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PERFORMANCE OF NEUTRON ACTIVATION ANALYSIS IN THE EVALUATION OF BISMUTH IODIDE PURIFICATION METHODOLOGY

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ABSTRACT

Bismuth tri-iodide (BrI_3) is an attractive material for using as a semiconductor. In this paper, BiI_3 crystals have been grown by the vertical Bridgman technique using commercially available powder. The impurities were evaluated by instrumental neutron activation analysis (INAA). The results show that INAA is an analytical method appropriate for monitoring the impurities of: Ag, As, Br, Cr, K, Mo, Na and Sb in the various stages of the BiI_3 purification methodology.

1. INTRODUCTION

Bismuth tri-iodide (BiI_3) is an attractive material for using as a semiconductor. 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 [1]. Small quantities of impurities present at concentrations below 1 ppb can have a significant effect on quality of semiconductor devices. In this paper, BiI_3 crystals have been grown by the vertical Bridgman technique 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 [2,3]. This study aimed to verify the performance of the INAA in evaluating the various stages of a purification methodology for BiI_3, with a view to future application of these semiconductor crystals as semiconductor radiation detector.

2. EXPERIMENTAL

2.1. Samples Analyzed

The samples used in the experiment were provided by the Laboratory of the Radiation Detector at IPEN that was developing the BiI_3 crystals growth, as pure as possible, to be used as radiation semiconductor detector. In this laboratory, the process originated from a BiI_3 salt with 99.9% (Alfa Aesar, A Johnson Matthey Company) of purity. For purification, BiI_3 crystals have been grown by the vertical Bridgman technique, based on the melting and nucleation phenomena [4]. After completion of the growth step, some crystals were selected from the bottom, middle and top of the system, for analysis of impurities. Another part was reprocessed, i.e. the entire process was repeated. Three repetitions were made which led to seven samples to be analyzed, since two of them were lost in the first step due to experimental problems. In order to obtain homogenous portions for elemental determination by INAA, each sample was ground in an agate mortar up to fine powder form.

2.2. Instrumental Neutron Activation Analysis (INAA)

Aliquots (BiI_3) 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 and Sb 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 for quality control of the analytical results.

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.

3. RESULTS AND DISCUSSION

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; $T_{1/2}$=24.9 minutes), making it impossible to determine impurities which

form radionuclides with half-lives of minutes or few hours, such as ^{66}Cu, ^{52}V, ^{51}Ti, ^{56}Mn by (n,ɣ) reaction.

Table 1: Nuclear characteristics of (n,ɣ) reaction of BiI_3 [5]

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 treatment of BiI3 purification executed within the Bridgman furnace are shown in Table 2a, 2b and 2c. Each result is the mean of two or three measures followed by the standard deviation. Samples corresponding to modules: bottom and top of the first purification step were lost.

Table 2a: Elemental concentrations (Mean ± Standard deviation) obtained in BiI_3 subjected to the first purification step

Element / **Unit**	**Module**
	Middle
Ag, µg kg^{-1}	3450 ± 331
As, µg kg^{-1}	624 ± 46
Br, µg kg^{-1}	720 ± 38
Cr, µg kg^{-1}	< 400*
K, mg kg^{-1}	12.5 ±0.4
Mo, µg kg^{-1}	< 600*
Na, mg kg^{-1}	11.15 ± 0.07
Sb, µg kg^{-1}	43 ± 6

***Detection Limit**

Table 2b: Elemental concentrations (Mean ± Standard deviation) obtained in BiI_3 subjected to the second purification step

Element / **Unit**	**Modules**		
	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	< 600*	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	< 4*

***Detection Limit**

Table 2c: Elemental concentrations (Mean ± Standard deviation) obtained in BiI_3 subjected to the third purification step

Element Unit	Modules		
	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}	< 600*	< 600*	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	< 4*

***Detection Limit**

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. Ag, As, Br and Sb were in agreement within 2-4%, while for Cr the concordance was approximately 15%. The detection limit was determined according to the IUPAC definition [6], the background radiation and the time of measurement are considered. In most cases, the accuracy of BiI_3 analyzes (Tables 2a, b and c) 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, Sb and Zn) in the various stages of the BiI_3 purification methodology.

The assessment the efficiency of the purification methodology based on the observed results (Tables 2 a, b and c) 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 BiI3 in order to distinguish the segregation of the impurities along the crystal, as shown in Tables 2a, b and c. 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 [7, 8].

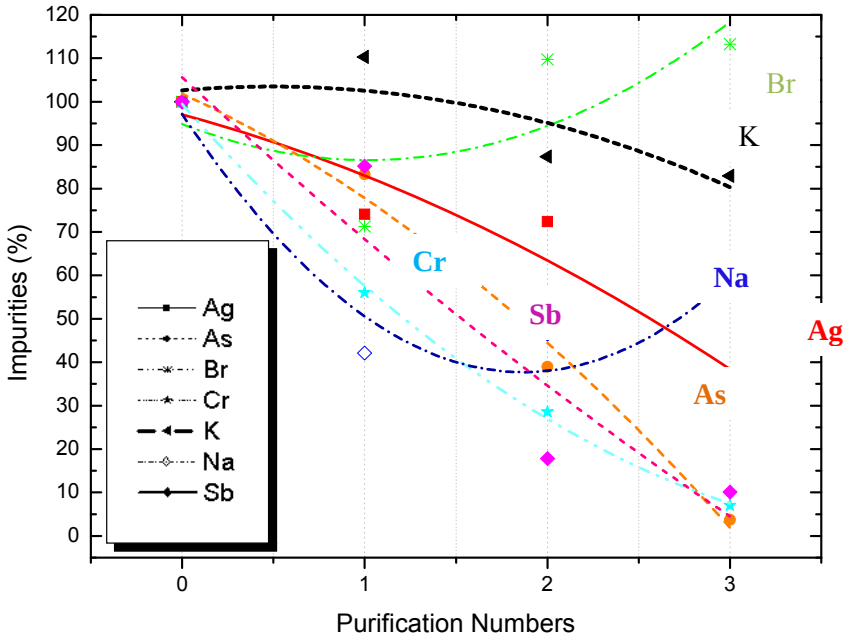

Figure. 1. **Tendency of the concentration decrease (b) in function of the purification number.**

4. CONCLUSIONS

INAA showed to be a special analytical technique to identify and quantify the impurities (Ag, As, Br, Cr, K, Mo, Na and Sb) in the BiI_3 crystals and to evaluate the reduction of the trace impurities, after each purification number.

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