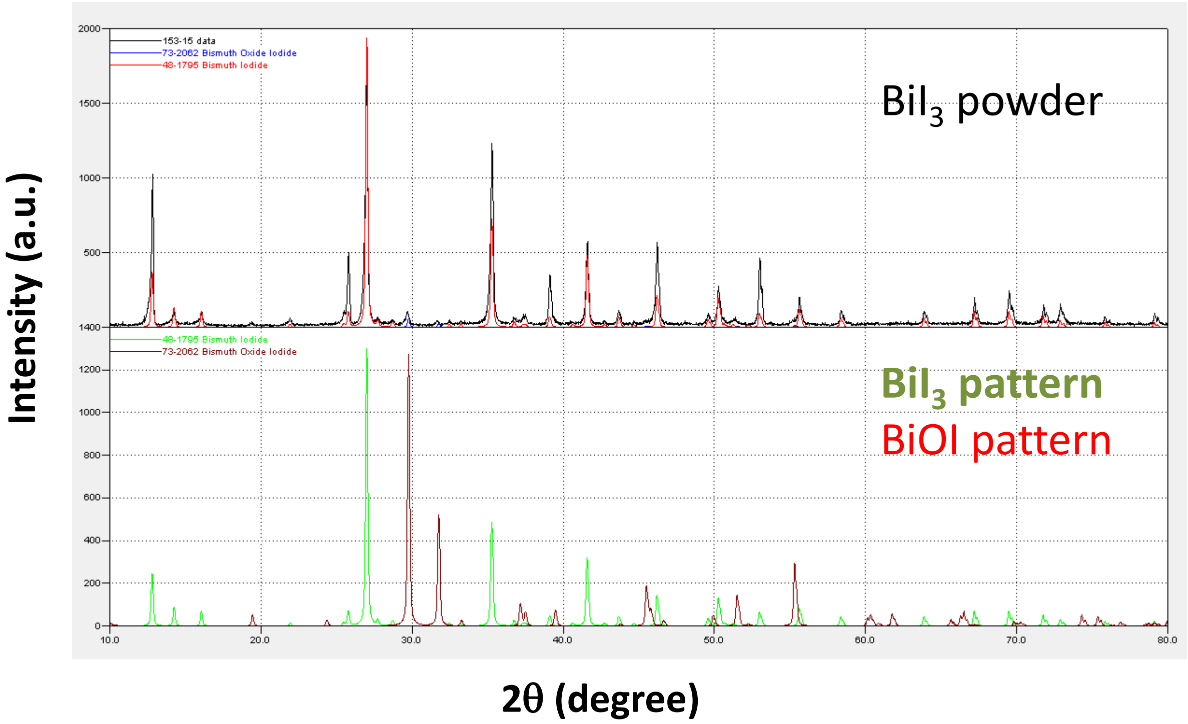


Figure 10. X-ray diffraction of the BiI_3 powder used; X -ray diffraction pattern of BiI_3 and BiOI (Card Information PDF Number: 48-1795) [10]

3. CONCLUSIONS

Concluding, the Repeated Vertical Bridgman Method showed to be effective to reduce the concentration of many impurities in BiI_3. After three purification procedures, most impurities such as, Mo, As, Cr and Sb, were practically removed. The Neutron Activation Analysis (INAA) showed to be a special technique to identify and quantify the impurities in the BiI_3 crystals and to evaluate the reduction of the impurities. The segregation of the majority of the total impurities to the ends of the crystal indicates that the purification method established in this work was efficient. No other crystalline phase in the BiI_3 purified twice and three times, by the Vertical Bridgman Method, were found; all detected peaks identified as belonging to BiI_3. For crystal purified only once, an important contribution from Bismuth Oxide Iodide (BiOI) was observed. Hence, the Repeated Vertical Bridgman Method showed to be an efficient technique for purification of BiI_3 aiming its use as raw material for the development of BiI_3 radiation semiconductor detector.

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