Multi-Elemental Segregation Analysis of Thallium Bromide Impurities Purified by the Repeated Bridgman Technique

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Abstract **– TlBr crystals were purified and grown by the repeated Bridgman method from commercial TlBr salt and characterized to be used as radiation detectors. To evaluate the purification efficiency, measurements of the impurity concentration were made after each growth, analyzing the trace impurities by inductively coupled plasma mass spectroscopy (ICP-MS). A significant decrease of the impurity concentration resulting from the purification number was observed. To evaluate the crystal as a radiation semiconductor detector, measurements of its resistivity and gamma-ray spectroscopy were carried out. The radiation response depended on the crystal purity. The repeated Bridgman technique improved the TlBr crystal quality used as a radiation detector. An exponential model was used to fit the impurity concentration as a function of the repetition number of the Bridgman growth.**

I INTRODUCTION

The thallium bromide crystal is a promising gamma and X ray radiation detector because it is a semiconductor composed of high atomic number elements (Z_{Tl}=81 and Z_{Br}=35), with high resistivity (>10^{10}Ωcm) and density (7,5g/cm^3). Its good response to X and gamma rays at room temperature makes it suitable for a number of applications such as radiation detector, photodetector and small dimension devices with high radiation efficiency like intra-operable surgical probes [1].

The performance of a radiation detector is controlled by both intrinsic and extrinsic factors. Carrier lifetime, mobility and the atomic number of the material used for radiation detectors represent intrinsic factors, while extrinsic factors, such as crystallographic imperfections and the concentrations of impurities can play an important role in the final performance of semiconductor radiation detectors [2]. Several studies about the preparation of TlBr detectors have been carried out and improvement in the methodology of purification, growth and characterization of the crystals has been observed [2-9]. There is agreement in the literature that the TlBr crystal purity is a crucial factor for its optimal performance as a radiation detector [2,10-13].

The problems of the TlBr detector are not yet completely resolved, among them the low collection efficiency of charge carriers, which is probably caused by impurities or defects created during crystal growth and subsequent treatment processes of the crystal [1,3,7,8]. However, as far as we know, few results on reduction of the TlBr impurities have been found in the literature. In this work, some aspects of the crystal impurity influence on the detector performance were evaluated, by systematic measurements of the gamma-ray spectrometry and resistivity. The crystal was purified, growing it by the Bridgman technique three times. The impurity decrease in the crystal was evaluated after each repetition number of the crystal growth using the ICP-MS technique. An exponential model was defined to calculate the coefficients for the migration of impurities.

II EXPERIMENTS

TlBr powder, with nominal purity of 99.99%, were used as the starting material for growing crystals intended for detector applications. TlBr crystal was grown by the vertical Bridgman technique, using a quartz crucible in vacuum. To reduce impurities, these materials were purified by Bridgman method. Preliminary, the crucibles were submitted to a rigorous chemical treatment and, subsequent thermal treatment, to avoid the adherence of the crystals in the tubes walls used in the melting. Afterward, the TlBr powder was introduced into a treated 50 cm long quartz tube of 20 mm diameter, evacuated to 10^{-6} Torr and sealed off. The crucible with TlBr was mounted into the vertical Bridgman furnace and the TlBr was melted at temperature of 550ºC. A crystal, around 20 mm diameter and 60 mm long, was obtained with a growth rate of 1 mm/h. The middle part of the crystal was sliced in wafers of about 0.65 mm thick, cut transversally to direction (110), using a diamond saw lubricated with glycerin during the cutting. From the first growth, two slices of TlBr crystal were cut to be used as detectors and a third slice was used to analyze its impurities by inductively coupled plasma mass spectroscopy (ICP-MS). A slice of the upper crystal, where most of the impurities are segregated, was also used for impurities quantification. The dimensions and details of the TlBr crystal sampling preparations are shown in the Fig. 1.

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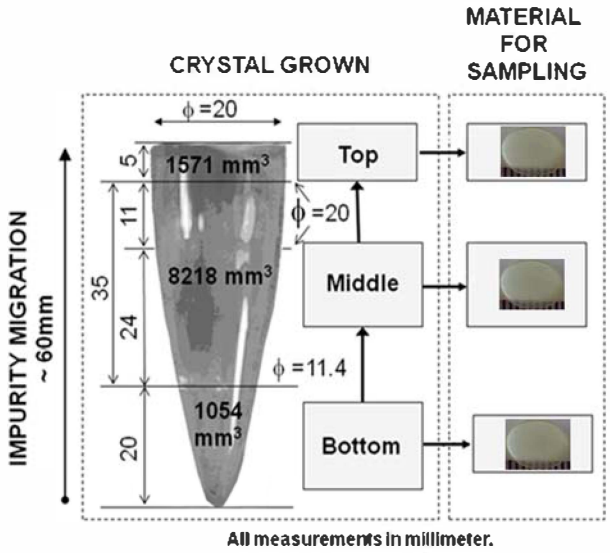


Fig. 1 – Dimensions and details of the crystal of TlBr

After each cutting, the TlBr slices surfaces were pre-treated using etching procedures previously described [4] and the detector assembled as showed in Fig 2.

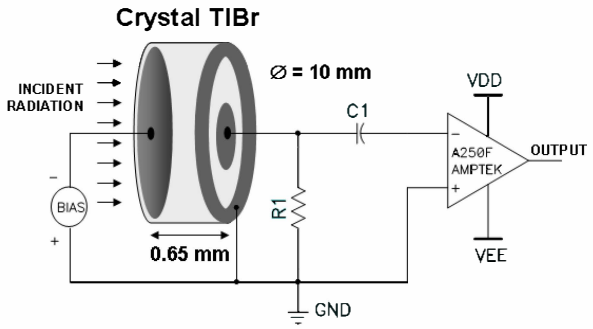


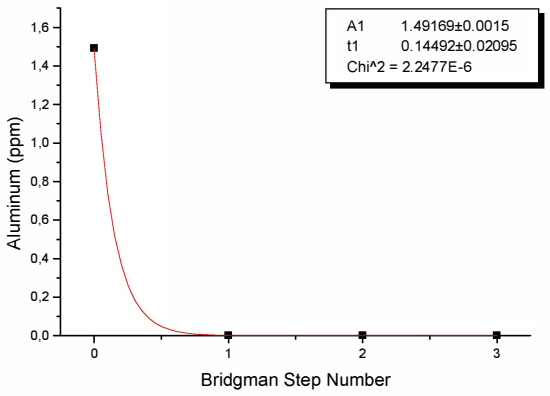
Fig. 2 – TlBr detector and preamplifier connections.

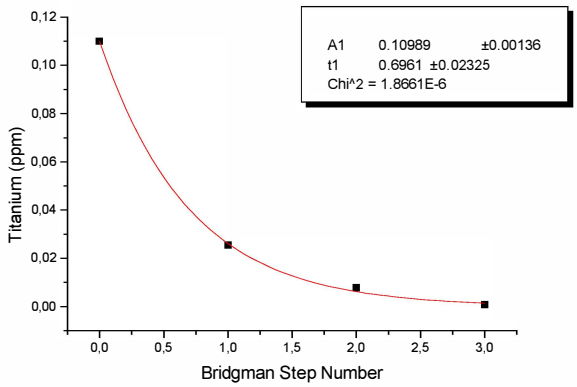
III Results and Discussion

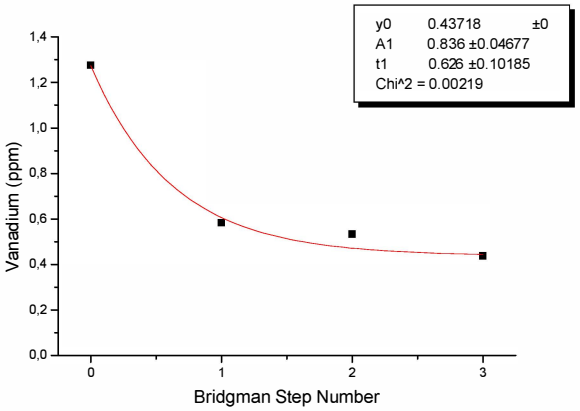
The concentration of ions found in the bottom, middle and top regions of the TlBr crystal measured by ICP-MS corresponding to three sequential crystals growth for the two salts used are shown in Table I and Fig. 3. An exponential model was used as mathematical model to explain and to fit the data of the impurity concentration as a function of the crystal growth repetition number. The exponential model was defined as $y=y_0 \times e^{-x/t}$ equation and it may be used to calculate the coefficients for the migration of impurities. This is useful for predicting the number of repetitions in Bridgman growth needed to achieve a desirable concentration value.

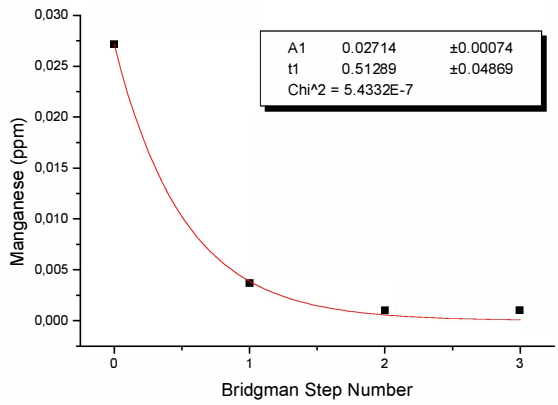
Table I - Impurity concentrations (ppm) in the TlBr salt and in the top and middle regions of the TlBr crystal, measured by the ICP-MS. technique. The values represents the mean one standard deviation (N=10 samples).

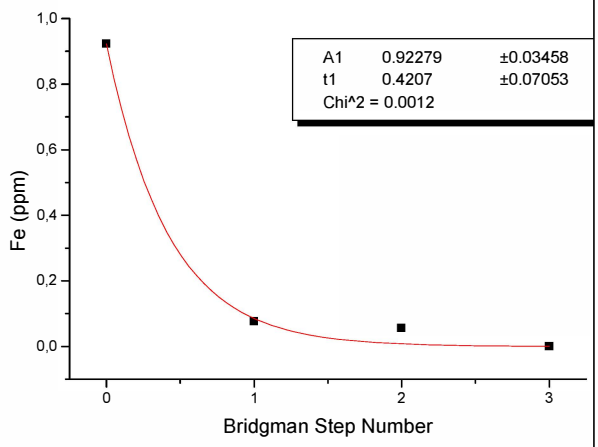
Impurities	CONCENTRATIO IN PARTS PER MILLION (ppm)									
	Raw material	Bottom			Middle			Top		
	0	Bridg #1	Bridg #2	Bridg #3	Bridg #1	Bridg #2	Bridg #3	Bridg #1	Bridg #2	Bridg #3
Al	1.49169	0.00150	0.00150	0.00150	0.00150	0.00150	0.00150	0.00150	0.00150	0.00150
Ti	0.10996	0.02546	0.00787	0.00075	0.01782	0.00689	0.00150	0.00075	0.02673	0.00075
V	1.27557	0.58232	0.53266	0.43718	0.55557	0.52989	0.47254	0.45901	0.64594	0.45445
Mn	0.02715	0.00368	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100	0.00100
Fe	0.92320	0.07673	0.05603	0.00060	0.07673	0.00060	0.00060	0.00060	0.44529	0.00060
Co	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040
As	0.52750	0.16415	0.15313	0.13149	0.15589	0.15431	0.13700	0.13464	0.17202	0.14959
Mo	0.02352	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040
Cd	0.11140	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.01300	0.00280	0.00040
Ba	0.03247	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040	0.00040
Zr	0.56119	0.00005	0.00005	0.00005	0.01250	0.00005	0.00005	0.00005	0.00005	0.00005

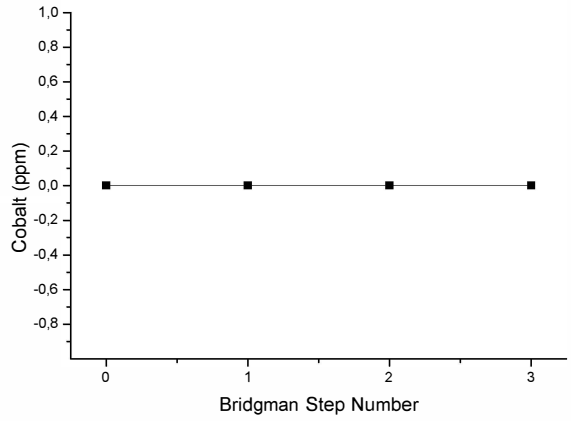

A1 1.49169±0.0015
t1 0.14492±0.02095
Chi^2 = 2.2477E-6
Aluminum (ppm)
Bridgman Step Number

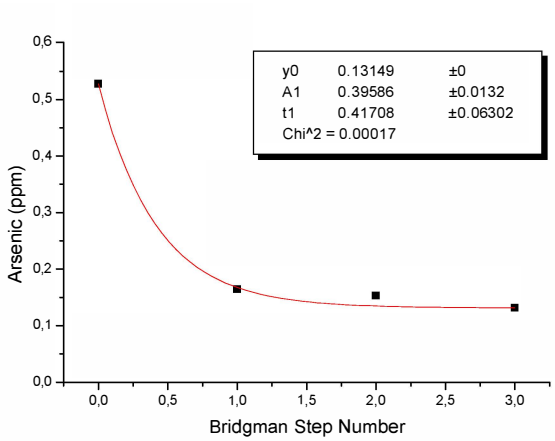

A1 0.10989 ±0.00136
t1 0.6961 ±0.02325
Chi^2 = 1.8661E-6
Titanium (ppm)
Bridgman Step Number

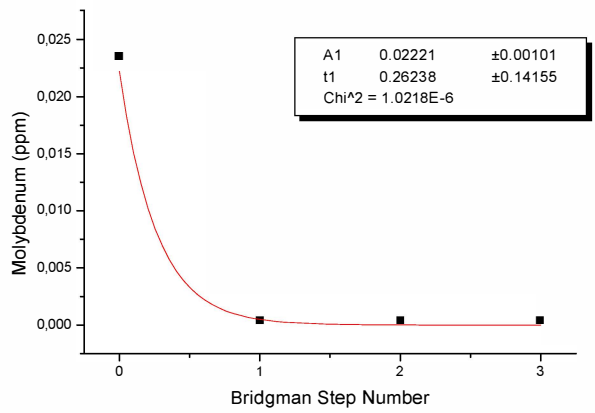

y0 0.43718 ±0
A1 0.836 ±0.04677
t1 0.626 ±0.10185
Chi^2 = 0.00219
Vanadium (ppm)
Bridgman Step Number


A1 0.02714 ±0.00074
t1 0.51289 ±0.04869
Chi^2 = 5.4332E-7
Manganese (ppm)
Bridgman Step Number


A1 0.92279 ±0.03458
t1 0.4207 ±0.07053
Chi^2 = 0.0012
Fe (ppm)
Bridgman Step Number


Cobalt (ppm)
Bridgman Step Number


y0 0.13149 ±0
A1 0.39586 ±0.0132
t1 0.41708 ±0.06302
Chi^2 = 0.00017
Arsenic (ppm)
Bridgman Step Number


A1 0.02221 ±0.00101
t1 0.26238 ±0.14155
Chi^2 = 1.0218E-6
Molybdenum (ppm)
Bridgman Step Number

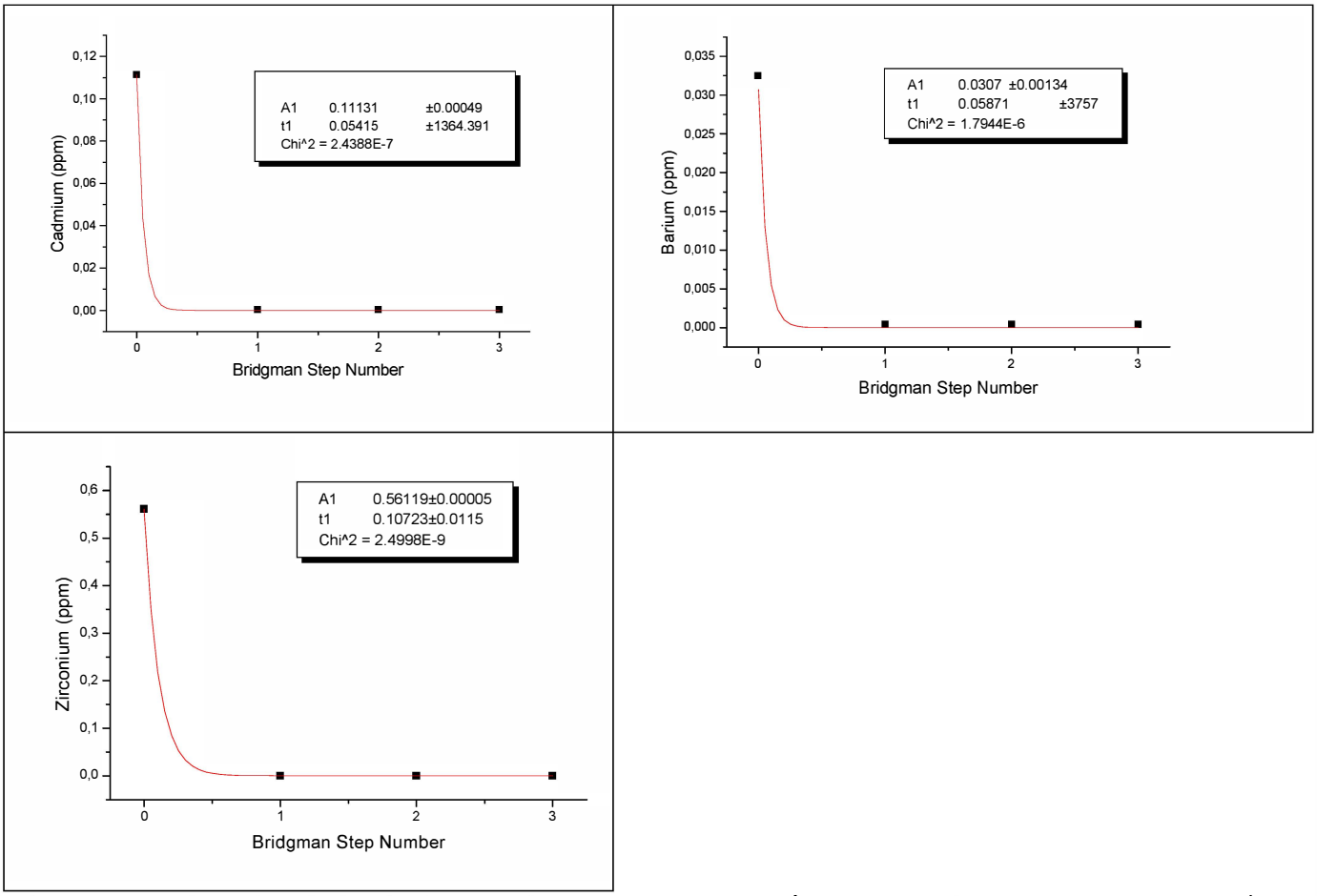


Fig. 4: Concentration of impurity ions in different regions of crystals: bottom, middle and top regions. The curves were fitted using a defined exponential model.

According to Table I and Fig. 4, the reduction level of the impurities in the crystal middle region, after the third growth, was of 99% (1-(0.00150/1.49169)) for Al, 98% (1-(0.00150/0.10996)) for Ti, 63% (1-(0.47254/1.27557)) for V, 96% (1-(0.00100/0.02715)) for Mn, 99% (1-(0.0006/0.92320)) for Fe, 74% (1-(0.13700/0.52750)) for As, 98% (1-(0.00040/0.02352)) for Mo, 99% (1-(0.00040/0.11140)) for Cd, 98% (1-(0.00040/0.03247)) for Ba and 99% (1-(0.00005/0.56119)) for Zn. No reduction level was observed in the Co concentration.

The number of Bridgman-steps required to reduce the impurity initial level of 100% to 1% and 0.1% were predicted from Fig. 4, which results are presented in the Table 2.

Table II - Predict number of Bridgman-steps needed to reduce the impurity from the initial level of 100% to 1% and 0.1%.

Impurity	Bridg# ↓ to 1%	Bridg# ↓ to 0.10 %
Al	0.7 ± 0.1	1.9 ± 0.2
Ti	3.2 ± 0.1	6.4 ± 0.2
V	2.9 ± 0.5	5.8 ± 0.9
Mn	2.4 ± 0.2	4.7 ± 0.4
Fe	1.9 ± 0.3	3.9 ± 0.6
Co		
As	1.9 ± 0.3	3.8 ± 0.6
Mo	1.2 ± 0.7	2.4 ± 1.3
Cd	0.2	0.5
Ba	0.3	0.5
Zr	0.5 ± 0.1	1.0 ± 0.1

The exponential model used to fit the curves of the impurity concentrations as a function of the crystal growth step number can be useful for predictive purpose, for example, in the present case, in order to know the number of Bridgman step to achieve 1% of initial concentration of Titanium (Ti), in the "middle" region, it will require approximately three (3) Bridgman grown steps, while to reduce for 0.1% it will be necessary around six (6) growth steps.

The "Repeated Bridgman" process was efficient for purification, as it can be inferred from Tables I and II and Fig. 4. Practically, after three growth steps, the impurities were reduced to 1%, compared to the initial concentration (TlBr powder). More studies for the improvement of the TlBr purification methodology evaluation should be carried out, aiming to establish the number of repeated growths, to achieve the maximum reduction of the impurities concentration to obtain high quality radiation detectors.

The X-ray diffraction pattern of TlBr powder exhibited a complete set of reflections (Fig. 3 (a)), while the typical X-ray diffraction pattern of TlBr crystals grown in this work presented only a reflection line (Fig. 3(b)). The diffractogram indicates that the crystal is preferentially oriented in the (110) direction (Fig.3 (b)). It is worthwhile to observe that there was no other crystalline phase in the grown crystal since all detected peaks corresponded to the TlBr peaks oriented in the (110) direction. These results

were obtained for the crystals grown once, twice and third times and are in agreement with the literature [4,10].

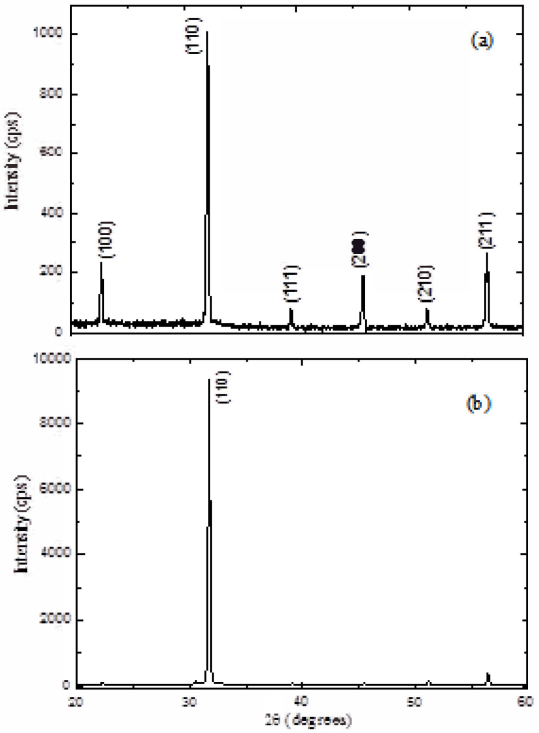


Figure 5: X-ray diffraction of TlBr powder (a) and TlBr crystal (b).

For the purpose of analyzing the effectiveness of the purification process, a spectrometric analysis was performed and the results were compared with the efficiency of the purification. The crystals grown by Repeated Bridgman technique were excited under a ^{241}Am gamma source, biased with 400 V and counted for 5 minutes. The pulse height spectra obtained (Fig. 6) suggest a significant improvement in their profiles when the purification step is increased. For the TlBr crystal grown once, it was not possible to observe the photopeak profile because the pulses generated fall in the electrical noise region. Otherwise, for the TlBr grown twice, it can be observed only the photopeak of 59 keV of ^{241}Am gamma source. For the third grown crystal, a multiple lines from ^{241}Am can be also observed, although without resolution enough to observe each one well separated, as it can be observed in the Fig. 6.

Fig. 7 and Table 2 present the TlBr resistivities found for crystals grown once, twice and three times. Concerning the repeated Bridgman, the resistivity show a positive slope tending to achieve a plateau after the third growth as can be inferred from Fig. 6. The resistivities found in this work are similar to that described by Hitomi et col. [13], which was obtained at room temperature. TlBr resistivities higher found by other authors [11,12] were obtained for measurements carried out at low temperature, since the resistivity is dependent of the temperature measurements.

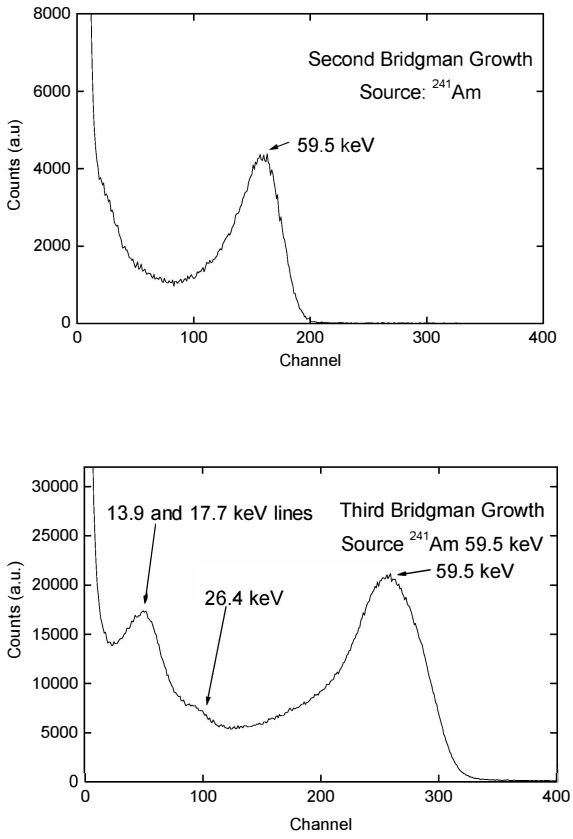


Fig. 6 - TlBr detector energy spectra under ^{241}Am excitations. Detectors were prepared using TlBr samples from the middle region of the crystals grown twice and three times.

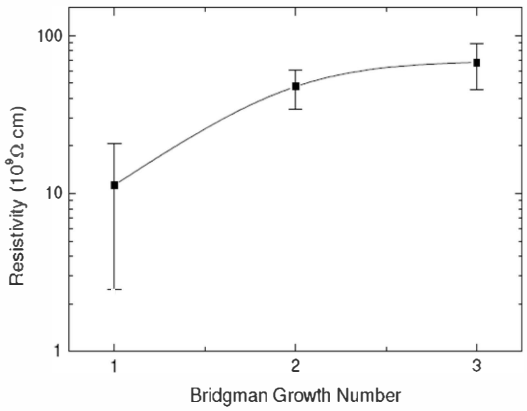


Fig. 7 – Resistivity of the slice samples (~0.65 mm thick) as a function of the Bridgman growth number. The bar error represents one standard deviation (N=3 samples).

VIII- CONCLUSION

The Repeated Bridgman method showed to be efficient to purify the TlBr crystal and to improve its performance as a radiation detector. A exponential model defined by $y=y_0e^{-x/t}$ equation may be used to calculate the coefficients for the migration of impurities. This is useful for predicting the number of repetitions in Bridgman growth required to achieve a desirable concentration value. The resistivity showed a positive slope, tending to reach a plateau after the third growth. Above 3 MΩ, the resistivity of the TlBr crystal seems to not affect the spectrometry quality of the detector.

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