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INFLUENCE OF IMPURITIES ON THE SURFACE MORPHOLOGY OF THE TlBr CRYSTAL SEMICONDUCTOR

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ABSTRACT

The impurity effect in the surface morphology quality of TlBr crystals was evaluated, aiming a future application of these crystals as room temperature radiation semiconductor detectors. The crystals were purified and grown by the Repeated Bridgman technique. Systematic measurements were carried out for determining the stoichiometry, structure orientation, surface morphology and impurity of the crystal. A significant difference in the crystals impurity concentration was observed for almost all impurities, compared to those found in the raw material. The crystals wafer grown twice showed a surface roughness and grains which may be due to the presence of impurities on the surface, while those obtained with crystals grown three times presented a more uniform surface: even though, a smaller roughness was still observed. It was demonstrated that the impurities affect strongly the surface morphology quality of crystals.

Key words: Radiation Detector, Semiconductor Crystal, TlBr Crystal

1. INTRODUCTION

The thallium bromide crystal is a promising gamma and X ray radiation detector since it is a semiconductor composed of high atomic number elements (Z_{Tl}=81 and Z_{Br}=35), with high resistivity (>$10^{10}\Omega$cm) and density (7,5g/cm^3). The performance of a radiation detector is controlled by both intrinsic and extrinsic factors These are important factors in applications where compact and small thickness detectors are necessary for X- and gamma ray measurements [1,2].

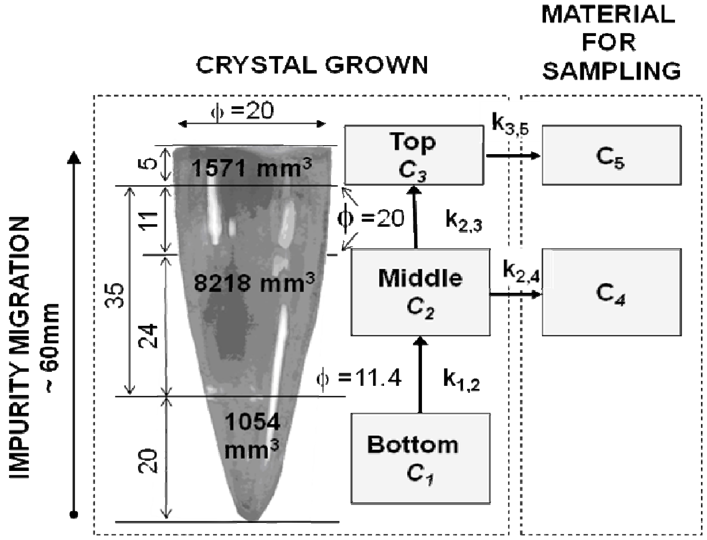
The performance of a radiation semiconductor detector depends on several factors related to the crystal quality, such as the carrier lifetime, mobility, crystallographic imperfections, the impurity concentrations and the surface morphology, present in the crystal. Several studies on the preparation of TlBr detectors have been carried out and improvements in the methodology of purification, growth and characterization of the crystals have been described, aiming to achieve all these factors [1,2,3]. However, as it can be observed in the literature [1,2,3,], the TlBr detector limitations are not yet completely resolved: primarily, the low collection efficiency of charge carriers, fact that is probably caused by impurities and defects created in the crystal growth or in the surface treatment process. There is a consensus in the literature that the TlBr crystal purity and surface quality are crucial factors for its optimal performance as a radiation detector [1,2].

The crystal cutting, surface polishing and subsequent etching are important processes during the manufacturing of the room temperature semiconductor radiation detectors, such as CZT, and TlBr. Both mechanical polishing and chemical etching can affect the surface leakage. The centers resulting from mechanical polishing may both enhance the carrier recombination on the surface by increasing surface trapping sites and affect the surface leakage current, by providing more conductive pathways and altered electrical-field distributions. Under some circumstances, the polarity effects can be introduced by surface processing and effectively removed by appropriate polishing and chemical etching [2,4].

Several works in the literature on the TlBr crystal surface treatment, describing the procedures of mechanical polishing and chemical etching with bromine methanol solution, have been found [1-5]. Cui et al. [4] and Wright et al. [5] have reported that different etchants change the surface morphology of the CZT surfaces. Their studies established a correlation between the roughness of the surfaces and the resulting values of the detector leakage currents, with the smoothest surface producing the lowest noise in detectors. Oliveira et al [2] studied the influence of the surface quality of the TlBr wafer on its performance as a radiation detector. In their work, the surface of the TlBr crystals was prepared with different mechanical and chemical treatments and the radiation response for detectors was prepared with these crystals was performed under ^{241}Am gamma radiation excitation. However, as far as we know, studies related to the impurity effect of the TlBr crystal on the surface morphology quality have not been previously reported. In this work, the surface morphology of the crystals purified once, twice and three times, and grown by the Repeated Bridgman method, were evaluated and compared.

2. EXPERIMENTAL PROCEDURE

Commercially available TlBr salt (Aldrich-Sigma), with nominal purity of 99.99%, was used as the raw salt for crystal growths. TlBr crystals were grown by the vertical Bridgman technique, using quartz tubes as crucibles in vacuum atmosphere. Preliminary, the quartz tubes were submitted to a chemical treatment. The tubes were, previously, washed with a cleaning agent solution (Extran MA 02, Merck) and, then, filled with a solution of hydrofluoric acid (5 per cent v/v); after 20 minutes, the tubes were rinsed three times with demineralized water. Subsequently, the quartz tubes were submitted to a thermal treatment at 250 ºC to avoid the adhesion of the crystals on the walls of the tubes. Afterward, the TlBr salt was introduced into one tube, evacuated to 10 was mounted into the vertical Bridgman furnace where the TlBr was melted at a temperature of 560 ºC. Crystals around 20 mm diameter and 60 mm long were obtained, with a growth rate of 1 mm/h. Following the same procedure, the crystals were grown repeatedly (three times) for purification (Fig. 2). In this procedure, the impurities tend to migrate to the extremities of the crystal during the growth, due to the segregation of impurities along the crystal. Thus, a better purity is expected to be found in the middle region. For each re-growth, the quartz tube was opened and two slice samples were taken from the crystals (Fig. 1). The “TOP” region refers to the upper ingot extremity (~5 mm), where most of the impurities migrate and, then, it was taken for chemical analysis. The “MIDDLE” region was considered the prime region (~35 mm thick) of the crystal, assuming that a good uniformity in the impurity concentrations exists in the middle region of the ingot. Samplings (2 x 0.65 mm thick slices) were taken, adjacently, from the middle of the crystal, for chemical analysis and detector preparation. The “BOTTOM” corresponds to the lower ingot extremity, which has a cone shape (~ 20 mm thick).



All measurements in millimeter.

Figure1: Compartmental model proposed to explain the migration of impurities in the TlBr crystal.

The crystalline quality of the TlBr crystal was analyzed by X-ray diffraction (XRD). X-ray diffraction patterns were obtained in a Siemens (D5005) Diffractometer CuKα radiation (2θ ranging from 20° to 60º).

The surface morphology and the stoichiometry of the TlBr crystal were analyzed by the scanning electron microscopy with back-scattered electrons (SEM-BSE) technique, using the scanning electron microscopy (SEM-BSE), LX 30 Philips model.

The impurity concentrations of the samples, taken from slices after each growth, were measured in an ICP-MS (Inductively Coupled Plasma Mass Spectrometer, mod. Elan 6100 ICP-MS, Perkin Elmer, USA). Previously, samples had been digested in a mixture of nitric acid (65%, Merck) and hydrogen peroxide (30%, Merck) by closed-vessel microwave digestion. The ICP-MS instrumental operating conditions were optimized for the measurement of elements. The impurities were expressed in parts per million (ppm).

3. RESULTS AND DISCUSSION

The crystal subjected to only one growing process suffered adhesion to the quartz tube and its structure was damaged, as shown in Figure 2 (a). After removal of samples for analysis, the crystal was subjected to a second growth process, resulting crystal with transparent appearance with some blackened spots which, again, adhered to the pipe (Figure

2 (b)). The same procedure was performed, growing a third time, when there was clear crystal and without adhesion to the quartz tube (Figure 2 (c)).

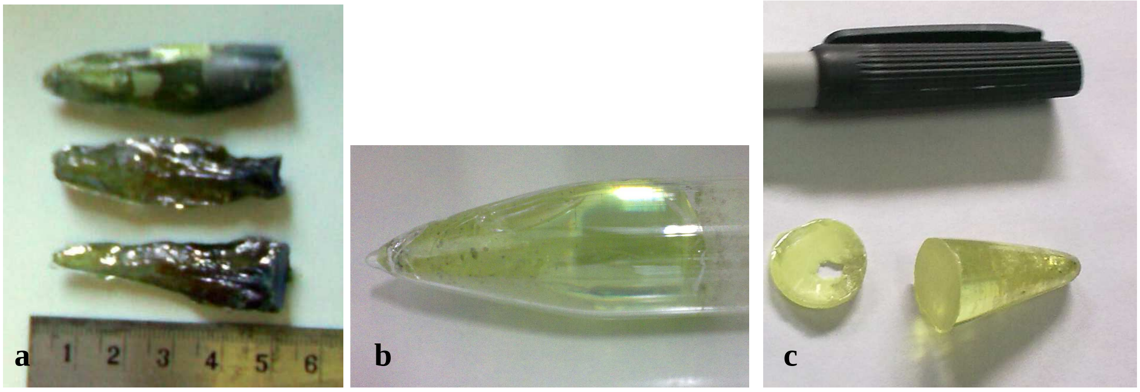


Figure 2: TlBr crystals grown by the Bridgman method: (a) subjected to one growth, (b) subjected to two-growth processes and (c) subjected to three-growth processes.

Figures 3 (a), 3 (b) and 3 (c) illustrate the X-ray diffraction pattern of TlBr crystals obtained for TlBr salt and the surfaces of the TlBr crystals grown twice and three times, respectively. The spectra obtained for all measures were similar, since there were no significant differences in the crystal structures obtained without purification and purified (two and three growths). The XRD patterns indicate that the crystals are preferentially oriented in the planes (110) and (111), with a structure similar to the TlBr crystalline cubic model. These results are in agreement with the literature [6,7].

Figure 4 and table 1 show the concentrations of impurities as a function of the number of growths. The samples were taken from the Middle region (Figure 1), which is the purest region of the crystal. Five impurities were found, Ti, V, Fe, As and Zr. As. As it can be observed from Fig. 4 and table 1, in the first purification, the amount of impurities in the middle region was, significantly, different from the TlBr raw material. After the first purification the impurity reduction is slower.

According to Table 1, the reduction level of the impurities in the crystal middle region for Ti was of 84% (1-(0.01782/0.10996)) after the growth with one purification; 94% (1-(0.00689/0.10996)) after two purifications, and 98% (1-(0.00150/0.10996)), after three purifications; for V was of 56% (1-(0.55557/1.27557)) after the growth with one purification, 58% (1-(0.52989/1.27557)) after two purifications and 63% (1-(0.47254/1.,27557)), after three purifications. For Fe it was of 91 % (1-(0.07673/0.92320)) after the growth with one purification, 99% (1-(0.00060/0.92320)) after two purifications and 99% (1-(0.00060/0.92320)) after three purifications. For As, it was of 70 % (1-(0.15589/0.52750)) after the growth with one purification, 71% (1-(0,15431/0,52750)) after two purifications and 74% (1-(0.13700/0.52750)) after three purifications. Finally, for Zr was of 97% (1-(0.01250/0.56119)) after the growth with one purification, 99% (1-(0.00005/0.56119)) after two purifications and 99% (1-(0.00005/0.56119)) after three purifications.

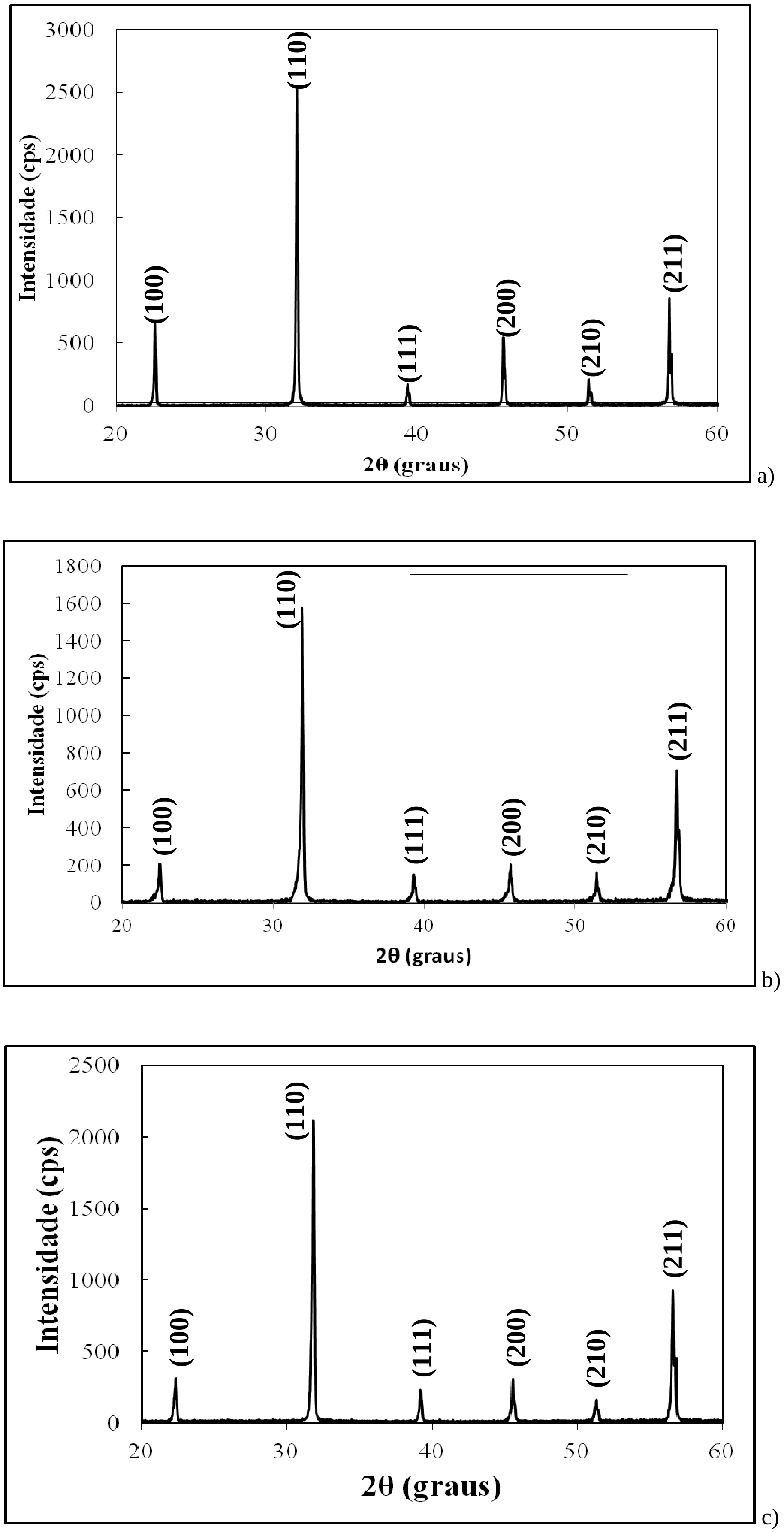


Figure 3: X-ray diffraction of TlBr powder (a) and TlBr crystals (b) and (c).

For Ti, Fe and Zr, the diminution levels of their concentrations were around 90%, after the first purification, afterward that the impurities decrease was slower, reaching a reduction of almost 100% after the third purification. On the other hand, for V a minimal reduction of ~56 % and a maximum of ~63% were obtained, while for As, the reduction levels between 70% and 74% were observed.

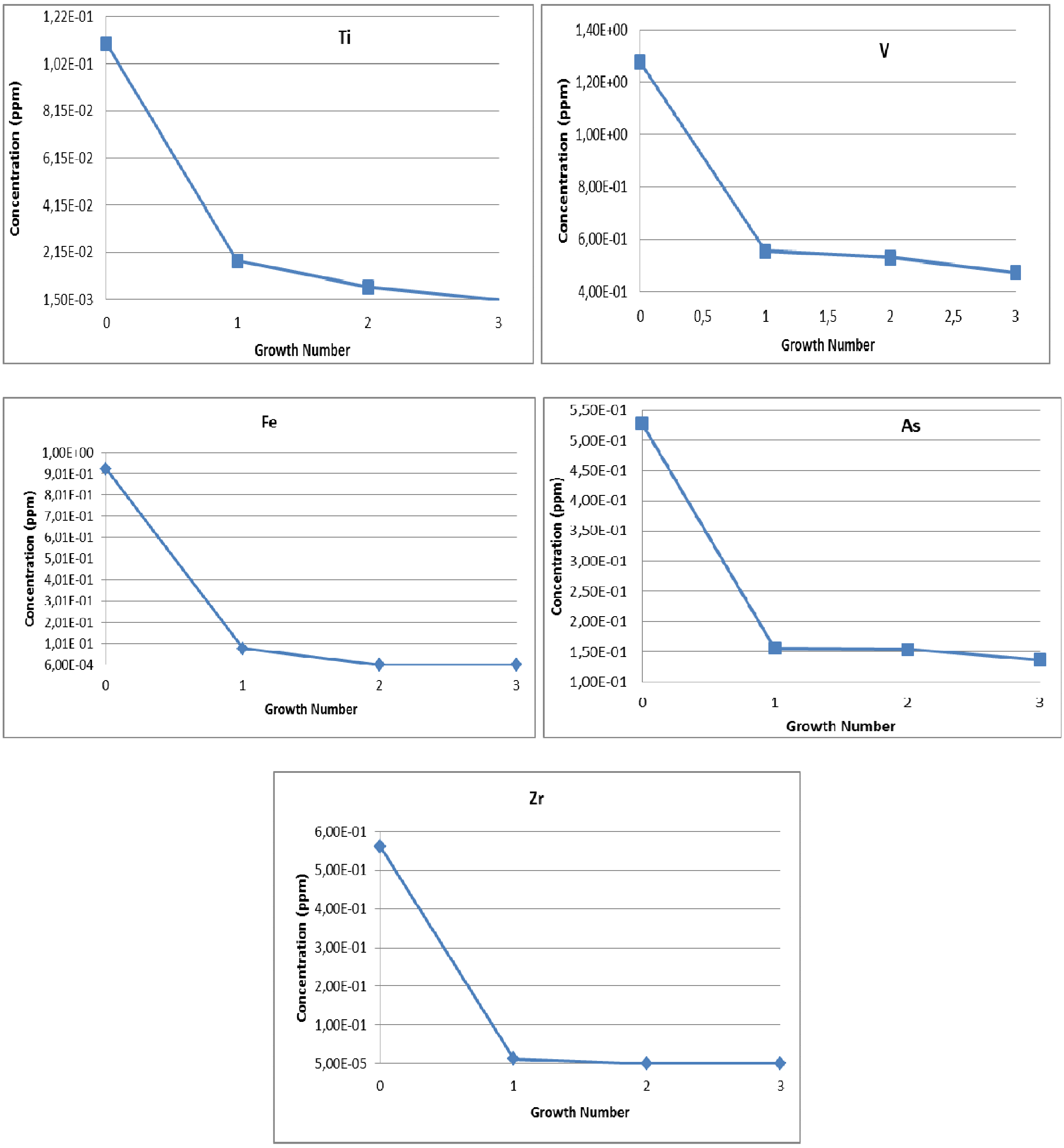
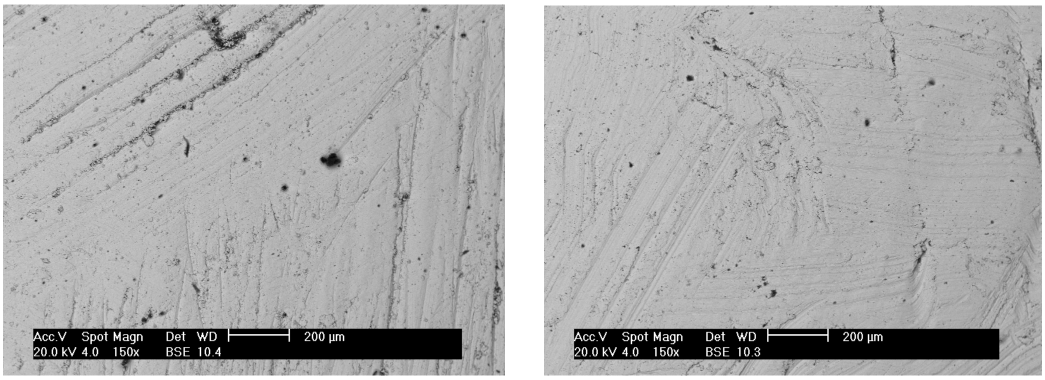


Figure 4: Concentration of impurities depending on the number of growth processes.

Table 1- Elemental composition of the TlBr crystal (ppm).

Growth Number	0	1	2	3
Impurities				
Ti	0.10996	0.01782	0.00689	0.00150
V	1.27557	0.55557	0.52989	0.47254
Fe	0.92320	0.07673	0.00060	0.00060
As	0.52750	0.15589	0.15431	0.13700
Zr	0.56119	0.01250	0.00005	0.00005

Figure 5 shows micrographs of the scanning electron microscopy with back-scattered electrons (SEM-BSE) carried out in the TlBr wafer, from the crystals grown after the second (Figure 5 (a)) and third (Figure 5 (b)) purifications. As it can be seen in Figure 5 (a), the crystal slice grown twice, magnified 150 times, shows the surface roughness and grain which may be due to the presence of impurities on the surface; crystals grown three times present a more uniform surface, although smaller roughness is still observed (Figure 5 (b) expanded 150 times). It was not possible to perform the experiment with crystals grown just once, due to the poor crystal formation, as shown in Figure 2 (a).



(a) **(b)**

Figure 5: SEM-BSE micrographs of the TlBr crystal surface grown twice (a) and three times (expanded 150X).

Additionally, using the technique of SEM-BSE scan, a semi-quantitative analysis of elements present in the crystal surface of the TlBr crystal was performed. As it can be seen from the Figure 6 and Table 2, a proper stoichiometry was found. The elemental composition of the crystals obtained by different numbers of crystal growth is shown in Table 2 and Figure 6. As observed in this Table, an appropriate stoichiometry was found in the crystals grown, being nearly one Tl atom to one Br atom. These results suggest that trace impurities present in the crystals did not affect the quality of the crystal stoichiometry.

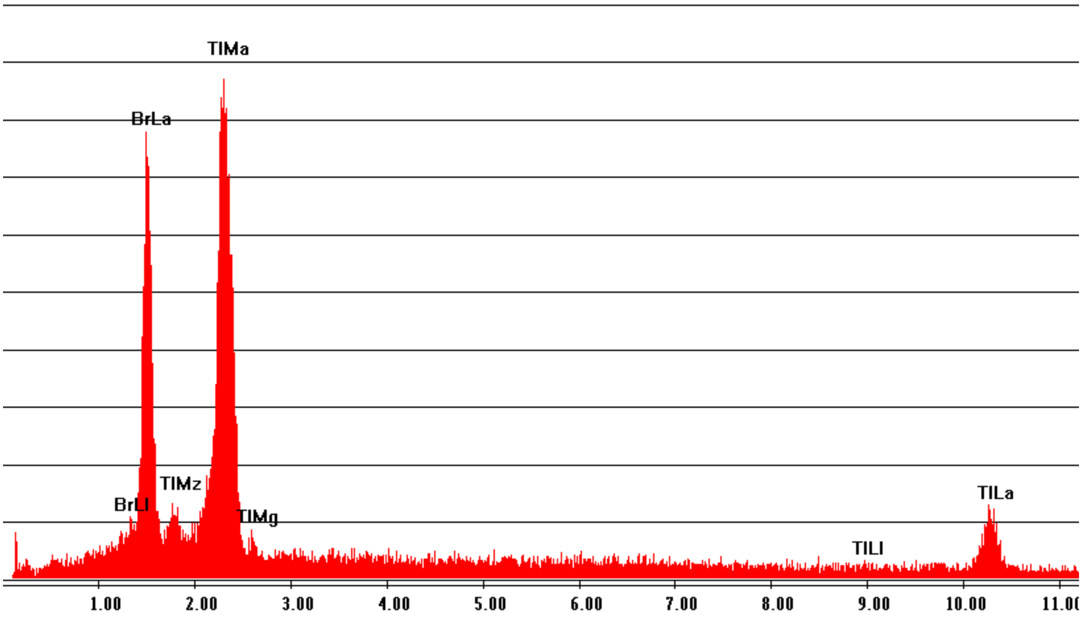


Figure 6: Spectrum of the TlBr crystal micrograph

Table 2: Elemental composition of the crystal grown twice and three times

Growth Number	Element	Atomic %	Standard Deviation
2	Br	52,94	1,72
	Tl	47,06	1,41
3	Br	53,09	1,63
	Tl	46,91	1,36

3. CONCLUSIONS

The repeated Bridgman method was efficient to purify the TlBr crystals. In the crystal middle region, a significant difference in the crystal impurity concentrations was observed for almost all impurities, compared to those found in the raw material. A significant improvement in the crystallinity and transparency was observed in the obtained crystal growth in the third growth, when compared to the second and first ones. These results demonstrate the efficiency of purifying with the repeated Bridgman technique. The level of impurity in the crystals studied did not interfere in their crystal structures. The TlBr crystals grown three times by Bridgman method presented better surface morphology quality compared to those grown twice. For crystals grown twice, the roughness and the incrustations of the distinct elements could be detected, clearly, while for crystals grown three times, a structure with uniform layer could be observed, indicating that the impurities affect strongly the crystal surface morphology quality. In our forthcoming paper, further research efforts will be directed on the study of the morphology effect in the radiation detector performance. Correlation among impurity concentrations, morphology and radiation response will be evaluated.

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