MULTIELEMENTAR SEGREGATION COEFFICIENT OF THALIUM BROMIDE IMPURITIES FROM INDUCTIVELY COUPLED PLASMA MASS SPECTROSCOPY MEASUREMENTS.

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Abstract - **Thallium bromide (TlBr) is a compound semiconductor with a high atomic number and wide band gap, being a very promising material to be used as room temperature radiation detectors. The commercial TlBr powder is used for growing crystals for detector applications. To reduce impurities, this material is purified by the zone refining technique. In this work the trace impurities at ppm level were analyzed using ICP-MS, before and after zone refining. The efficiency of the purification was analyzed theoretically from the experimental data of the segregation coefficient estimated. Three impurities were described in this work: lithium (k=0.381), barium (k=0.699) and chromium (k=0.546).**

Index Terms – **Thallium bromide, zone refining, radiation detector, segregation coefficient.**

I. 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 in the field of X and gamma ray measurements, operating at room temperature [1-4]. Layered semiconductor materials have a number of properties that make them attractive for such application. However, the role of the crystal impurities on the detector performance is crucial, and then improvements on the chemical purification and the impurity reduction analysis should be achieved [5,6].

TlBr is a layered semiconductor material which has a set of special characteristics, such as: (a) wide band gap energy (Eg = 2.68eV), (b) high resistivity ($10^{11}\Omega$cm), (c) high density (7.5 g/cm^3) and (d) high atomic number elements (Z_{Tl}= 81, Z_{Br} =35) [3-5]. These properties become the TlBr a suitable material to be used in the X and γ ray spectrometry, at room temperature. Successful

growth of high optical and electrical quality of the TlBr crystal detector is largely dependent on the purity of the substrate used [5,6]. The zone refining is one of the more efficient techniques to obtain a purified crystal substrate. The zone refining principle is based on the capacity of the impurities to migrate along the ingot, displaced by the action of its solubility in the melting zone. The impurity migration efficiency can be characterized by a parameter *k* named as segregation coefficient. The knowledge of *k*, for each one impurity present in the crystal substrate, is important in order to predict the refining pass numbers necessary to obtain an ingot with a desirable purity grade [8].

The purpose of this work is to estimate the segregation coefficient, *k*, for the Li, Cr and Ba impurities in the TlBr ingot. The impurities were measured by the ICP-MS technique and the Excel Solver routine was applied for the *k* calculations.

II. MATERIAL AND METHODOS

Commercially available TlBr powder with Optical purity grade was uniformly distributed in a quartz tube occupying a length of 40 cm inside the ampoule (Fig.1). Subsequently, the powder salt was solidified, submitting it to one pass zone refining process [6]. Firstly, the ampoule containing the powder substrate was evacuated to 10^{-5} Torr and sealed off. It was mounted in the zone refining furnace (Fig. 1) and the heater was moved at a speed of two cm/hr along the length of the quartz ampoule. The length of the melting zone was about three cm. The furnace temperature was set to approximately 480ºC. The solidified TlBr ingot was cut into 40 pieces of 1 cm each, using clean stainless scissors. The impurities segregation was evaluated by inductively coupled plasma mass spectroscopy (Perkin-Elmer ICP-MS, ELAN 6100) technique [9].
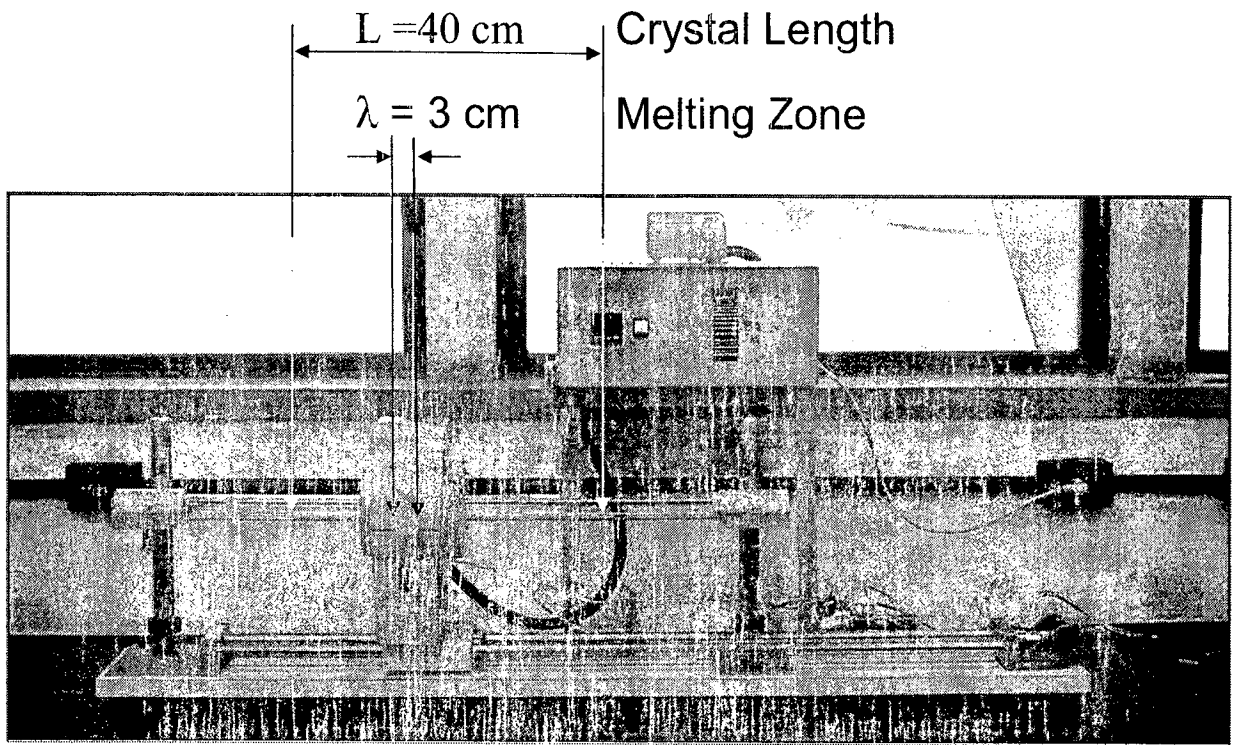
9900

L =40 cm   Crystal Length

λ = 3 cm   Melting Zone

Fig. 1. Zone refining furnace system. Melting zone = 3 cm. Heater speedy = 2 cm/hr
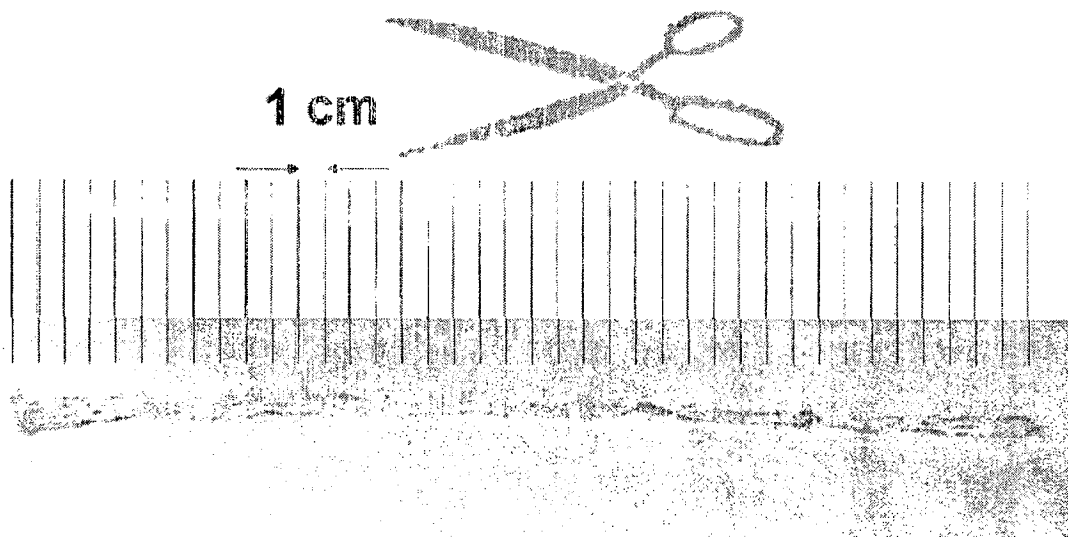
1 cm

Fig. 2. Final aspect of the TlBr crystal solidified by one pass of zone melting refining. The entire section of the crystal was cut into small pieces of one cm, carried out with clean stainless scissors.

The ICP-MS measurements identified, consistently, the presence of three metals: Lithium, Barium and Chromium. After that, for each of those metals, and to express the results in terms of the zone melting length (3 cm), the 40 samples were averaged each three samples at a time.

For the calculation of the segregation coefficient **k** some idealized hypothesis were assumed: (1) the concentration of the metals in the powder was constant in all extension of its distribution in the quartz ampoule; (2) constant ingot cross section; (3) constant segregation coefficient along the ingot length; (4) the initial concentration in each 3 cm sequence of the ingot corresponds to the sum of the ICP-MS in the entire ingot, divided by the number of elements considered, i.e.,

$$C_0 = l \times \frac{\sum_{i=0}^{N}[impurity]_i / cm}{N} \tag{1}$$

where: N in this work = 40; l (the melting zone length) = 3; $[impurity]_i$ corresponds to the ICP-MS measurement for the metal in the i-segment of the TlBr ingot, and finally, (4) the last $\frac{N}{l}$ section of the ingot the impurity concentration C_x equals:

$$C_{x.\frac{N}{l}} = \frac{N}{l} \times C_0 - \sum_{j=1}^{\frac{N-l}{l}}[impurity]_j \tag{2}$$

The predictable mathematical model to calculate the concentration C_x was:

$$C_x = C_0 \times [1 - (1 - k) \times e^{-k \cdot \frac{x}{l}}] \tag{3}$$

After these considerations, the segregation coefficient **k** was estimated using the Microsoft Excel routine named **Solver**. In this routine the (Set) **Target Cell** was assumed as the parameter:

$$\chi^2 = \sum \frac{(C_{x,obs} - C_{x,cal})^2}{C_{x,cal}} \tag{4}$$

and the "(By) **Changing Cell**" as the k values, initially assumed as 0.1 (the Solver routine recalculated this first estimate to a convergent value).

As an example, the Lithium input data set is showed in Fig. 3. In this figure the column "**B**" (C_0(ppm)) represents the initial salt concentration of the impurity, column "**C**" the ICP-MS experimental values, column "**D**" the respective theoretical value calculated from the equation 3.

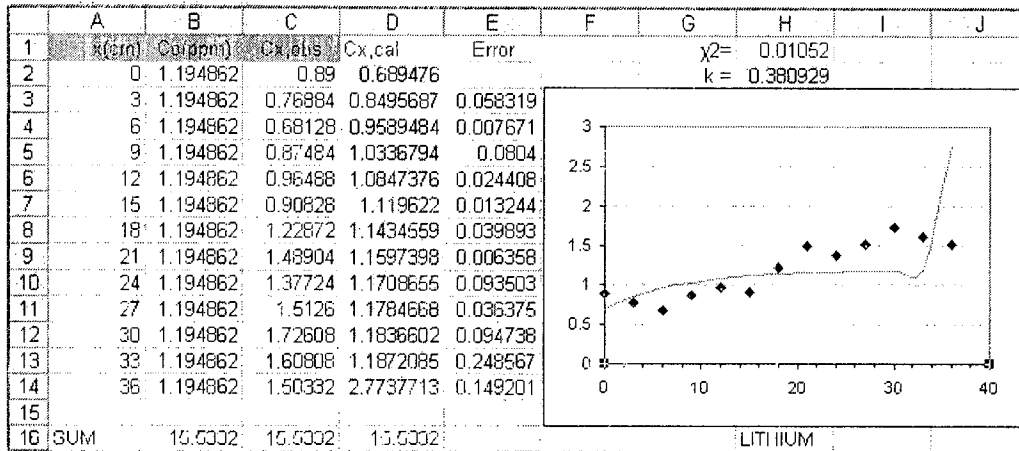|	A	B	C	D	E	F	G	H	I	J
1	X(cm)	C0(ppm)	Cx,obs	Cx,cal	Error		χ2=	0.01052		
2	0	1.194862	0.89	0.689476			k =	0.380929		
3	3	1.194862	0.76884	0.8495687	0.058319					
4	6	1.194862	0.68128	0.9589484	0.007671					
5	9	1.194862	0.87484	1.0336794	0.0804					
6	12	1.194862	0.96468	1.0847376	0.024408					
7	15	1.194862	0.90828	1.119622	0.013244					
8	18	1.194862	1.22872	1.1434559	0.039893					
9	21	1.194862	1.48904	1.1597398	0.006358					
10	24	1.194862	1.37724	1.1708655	0.093503					
11	27	1.194862	1.5126	1.1784668	0.036375					
12	30	1.194862	1.72608	1.1836602	0.094738					
13	33	1.194862	1.60808	1.1872085	0.248567					
14	36	1.194862	1.50332	2.7737713	0.149201					
15										
16	SUM	15.5332	15.5332	15.5332						

Fig. 3. Example of the MS-Excel input of data for the calculation of the segregation coefficient **k** for Lithium

III. RESULTS AND DISCUSSIONS

Table I sumarizes the results of the Lithium, Barium and Chromium in the TlBr ingot. Segregation; coefficient **k**.

Figures 4 to 6 show a projection of the improvement in the TlBr crystal purity in function of the increase of the zone refining pass numbers.

Table 1 – The coefficient of segregation and the fitting parameter χ^2.

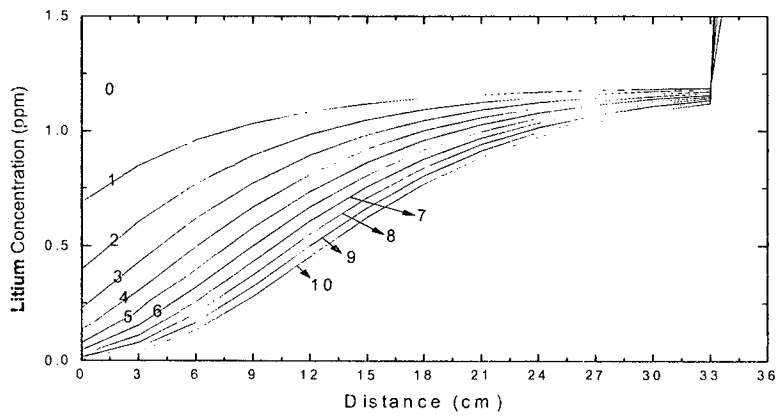| IMPURITY	k	χ^2
Lithium	0.381	0.0105
Barium	0.699	15.01
Chromium	0.546	0.0302

Fig. 4. The zone refining pass number effect in the ingot of TlBr for Lithium.
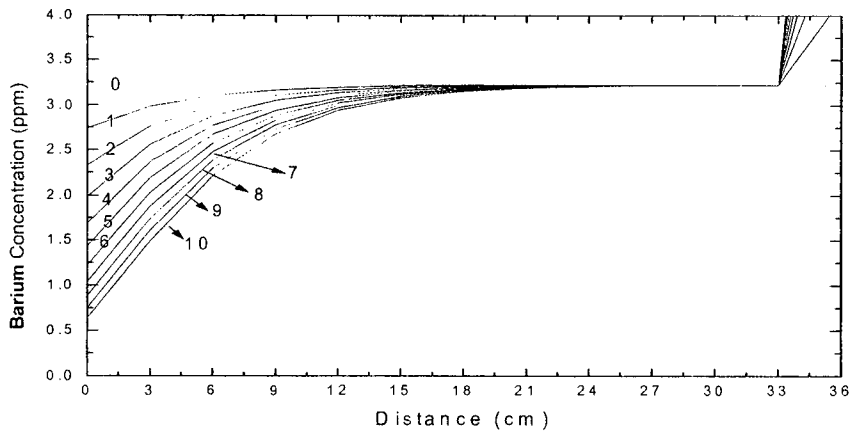

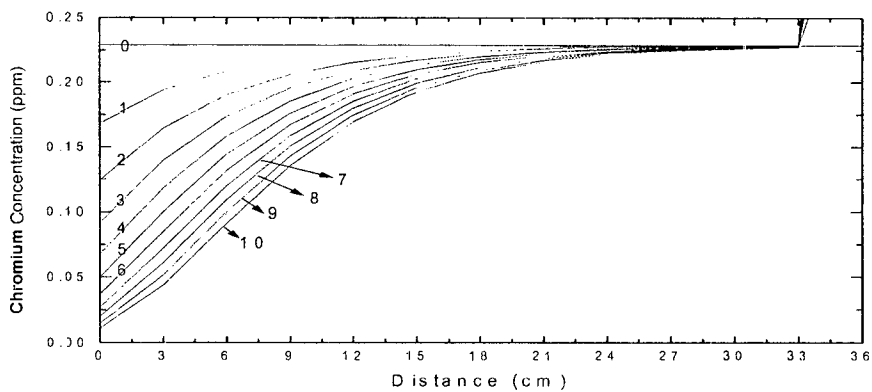Fig. 5. The zone refining pass number effect in the ingot of TlBr for Barium.

Fig. 6. The zone refining pass number effect in the ingot of TlBr for Chromium.

In the initial portion of the TlBr crystal, lithium is able to achieve a level of impurity of only 0.4% after the tenth pass. However, in the middle of the ingot (18 cm), the level of lithium concentration decreased only 64% after 10 passes, suggesting to be necessary more pass numbers if a higher purity grade is aimed.

Similar observations can be described for chromium, while the worst situation was found for barium. For this element, the initial portion had a clearance of only 20% after the tenth pass. In the middle portion it is expected only a clearance factor of 3% after ten passes of zone refining.

The technique ICP-MS with a laser sampling system used to quantify TlBr ingot impurities in solid samples showed a some imprecision in the results. It is expected that measures carried out in ICP-MS, diluting TlBr ingot samples in a liquid solution present better precision, although this is a destructive technique. Further measurements with samples diluted in solution should be carried out.

IV. CONCLUSION

The semiconductor of TlBr can be an important radiation detector provided suitable quality crystals can be routinely produced. One of the obstacles to be overcome is related to the impurities in the crystal. In this work we present an analysis of measures using modern technology (ICP-MS) allied to a traditional calculation of the segregation coefficient, now renewed by use of computational facilities.

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