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Purification and Crystal Growth of the Bismuth (III) Iodide-influence of Trace Impurities on the Crystal Quality

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Abstract

This work describes the experimental procedure of purification and preparation of BiI_3 crystals by Repeated Vertical Bridgman technique, aiming a future application of this semiconductor crystal as a room temperature radiation detector. The BiI_3 powder used as raw material was purified three times and, at each purification, the crystal was evaluated by systematic measurements of the reduction of the impurities, crystalline structure, stoichiometry and surface morphology. The reduction of the trace metal impurities in the BiI_3, at each purification, was analyzed by Instrumental Neutron Activation Analysis (INAA), in order to evaluate the efficiency of the purification technique established in this work. It was demonstrated that the Repeated Bridgman technique 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 BiI_3 pattern. However, for BiI_3 powder and purified once, an intensity contribution of the BiOI was observed in the diffractograms. Improvement in the stoichiometric ratio was observed at each purification step, as well as the crystal surface morphology.

Keywords: bismuth (III) iodide, crystal growth, semiconductor crystal, INAA

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 gamma ray spectrometer, operating at room temperature (McGregor & Hermon, 1997; Martins et al, 2012; Oliveira et al, 2004). Layered semiconductor materials have a number of properties that make them attractive for such application. However, the common factor among the semiconductor materials to operate as room temperature semiconductor radiation detectors is their difficulty to obtain crystals with high purity, high crystallographic perfection and good chemical stoichiometry. It is know that the role of the impurities is crucial to grow crystals with these required characteristics, thus, improvements on the chemical purification and the impurity reduction analysis should be achieved (Martins et al, 2012; Oliveira et al, 2004).

Several studies are found in the literature on 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 80s (Martins et al, 2012; Oliveira et al, 2004; Oliveira et al, 2002; Hitomi &Matsumoto, 2002).

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 (Martins et al, 2012; Oliveira et al, 2004; Oliveira et al, 2002; Hitomi &Matsumoto, 2002;Matsumoto et al, 2002;Qiu, 2010, Gokhale et al. 2014, Garg et al, 2014; Gokhalea et al, 2015; Santos et al. 2012), problems found in the room temperature semiconductor detectors are not yet completely resolved. Among them, the low collection efficiency of charge carriers and their stability, which are probably caused by impurities or defects created during the crystal growth. The semiconductor crystal purity is a crucial factor for its optimal performance as a radiation detector (Martins et al, 2012; Oliveira et al, 2004; Oliveira et al, 2002; Hitomi &Matsumoto, 2002; Matsumoto et al, 2002;Qiu, 2010, Gokhalea et al. 2014).

More recently, BiI_3 has emerged as a particularly interesting material well suited for use as X ray and γ ray spectrometers at room temperature, in view of its wide band gap (1.67eV), large density (5.7g/cm^3), high atomic

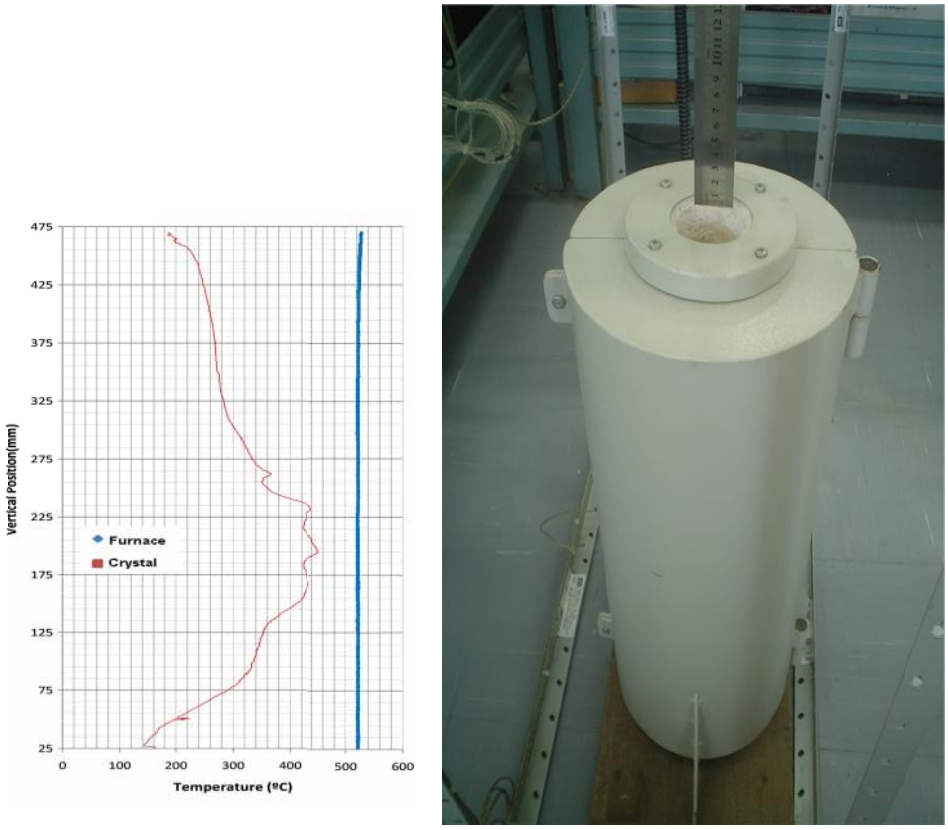
number elements (Z_{Bi}= 83, Z_I =53) and high resistivity (>109Ωcm) (Matsumoto et al, 2002; Gokhalea et al. 2014). However the behavior of semiconductor devices is strongly influenced by the presence of impurities or contaminants remaining due to incomplete purification of the semiconductor material (Matsumoto et al, 2002). Small quantities of impurities present at concentrations below 1 ppb can have a significant effect on quality of semiconductor devices. Nevertheless, as far as we know, few studies on impurities reduction methodology in BiI_3 semiconductor crystals have been found in the literature.

In this paper, BiI_3 crystals have been grown by the vertical Bridgman technique (Pfann, 1958) using commercially available powder. Efforts have been concentrated on the purification of the BiI_3 and, the purification efficiency was assessed by analyzing the crystals, through instrumental neutron activation analysis (INAA). The analyzed crystals came from the impurity reduction process occurred after each purification by the Repeated Vertical Bridgman method. INAA is the elemental analysis method usually chosen for these projects because of some features such as: small amount of sample available, minimal sample handling and high sensitivity for many elements (Alfassi, 1998; Hamada, 2003). Also, the stoichiometry, the crystalline structure and the surface morphology were evaluated for each crystal grown by Vertical Bridgman methodology, as a function of purification number.

2. Methodology

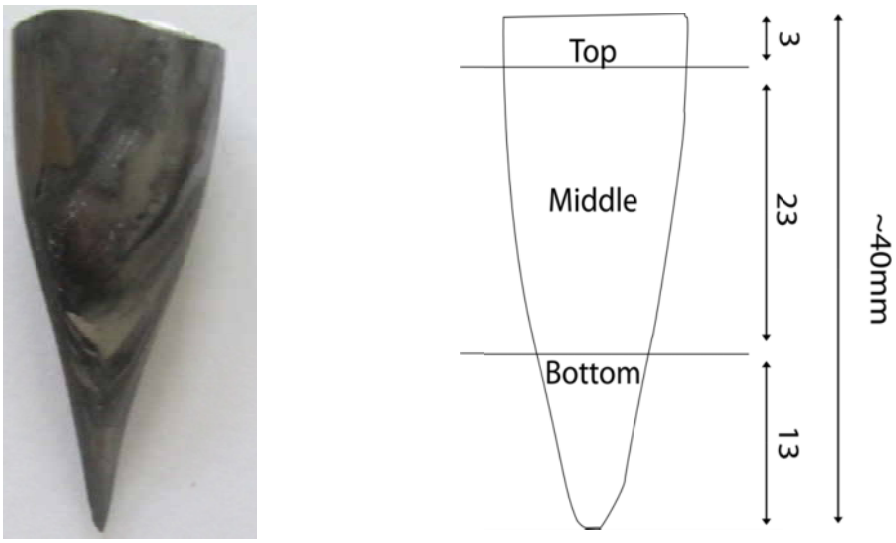
Commercially available BiI_3 powder (Alfa Aesar, A Johnson Matthey Company), with nominal purity of 99.99%, was used as the starting material for growths of the BiI_3 semiconductor crystals. BiI_3 crystals were grown by the vertical Bridgman technique, using borosilicate glass tubes as crucibles in vacuum atmosphere. Preliminary, the tubes were submitted to a chemical treatment. The 2.0 mm diameter x 150 mm long borosilicate glass tubes were previously washed with a cleaning agent solution (Extran MA 02, Merck) for removal of possible dust particles and plumb. Afterward, the tubes were washed repeatedly with distilled water and, then, filled with a 30% NH_3 solution; after 10 minutes, the tubes were rinsed three times with demineralized water. Subsequently, the tubes were submitted to a thermal treatment at 530 ºC to avoid the adhesion of the crystals on the walls of the tubes. Subsequently, 15 g of BiI_3 powder was introduced into the treated tube, evacuated to 10-5 Torr and sealed off. The tube containing BiI_3 powder was mounted into the vertical Bridgman furnace (Fig. 1A) and BiI_3 was melted at a temperature of 530°C; afterwards, the tube with BiI_3 was moved vertically with a rate of 2 mm/hr into the furnace. Fig. 1(B) 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.

Crystal around 2.0 mm diameter x 40 mm long was obtained, after each purification step. For each re-growth, the tube was opened in the clean room and the crystal was cleaved in the following dimensions: the “TOP” sample (upper region) with ~3 mm thick, the “MIDDLE” sample with ~23mm thick and the “BOTTOM” with ~13mm thick, as shown in Figure 2. Samples from each crystal region were taken for performing the physical-chemical characterizations, after each purification step. After taking a small piece from the MIDDLE region, this was used for new purification. Following the same procedure, the crystals were 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.



(A) (B)

Figure 1. Typical curve of furnace temperature: redline crystal growth temperature and blue line furnace temperature (A) and Vertical Bridgman Furnace used for BiI_3 purification (B)



(A) (B)

Figure 2. Crystal obtained by Repeated Bridgman purification (A); Crystal dimensions and cleavage proportions (B)

A small amount of about 150 mg of sample was taken from each slice (samples TOP, MIDDLE and BOTTON) 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 (Oliveira, 2002). For this, BiI_3 aliquots ranging from 40 to 120 mg were transferred to polyethylene bags, which had been cleaned by leaching with a diluted HNO_3 (1:5) and purified water. Certified standard solutions (Spex Certiprep) of Ag, As, Br, Cr, K, Mo, Na, Sb and Zn were used to prepare the standards. Aliquots (50-100 μL) of these solutions were transferred to small sheets of analytical filter paper (Whatman number 42). After drying, these filter papers were placed into polyethylene bags for irradiation. Irradiations were carried out at the IEA-R1 nuclear research reactor of IPEN-CNEN/SP. The thermal neutron flux utilized ranged from 0.1 to 1,2 x 10^{12} n cm^{-2} s^{-1}. Samples and standards (Ag, As, Br, Cr, K, Mo, Na and Sb) were irradiated simultaneously in an aluminum container for 7 h. The ^{76}As, ^{82}Br, ^{42}K, ^{99}Mo, ^{24}Na and ^{122}Sb activities were measured after 3 days of decay time, while ^{110m}Ag and ^{51}Cr were measured after, at least, 8 days of decay time. In addition, analyses of certified reference material NIST 2710 Montana Soil was also carried out simultaneously to take control of the analysis process. The equipment used to measure the gamma-radiation was a model GX2020 hyperpure Ge detector, coupled to a model 1510 Integrated Signal Processor and MCA System 100, both from Canberra. The detector used had a resolution (FWHM) of 0.9 keV for 122 keV gamma rays of ^{57}Co and 1.9 keV for 1332 keV gamma-ray of ^{60}Co.

The crystalline quality was analyzed by X-ray diffraction (DRX) (Keller, 1996) for samples from the regions (Top, Middle, Bottom) at each growth process. An X-ray diffractometer Phillips Model DR 714020 with Cu Kα radiation target (40kV, 35mA, in the 2θ range from 0 to 60º) was used for structural characterization of BiI_3 crystal grown with different impurities.

Scanning electron microscopy analyses were performed to verify the morphology and elemental chemical composition of the BiI_3 crystals at different levels of purification, as well as to investigate the surface quality in the Top, Middle and Bottom regions from the crystals purified once, twice and three times. This method allows observing the surface homogeneity and structural quality on a much larger scale (10-20,000 X). Both, analyses the surface morphology and the stoichiometry BiI_3 crystals were evaluated by SEM-BSE technique, using a scanning electron microscope LX 30, from Philips. For these experiments, 0.50 mm slices were cleaved from the three regions at each growth.

3. Results and Discussion

Figure 3 shows a typical crystal of BiI_3 obtained by the Bridgman technique before and after purification. The crystals obtained in the first growth showed a blackish gray coloration. A better crystal quality was observed in the crystals with higher purity. These crystals had fewer imperfections and high translucency and uniformity. No significance difference was observed in the crystal visual aspects between two and three purifications.

Before (A) After (B)

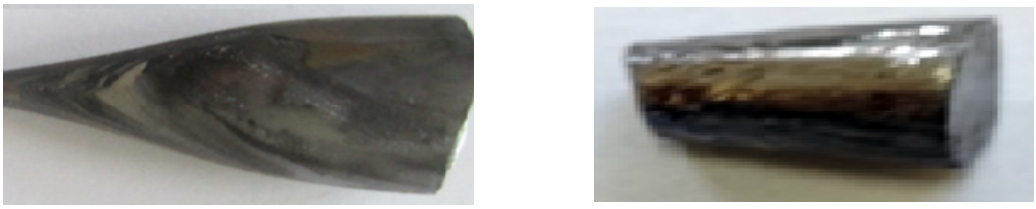


Figure 3. Pictures of the BiI_3 crystals without (A) and after three purifications (B)

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

In order to evaluate the performance of INAA for the determination of impurities in BiI_3 is important to take into consideration certain nuclear characteristics of the radionuclides formed by the reaction (n, ɣ) on the matrix (Table 1). As can be seen, the probability of formation of bismuth radionuclides is very small. For this reason, bismuth does not prevent the application of INAA in this study. However, the reaction of formation of the ^{128}I is very effective (σ = 6200 Millibarns). It is a produced radionuclide ($T_{1/2}$=24.9 minutes) making it impossible to determine impurities whose reaction (n,ɣ) form radionuclides whose half-lives are of the order minutes or few hours, such as ^{66}Cu, ^{52}V, ^{51}Ti, ^{56}Mn.

Table 1. Nuclear characteristics of reaction (n,ɣ) on the BiI_3 (Travesi, 1975).

Parameters					
Stable isotope	Isotopic abundance	Nuclear reaction	Cross section	Isotope produced	Half - life
-	**%**	-	**Millibarns**	-	**Y, D or M***
^{209}Bi	100.00	(n,ɣ)	15.0	^{210m}Bi	0.3 E + 07 Y
^{209}Bi	100.00	(n,ɣ)	19.0	^{210}Bi	5.01 D
^{127}I	100.00	(n,ɣ)	6200.0	^{128}I	24.90 M

* Y = year; D = day; M = minute

The results of the analysis of impurities in the samples obtained from the BiI_3 purification carried out by Bridgman technique are shown in Table 2. Each result is the mean of two or three measures followed by the standard deviation.

The results obtained in the certified reference material NIST 2710 Montana Soil, used for quality control, showed good agreement with the certified values, for most of elements. In most cases, the accuracy of BiI_3 analyzes (Table 2) were below 20%. As such, the results showed that INAA can be a useful instrument to monitor impurities (Ag, As, Br, Cr, K, Mo, Na and Sb) in the various stages of the BiI_3 purification methodology.

The efficiency assessment of the purification methodology based on the observed results (Table 2) depends on the knowledge of the segregation coefficients of the elements in the surroundings, which is beyond of the scope of the present study. However, it should be emphasized that INAA demonstrated to be a sensitive analytical technique useful to identify both qualitative and quantitative multi-element analysis of trace elements in BiI_3 in order to distinguish the segregation of the impurities along the crystal, as shown in Table 2. It was observed a trend for impurities to segregate to the upper part of the ingot (last to freeze), as a consequence of their segregation during the growth process, suggesting that the segregation coefficient (k) of this element is $k > 1$. It also appears that the most of impurity concentrations is smaller towards the middle of the ingot, indicating that for these elements the segregation coefficient is below or above unity. So, these impurities segregate to the first or last parts of the ingot to freeze (Oliveira, 2004, 2005).

The impurity concentration tendency of the middle region to decrease in function of the purification number of the BiI_3 is illustrated in the Fig. 3. As it can be observed, there was a significant reduction of most impurities according to the purification numbers, 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. Mo was fully removed at the first purification, while, As, Cr and Sb impurities decreased significantly after the third purification. Almost all impurities decreased, excepting Br, whose quantity, contrarily, increased after each purification number. Probably, the segregation coefficient is less than 1 ($k < 1$) or some contamination may have occurred during the experiments. Further studies should be carried out to elucidate this result. It should be emphasized that there is few literature describing the impurities present in the starting material (powder) for BiI_3 crystal growth and, even among these few references, there is no consensus among the elements found (Matsumoto et al, 2002; Qiu, 2010, Gokhale et al. 2014, Garg et al, 2014; Gokhalea et al, 2015).

Table 2. Elemental concentrations (Mean ± Standard deviation) determined in BiI_3 crystals purified once, twice and third times, by INAA methods

Element / Unit	1st Purification		
	Botton	**Middle**	**Top**
Ag, µg kg^{-1}	3519 ± 389	3450 ± 331	4312 ± 436
As, µg kg^{-1}	1996 ± 153	624 ± 46	3556 ± 531
Br, µg kg^{-1}	872 ± 91	720 ± 38	679 ± 61
Cr, µg kg^{-1}	1736 ± 54	1054 ± 16	6625 ± 54
K, mg kg^{-1}	15 ± 0,9	12.5 ±0.4	25 ± 3,0
Mo, µg kg^{-1}	28 ± 1,0	ND	82 ± 3,9
Na, mg kg^{-1}	13 ± 0,8	11 ± 0.07	22 ± 1,1
Sb, µg kg^{-1}	ND	43 ± 6	75 ± 3,9
Element / Unit	**2nd Purification**		
	Botton	**Middle**	**Top**
Ag, µg kg^{-1}	3518 ± 318	3371 ± 50	4351 ± 307
As, µg kg^{-1}	425 ± 82	358 ± 115	759 ± 20
Br, µg kg^{-1}	1255 ± 268	1109 ± 178	1074 ± 8
Cr, µg kg^{-1}	1007 ± 278	752 ± 186	7615 ± 705
K, mg kg^{-1}	11.9 ± 0.1	9.9 ± 0.2	19 ± 2
Mo, µg kg^{-1}	871 ± 231	ND	3026 ± 278
Na, mg kg^{-1}	13.5 ± 0.6	12.3 ± 0.1	25.3 ± 0.5
Sb, µg kg^{-1}	15 ± 2	9 ± 1	ND
Element / Unit	**3rd Purification**		
	Botton	**Middle**	**Top**
Ag, µg kg^{-1}	1879 ±102	1651 ± 86	2851 ± 1039
As, µg kg^{-1}	50 ± 4	28 ± 6	716 ± 34
Br, µg kg^{-1}	1281 ± 33	1145 ± 3	1184 ± 181
Cr, µg kg^{-1}	557 ± 124	184 ± 51	9062 ± 431
K, mg kg^{-1}	11 ± 2	9.4 ± 0.5	81 ± 7
Mo, µg kg^{-1}	ND	ND	7556 ± 629
Na, mg kg^{-1}	19.8 ± 0.6	15.0 ± 0.7	516 ± 23
Sb, µg kg^{-1}	6 ± 1	5.1 ± 0.3	ND

ND – not detected

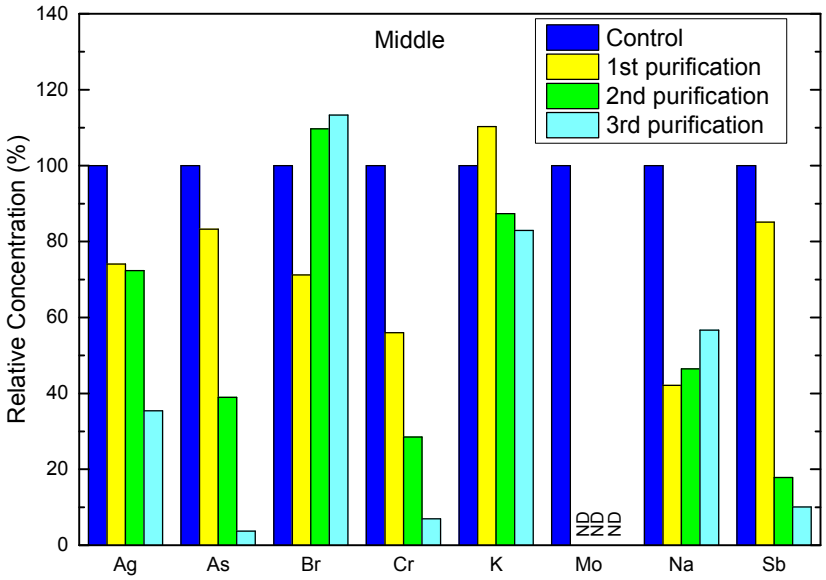


Figure 4. Impurity reduction of the concentration in function of the Bridgman purification number

ND = no detected

Fig. 4 and 5 present the X-ray diffraction characterization of samples from the bottom, middle and top regions of the crystal purified twice and three times, respectively, and the X-ray diffraction pattern of BiI_3. As it can be observed from Fig. 4 and 5, crystals purified twice and three times present a similar structure with the rhombohedral crystalline pattern to BiI_3 crystal (Matsumoto et al, 2002;Qiu, 2010). On the other hand, the diffractograms of BiI_3 powder and the samples from crystal growth once (one purification) presented not only the peaks belonging to BiI_3 crystals, but also, an intensive contribution from Bismuth Oxide Iodide (BiOI) appears at the angles, as it may be observed in Fig. 6 and 7. A background intensity contribution, which appears at the angles, probably due to some traces impurities, is still present in the crystal. However, the trace impurities did not affect, significantly, the crystalline structure, suggesting that the impurities did not enter in the crystal structure during the growth. Finally, it is worthwhile to observe that there were no other crystalline phases in the grown samples, above two times since all detected peaks were identified as belonging to BiI_3.

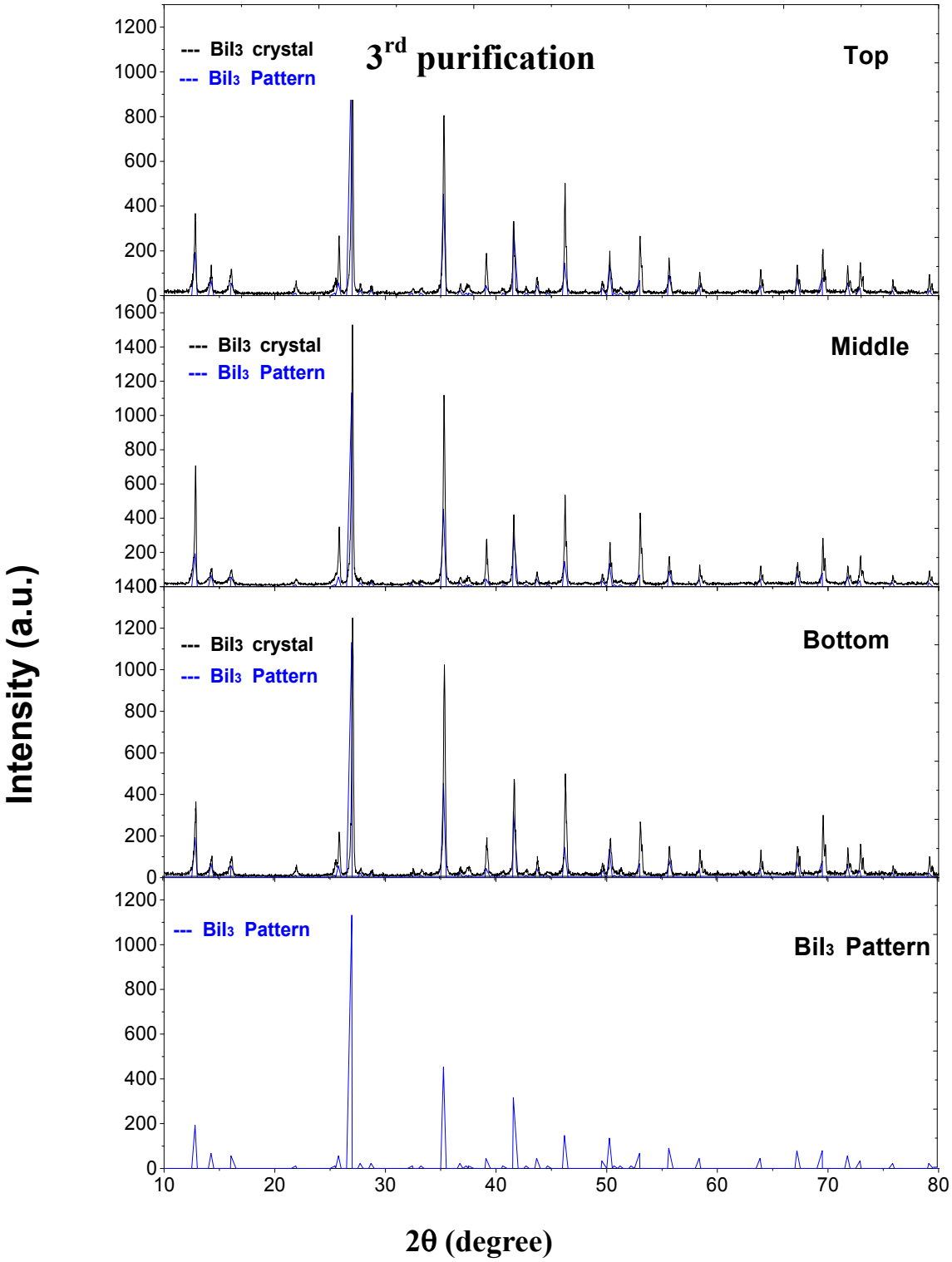


Figure 5. X-ray diffraction of the Top, Middle, Bottom samples from BiI_3 crystal purified three times X-ray diffraction pattern of BiI_3 (Card Information PDF Number: 48-1795) (Sillen, 1941).

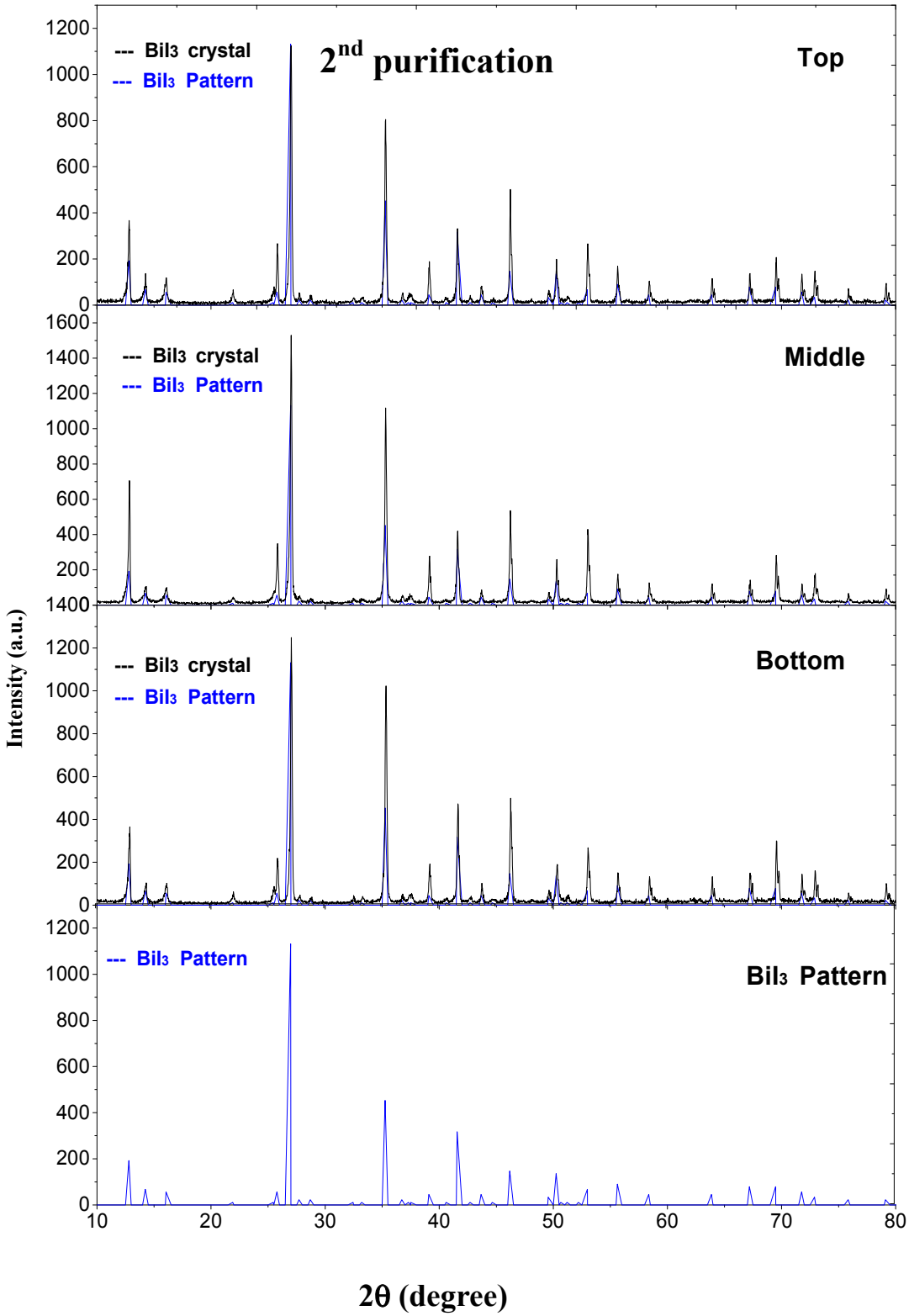


Figure 6. X-ray diffraction of the Top, Middle, Bottom samples from BiI_3 crystal purified twice X-ray diffraction pattern of BiI_3 (Card Information PDF Number: 48-1795) (Sillen, 1941).

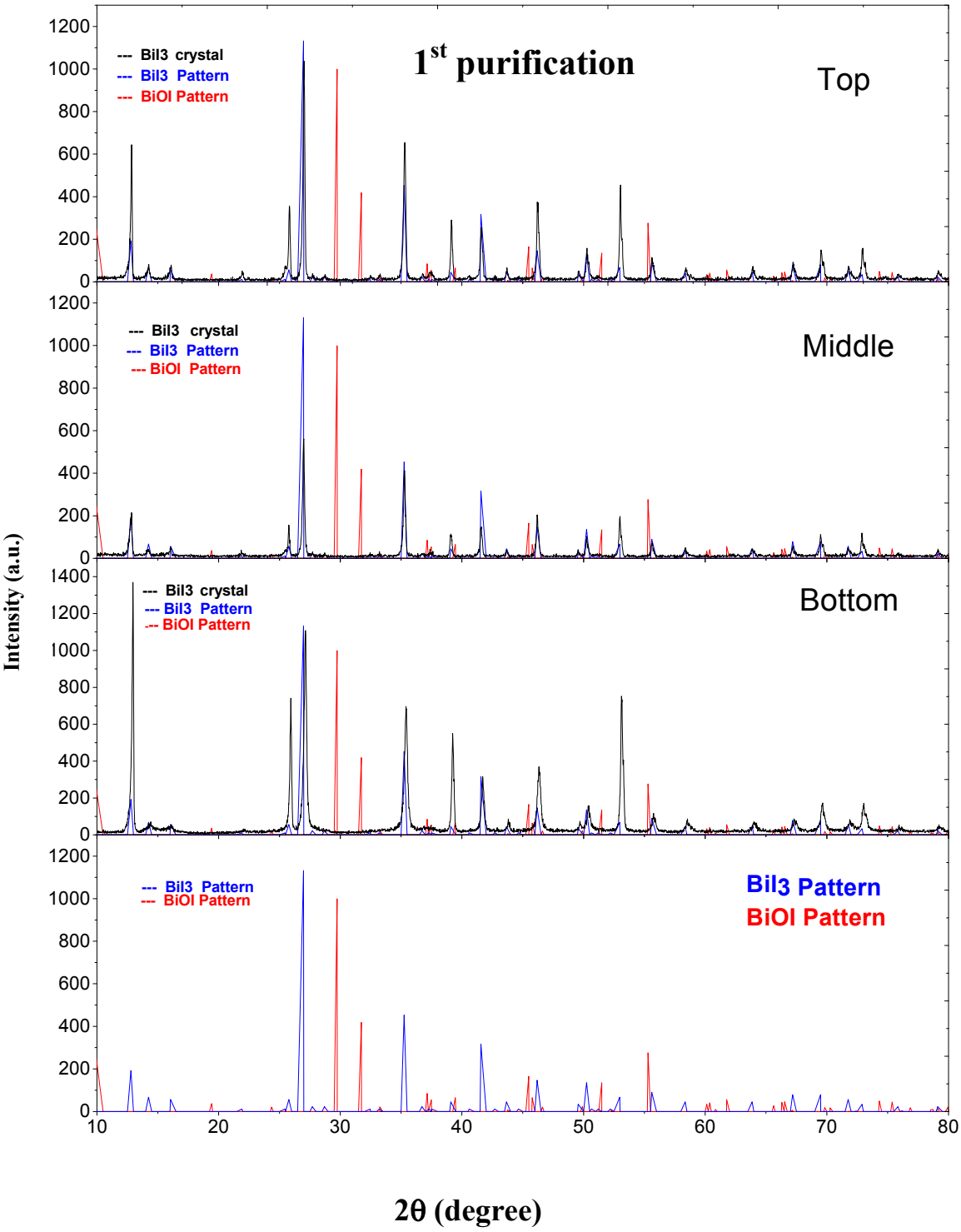


Figure 7. X-ray diffraction of the Top, Middle, Bottom samples from BiI_3 crystal purified once X-ray diffraction pattern of BiI_3 and BiOI (Card Information PDF number: 48-1795) (Sillen, 1941).

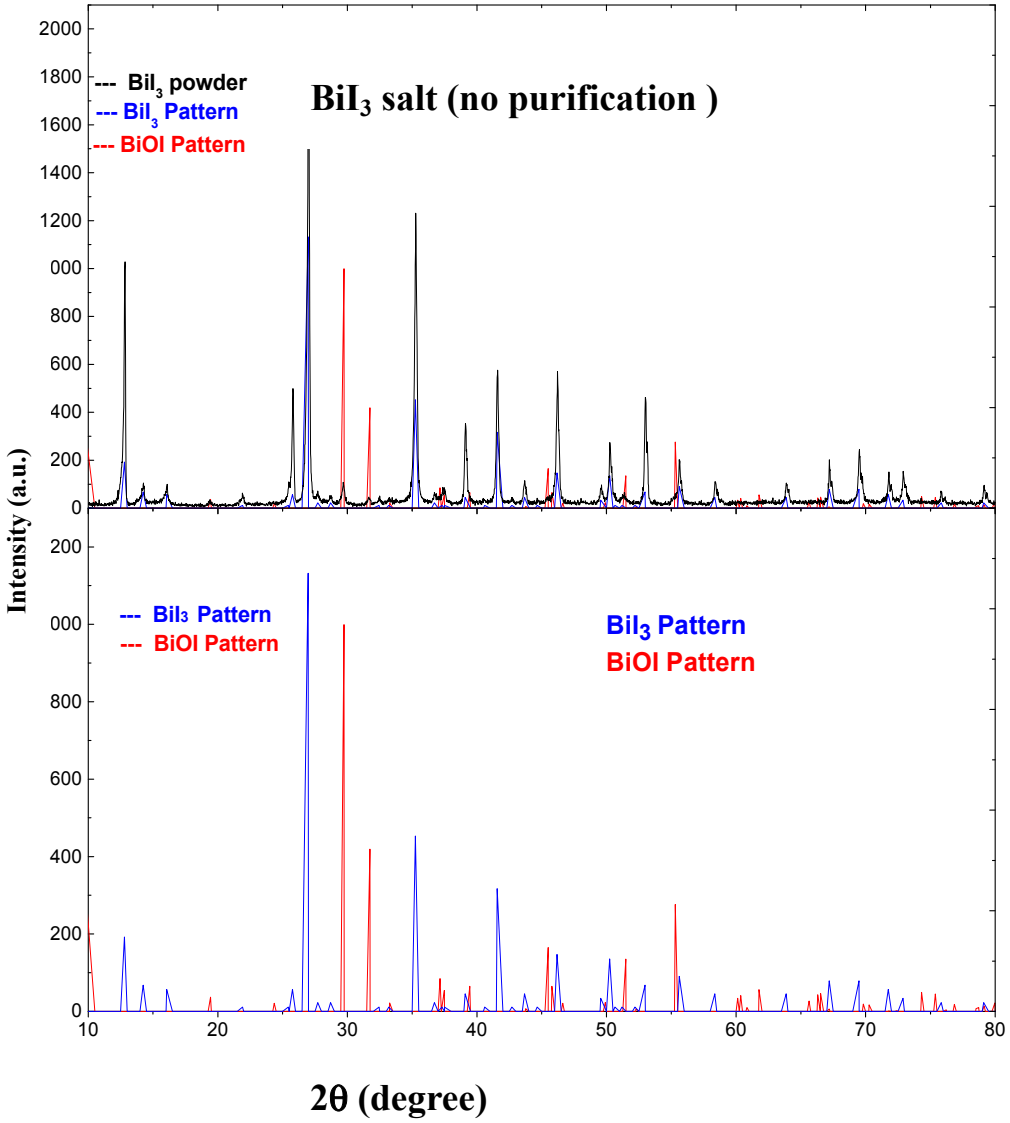


Figure 8. X-ray diffraction of BiI_3 powder used.

X - ray diffraction pattern of BiI_3 and BiOI (Card Information PDF Number: 48-1795) (Sillen, 1941)

A semi-quantitative scanning of the elements present on the crystal surface was performed using SEM-BSE technique, in order to evaluate the stoichiometry of BiI_3. The elemental composition of the surface of the starting powder and crystal samples from each region (Top, Middle and Bottom) obtained by different purification numbers is shown in Table 3. The molar stoichiometric ratio of the crystal is practically 1 atom of Bi to 3 Iodine atoms, that is, 25% of the compound will be Bi and 75% of Iodine.

Table 3. Elemental composition of crystal surface obtained by three purifications

	Element	% Atomic	% Error	I/Bi
Powder	I	74.57	3.78	2,98
1st Purification				
	Element	**% Atomic**	**% Error**	**I/Bi**
Bottom	I	70.22	4.06	2,36
	Bi	29.78	8.12	
Middle	I	72.07	3.98	2,59
	Bi	27.93	7.88	
Top	I	66.82	4.23	2,01
	Bi	33,24	10.2	
2nd Purification				
Bottom	I	68.83	4.13	2,21
	Bi	31.17	7.30	
Middle	I	72.67	3.87	2,66
	Bi	27.33	8.62	
Top	I	66.34	4.60	1,97
	Bi	33.66	7.58	
3rd Purification				
Bottom	I	74.81	3.67	2,94
	Bi	25.19	9.57	
Middle	I	75.85	3.62	3,1
	Bi	24.15	8.57	
Top	I	61.06	4.98	1,56
	Bi	38.94	5.73	

As it can be seen from Table 3, a proper stoichiometry was found in the starting powder, at a very close value of 3: 1 (2.98: 1). However, in the first purification, a lower ratio was found compared to that present in the starting salt, with 2.59: 1 for the Middle region, that corresponds to 72.07% of I and 27.93%, of Bi. For the Top and Bottom regions the findings were determined to be 2.01: 1 and 2.36: 1. These results suggest that the impurities present in the salts used as starting material may interfere with the stoichiometry of the crystal, during its growth.

On the other hand, an improvement in the stoichiometric ratio was observed at each purification number, that is, the stoichiometry improved as a function of the reduction of impurities in the crystal. In the 3rd purification, the stoichiometric ratio was very close to 3:1, being 3:1.1 in the Middle region and 2.94: 1 in the Bottom region, suggesting that the impurities migrated to the upper end of the crystal, i.e. in the end of the crystal growth, indicating that most trace elements, present as impurity, have k>1.

Figure 8 shows the micrographs of the scanning electron microscopy with back-scattered electrons (SEM-BSE) carried out in Bottom, Middle and Top regions from the crystal surface obtained after first, second and third purification, in order to evaluate the quality of BiI_3 wafer surface.

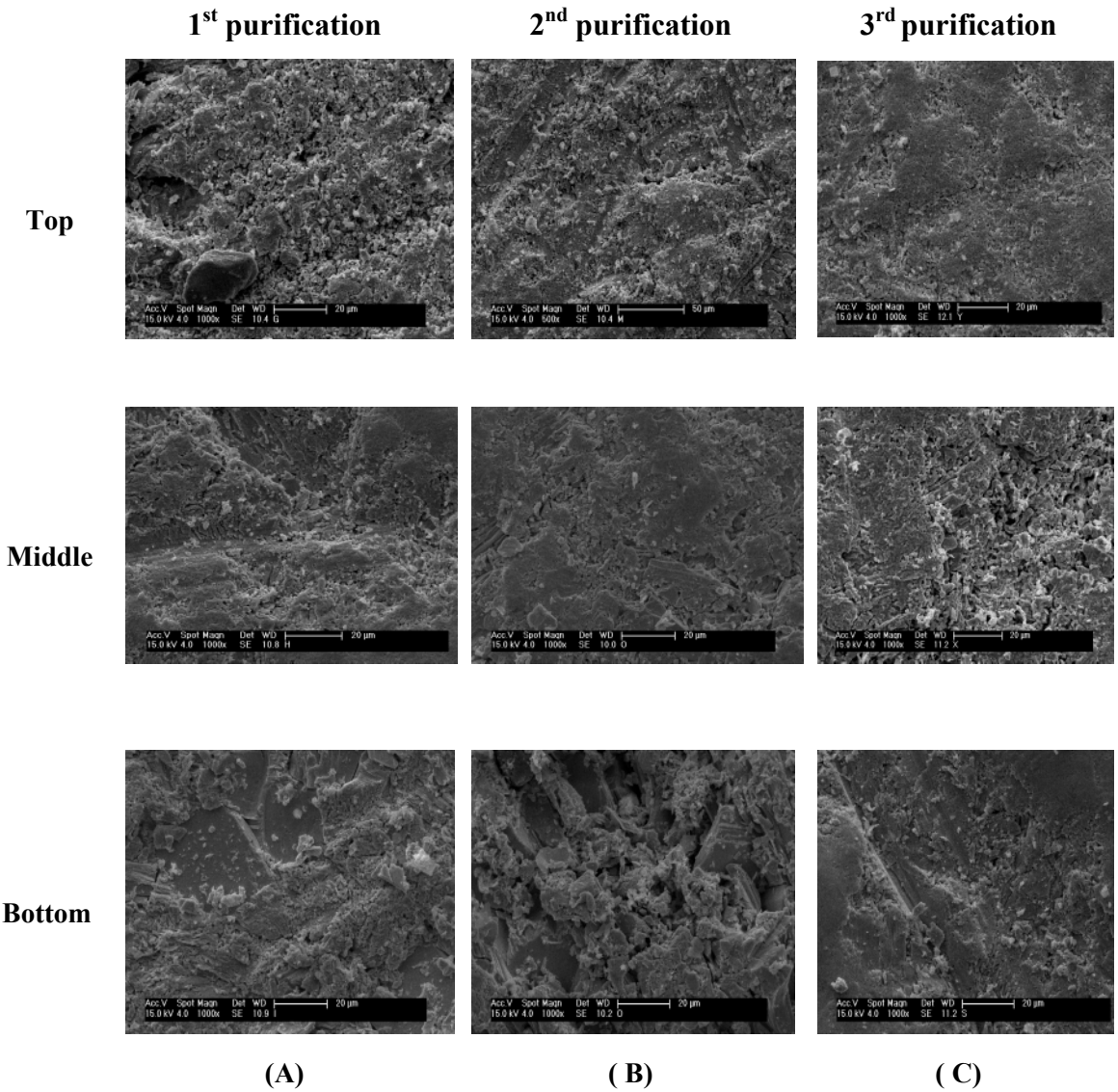


Figure 10. Micrographs of the BiI_3 crystal surface purified once (A); twice (B) and third times (C) expanded 1000X

As it may be observed from Figure 8, for crystals purified once (Figure 8A), the Middle and Top regions present polycrystalline structures, while the Bottom region shows only an amorphous structure with roughness.. This may be due to the presence of impurities and/or defects in the surface of the crystal. For the crystal purified twice (Fig 8B), the Bottom region still presents an amorphous structure, while the Top region shows more crystals forming in its structure. In the Middle region, crystal structures may still be observed, but with impurities traces. These impurities present in the Middle region may have migrated from the Bottom region at a slower rate than the others present in the Top region, in other purifications, because their impurity segregation constant (k) is different. For crystal purified three times (Fig 8C), the Bottom and Top regions show amorphous structures due to the impurities present and which had not migrated in the previous purifications yet and the Middle region still presents more crystals forming, but the presence of impurities is not practically observed.

Validation of the methodologies for purification process and growth of the BiI_3 by the Vertical Bridgman technique, as well as the establishment of a method for accompanying the reduction of the impurities, after each purification process are important for future works on the application this crystal as a room temperature radiation semiconductor detector. It is known that semiconductor detectors fabricated from high purity crystal exhibit significant improvement in their performance compared to those produced from low purity crystals.

4. Conclusion

The Repeated Vertical Bridgman Method showed to be effective to reduce the concentration of many impurities in BiI_3. After three purifications, most of the impurities, such as Mn, As, Cr and Sb were, practically, removed. Neutron Activation Analysis (NAA) 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 most 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 Vertical Bridgman Method was found; all detected peaks were identified as belonging to BiI_3. For crystal purified only once, an intensity contribution from Bismuth Oxide Iodide (BiOI) was observed. The sample from the Middle region of the BiI_3 crystals, purified three times, presented a better result of stoichiometry evaluated by the analysis of MEV-BSE compared to that with less purification. By the analysis of SEM-SE, a crystalline structure was observed in the middle region of the crystals purified two and three times. The other regions showed an amorphous structure.

Acknowledgements

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