BRAZILIAN JOURNAL
OF
RADIATION SCIENCES
10-03B (2022) 01-14

Zonal Refining and Bridgman Technique for CsI:Tl Scintillation Crystal Growth

Suzart[a] K.F., Pereira[a] M.C.C., Hamada[a] M.M., Mesquita[a] C.H.

[a] *Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN - SP)/ 05508-000 São Paulo, SP, Brazil*

e-mail : karolinesuzart@usp.br

ABSTRACT

This work describes the development of the crystal cesium iodide doped with thallium (CsI:Tl) for use as a radiation detector. For CsI salt purification the zonal refining methodology using a horizontal oven at a constant temperature of 700 °C was used. The high temperature region corresponds to approximately 10% of the salt bed containing (260 mm). This region moves at a speed of 50 mm/h. The crystal growth was carried out by Bridgman technique, using a vertical oven at speed of 1 mm/h.

ISSN: 2319-0612
DOI: https://doi.org/10.15392/2319-0612.2022.1925
Submitted: 2022-01-30
Accepted: 2022-08-01

Keywords: **Scintillator Detector, Zonal Refining Technique, Bridgman Technique, CsI:Tl Crystal**

1. INTRODUCTION

The CsI:Tl inorganic scintillator was selected due to its characteristic of withstanding mechanical shocks, sudden temperature changes and for having adequate efficiency in the detection of gamma radiation when compared to other scintillator detectors [1]. Its potential in applications, such as high energy physics research, environmental monitoring, petroleum research, geological research [2], nuclear medicine [3], security incidents and defence techniques [4], detectors to measure dose rate in contaminated environments [5]. These subjects indicate the CsI crystal looks very promising scintillator to be used as a radiation detector. Conversion of scintillations into electronic signals may be achieved with a PIN-type photodiodes or a bialkaline-photomultipliers. If doped with Na in place of Tl, the PIN photodiode may be replaced by a bialkaline photomultiplier (PMT). When gamma radiation transfers its energy to the valence shell it may be brought to a level excitation. When it returns to steady state, it emits a photon of green light at 540 nm if doped with Tl and near UV at 420 nm, if doped with Na.

Cesium iodide (CsI) crystals have high gamma-ray stopping power due to their high density and high atomic number of their chemical constituents [6]. These properties make the CsI crystal as an optimum gamma ray detector [7, 8]. CsI crystals are stable physicochemical structures due to the absence of a cleavage plane and have better chemical stability when compared to sodium iodide (NaI) crystals due to their less hygroscopic nature. Doping the CsI crystal matrix with thallium (Tl) or sodium (Na) produces a reduction in the crystal band gap and consequently increasing the efficiency of this crystal as a radiation detector [1].

An important advantage of CsI:Tl is that it can be coupled to photodiodes PIN type that operate with reverse bias of approximately 10 to 40 volts. Alternatively, can be used bialcaline-photomultipliers that operates at approximately between 700 and 1800 volts [9].

The objective of this work was to grow cesium iodide crystals activated with thallium ions (Tl^+) to use as radiation detectors. The Zonal Refining or Zonal Fusion technique [10, 11] was applied to obtain a Cesium Iodide salt as pure as possible. For crystal growth, the Bridgman technique was used [12].

2. MATERIAL AND METHODS

The Cesium Iodide crystal, doped with 10^{-3}M of Thallium was produced at IPEN/CNEN/SP, using the Bridgman technique. The cesium iodide salt was weighed and then placed in a properly cleaned quartz crucible. To clean the quartz crucible, Extran 10% was used, in which it was soaked for 24 hours. Then, a 5% hydrofluoric acid solution was prepared, where the crucible remained for 40 minutes and rinsed with milli-Q water.

The quartz crucible containing the CsI salt was left in a vacuum of 10^{-5} Pa and then sealed and taken to the horizontal furnace for the zonal refining procedure. The melting point of CsI is 626°C [13] and therefore the temperature of 700°C was selected for the zonal refining procedure, as this guaranteed the melting of the CsI salt. Zonal refinement is a technique for purifying solid materials by liquefying a small region capable of dragging impurities to the ends of the solid material. [14, 15] According to Figure 1- (a), it is possible to observe the solid formed after the zonal refining. Upon removal from the tube disregarding the ends, the CsI solid was macerated and placed in another properly cleaned quartz crucible, as shown in Figure 1 (b).

Figure 1- *(a) CsI solid after zonal refining and (b) after the mass of crystals are macerated*.

Source : The Author

After purification of the CsI salt by zonal refinement, Thallium Iodide was added and then the crucible was taken to a vacuum for the thermal treatment of the salt. Iodine was added to the crucible inside a glove box in an argon gas atmosphere, in order to prevent oxygen from entering the crucible. After the quartz crucible was sealed both CsI salt previously purified by the zonal refining and Tl they were placed in a vertical oven to obtain the CsI:Tl crystal grown by the Bridgman method [16,17], as shown in Figure 2 (a). Subsequently, heat treatment was performed on the obtained crystal to eliminate the coloring due to excess iodine, as shown in Figure 2 (b). The CsI:Tl crystal was cut with a diamond edged cutting wheel and using ethylene glycol as a lubricant.

Then the crystal was polished having the final geometry of a parallelepiped with dimensions of 12.22 x 12.22 x 18.80 mm^3 (parallel square face and thickness), as shown in Figure 2 (c) and (d).

Figure 2- *(a) CsI crystal (Tl) after the Bridgman method. (b) CsI crystal:Tl after heat treatment. (c) CsI :Tl crystal in cutting process. (d) Final geometry of the CsI :Tl crystal.*

Source : The Author

Transparency is a critical factor for scintillators quality. Photons emitted with energy in thevisible region need to reach the photosensor efficiently. Transparency can be assessed by a direct measurement of light transmittance over a given wavelength range. The transmittance tests were performed on samples of CsI:Tl crystals and pure CsI, using a UV-visible spectrophotometer (Shimadzu UV-1601 PC). The spectral profile was from 190 nm to 1100 nm, and the optical path length was 3 mm.

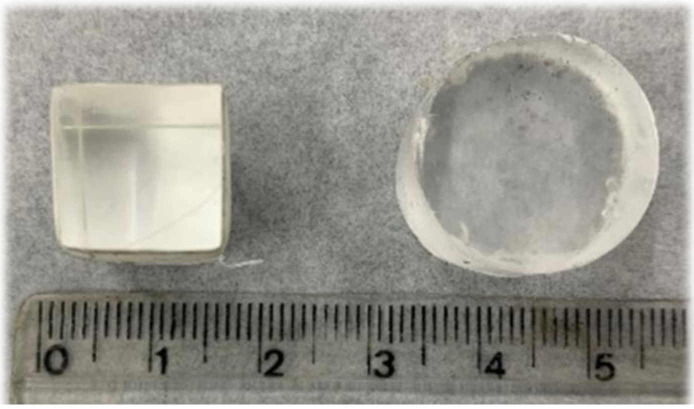
Luminescence emission spectra for the CsI:Tl and pure CsI crystals were evaluated by photometric analysis of the stimulated crystals, with a radioactive source of ^{137}Cs (662 keV) in front of each crystal samples coupled to the monochromator input. The pulses of light from the scintillators were converted into electrical pulses by means of a photomultiplier tube, optically coupled to the output of the monochromator.

3. RESULTS AND DISCUSSION

After the steps of the Zonal Refining and Bridgman techniques, the CsI:Tl crystals were obtained with the dimensions (a) 12.22 x 12.22 x 18.80 mm^3 (parallel square face and thickness) and (b) Ø 20.1 mm x ↑11.9 mm (circular face and thickness) both used for radiation measurements.

The Figure 3 show crystals with the different profiles.

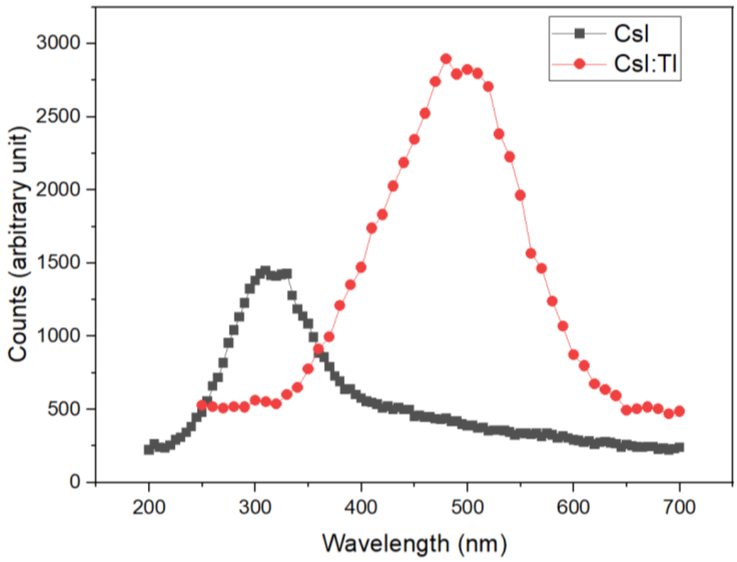
Figure 3- *CsI:Tl crystals with geometries of □12,22 mm ↑ 18,80 mm and Ø 20,1 mm ↑ 11,9 mm*



Source : The Author

The Figure 4 shows the luminescence curves for CsI pure and CsI:Tl crystals. The peak intensity at 520 nm for CsI:Tl crystal is attributed to the presence of thallium ions in the crystal [18]. The pure CsI crystal used for comparison purposes showed an emission peak of luminescence at 310 nm.

Figure 4- *Luminescence curves as a function of wavelength for the pure CsI and CsI:Tl crystals.*

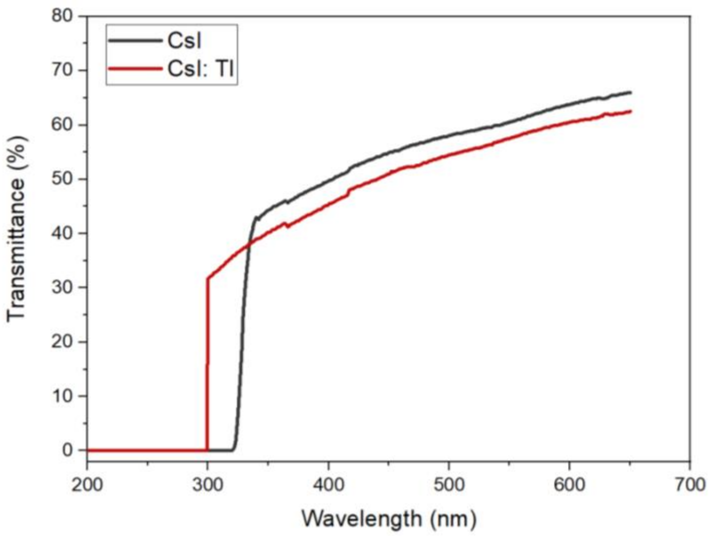


Source : The Author

The effect of thallium on the CsI matrix is to decrease the band gap (an energy gap between the valence band and the conduction band). According to figure 4, the luminescence peaks λ_{CsI}= 310 nm and $\lambda_{CsI:Tl}$= 520 nm. The energetic relationship between the wavelength of luminescence and the photon energy is estimated by the Planck–Einstein formula $\boldsymbol{E=h.\nu}$, being the Planck constant, equal to 6.626x10^{-34} m^2.kg/s and the frequency $\boldsymbol{\nu}$ of electromagnetic radiation in hertz (Hz). The relationship of wavelength and $\boldsymbol{\nu}$ is equal to $\boldsymbol{\nu = c/\lambda}$, then $\boldsymbol{E=h.c/\lambda}$, where $\boldsymbol{c}$ is the light velocity in the vacuum (~ 3.10^8 m/s). In this maner, E_{CsI} = 4.002 eV and $E_{CsI:Tl}$ = 2.384 eV, that is, the addition of thallium will halves the band gap energy of the crystal. Consequentely, it will improve the sensibility of the cintilation detection by a factor of approximately a double. Decreasing the band gap will produce more light photons per incident radiation.

According to Figure 5, the optical transmitance of the pure CsI crystal at the wavelength of 650 nm was 66%, falling practically to the zero level for wavelength below 320 nm. The same analise applied to optical transmittance of the CsI:Tl crystal was 62.5% for the wavelength of 650 nm. In the peak of maximum luminescence emission was approximately 56% (Figure 4). These results reveal an adequacy between the transmittance capacity of the CsI:Tl crystal and its luminescence peak (520 nm). The same is not observed for the pure CsI crystal due to its maximum emission peak being at 320 nm and located close to the transmittance slope.

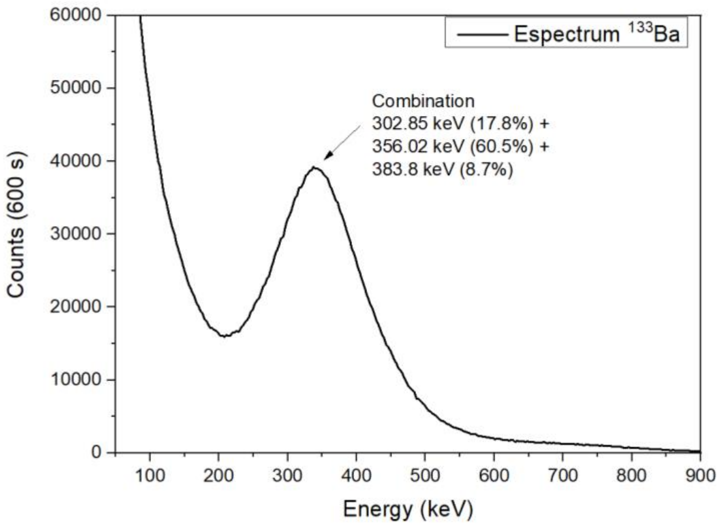
Figure 5 – *Transmitance curves as a function of wavelength for the pure CsI and CsI:Tl crystals.*



Source : The Author

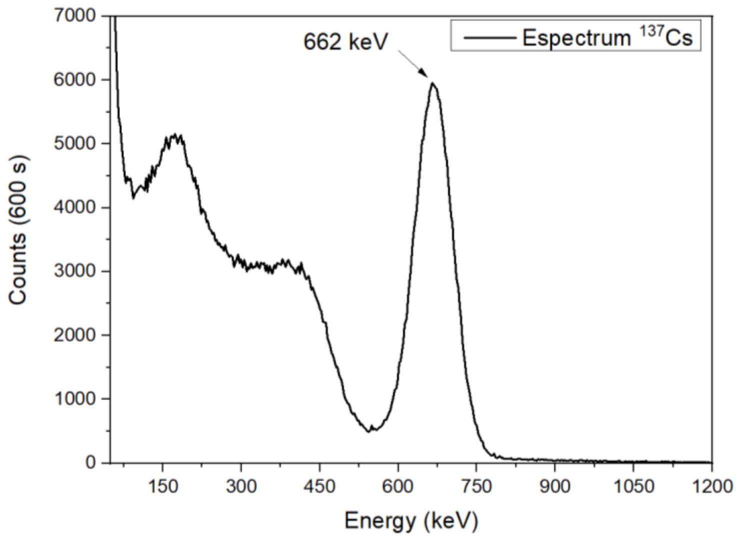
To know the energy resolution capability of the CsI:Tl crystal developed in this work, gamma spectra from different radioactive sources in the energy range of 355 keV to 1333 keV were used, as following: ^{133}Ba (~355 keV), ^{137}Cs (662 keV), ^{22}Na (511 keV and 1275 keV) and ^{60}Co (1173 keV and 1333 keV). Figures 6, 7, 8 and 9 shows the spectra obtained for these sources.

Figure 6- *Spectrum obtained for the sources of ^{133}Ba of the CsI :Tl crystal.*



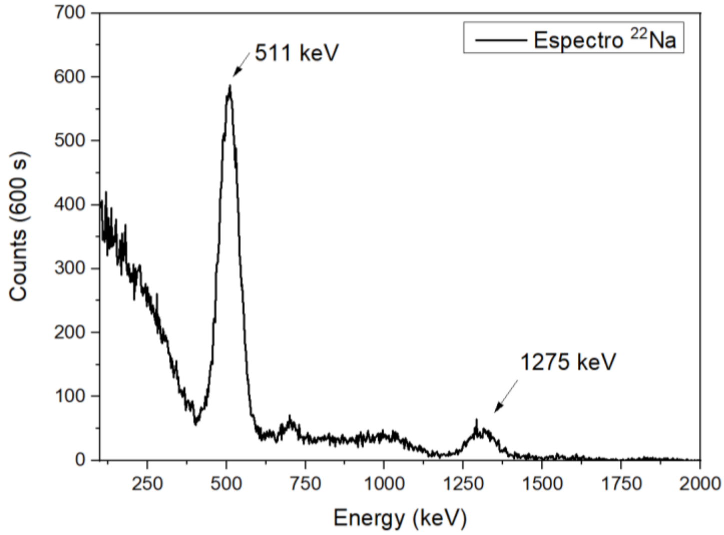
Source : The Author

Figure 7- *Spectrum obtained for the sources of ^{137}Cs of the CsI :Tl crystal.*



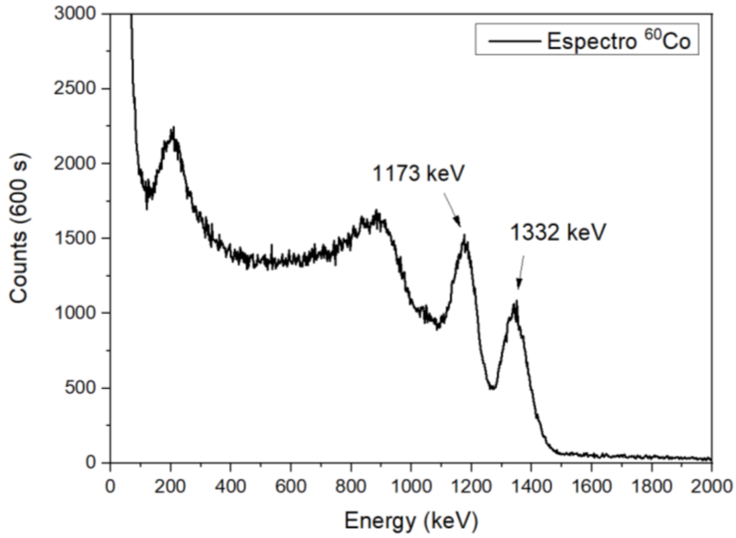
Source : The Author

Figure 8- *Spectrum obtained for the sources of (a) ^{22}Na of the CsI :Tl crystal.*



Source : The Author

Figure 9- *Spectrum obtained for the sources of (c) ^{60}Co of the CsI :Tl crystal.*



Source : The Author

Table 1 presents the energy resolutions for the developed CsI:Tl crystal coupled to the PIN-type photodiode and using a set of gamma radiation sources, containing energy photopeaks ranging from 355 keV to 1332 keV. The FWHM parameter is defined as the total width at half of its maximum which was used to estimate the resolution.

The reduction of impurities in the CsI salt promoted by the zonal refining technique proved to be effective due to the high count-efficiency and the adequate values of the energy resolution presented (Table 1) by the CsI:Tl scintillator crystals.

Table 1- Percentage resolution of the CsI:Tl crystal coupled to the photodiode

Source	Energy (keV)	Resolution (%)
^{133}Ba	356	13,4
^{137}Cs	662	7,0
^{22}Na	511	9,9
^{22}Na	1275	6,9
^{60}Co	1173	5,8
^{60}Co	1333	5,3

CONCLUSION

The zonal refining technique is a powerful method of purifying salts used in crystal growth for radiation detection purposes. By means of this purification technique, it is possible to use commercial salts with a low degree of purity and after purification by the zonal refining technique, high quality scintillator crystals can be grown.

The results demonstrated that Thallium Activated Cesium Iodide crystals grown by the Bridgman Technique in the IPEN laboratory proved to be sensitive to the detection of gamma radiation.

The luminescence spectrum of the CsI:Tl crystal showed maximum emission at 520 nm, evidencing an adequate overlap with the quantum efficiency of PIN-type photodiodes.

The optical transmittance of the CsI:Tl crystal was 56% at the wavelength of 520 nm, demonstrating suitable overlap between the transmittance capacity of the crystal and its maximum luminescence region. The analysis of the luminescence and transmittance spectra as a function of wavelength showed an adequate overlap between the luminescence and transmittance curve, thus ensuring that the crystal is practically transparent to its own scintillation.

From the analysis of the luminescence curve and the Einstein-Planck formula $E=h.v$ it is possible to infer that the presence of Tl in the CsI crystal matrix reduces the band-gap to approximately half. Consequently, the Tl contributes to generating the double of light photons (sensitivity parameter) in the CsI:Tl detector.

Spectra with defined energies were obtained using the CsI:Tl radiation detector, for energies (~355 keV) of the ^{133}Ba source, (662 keV) of ^{137}Cs and (511 and 1275keV) of ^{22}Na. The spectra shown in Figures 6-9 are similar to those described in the literature for the CsI:Tl detector.

The energy resolution values show good results for the CsI:Tl scintillator crystal coupled to the photodiode PIN type.

ACKNOWLEDGMENT

The authors express their thanks to CNPq for the scholarship in developing the work and granting the CNEN / IPEN grant to the first author.

REFERENCES

[1] KNOLL, G. F. **Radiation Detection and Measurement**, 4th Edition, United States of America, 2010.

[2] ZHANG, Z.; ZHAO, Q.; Li, Y; OUYANG, X.P. Electronic structure and optical properties of CsI, CsI(Ag), and CsI(Tl). **Journal of the Korean Physical Society**, v.68, 2016, p.1069–1074.

[3] ALBAGLI, D.; HUDSPETH, H.; POSSIN, G.; LEE, J.; NISKAYUNA, P.; GRANFORS, B.; GIAMBATTISTA, G.E. Performance of Advanced a-Si / CsI-based Flat Panel X-ray Detectors for Mammography, **Medical Imaging 2003: Physics of Medical Imaging,** M. J. Yaffe, L. E. Antonuk, Editors, Proceedings of SPIE v. 5030, 2003.

[4] PURSLEY, J. Determination of Thallium Doping in Cesium Iodide Scintillator Crystals, **NSCL**, Michigan State University, East Lansing, MI 48824, 2001.

[5] SHUICHI T.; KIMIAKI S. Spectrum dose conversion operator of NaI(Tl) and CsI(Tl) scintillation detectors for air dose rate measurement in contaminated environments. **Journal of Environmental Radioactivity** v. 166, 2017, p. 419-426.

[6] KIM, H.; KHAN, A.; DANIEL, J.; ROOH, G.; VOUNG, P. Q. Thallium-based heavy inorganic scintillators: recent developments and future perspectives. **Royal Society of Chemistry** CrystEngComm, Issue 3, 2022.

[7] MESQUITA, C.H.; DANTAS, C.R.; COSTA, F.E.; CARVALHO, D.V.S.; MADI FO, T.; VASQUEZ, P.A.S.; HAMADA. M.M. Scintillation Response of CsI:Tl Crystal under neutron, gama, alpha particles and beta excitations. **2010 IEEE Nuclear Science Symposium Conference Record**, 2010, p.19-22.

[8] PEREIRA, M., C., C.; FILHO, T. M.; LOPES, V. M.; BERRETA, J. R.; CÁRDENAS J. P. N. Scintillation Response of CsI:Tl Crystal under neutron, gama, alpha particles and beta excitations. International Nuclear Atlantic **Conference** - INAC São Paulo, SP, Brazil, October 4-9, 2015.

[9] BLANCO, M.; BARELLI, N.; BENEDETTI. A. V.; FLOR, S. W. A. Desenvolvimento de um dispositivo para obtenção de monocristais de ligas à base de cobre, **Quim. Nova**, v. 26, N° 5, 2003, p. 757-762.

[10] PAMPLI, B. R. **Crystal Growth**. 2nd ed. Oxford : Pergamon Press, 1980, p. 609.

[11] PFANN, W. G. **Zone Melting**. 2nd ed. New York: John Wiley & Sons, Inc., 1966, p.309.

[12] RAVI, B. and RAJARAJAN, G. Study on Growth and Optical, Scintillation Properties of Thallium doped Cesium Iodide- Scintillator Crystal. Oriental **Journal of Chemistry**. p. 581-586, 2014.

[13] "Ficha de Dados de Segurança, Sigma Aldrich", Microsoft Word - r8173339.rtf (usp.br), 2021.

[14] ZAVARTSEV, Y., D., ZAGUMENNYI, A., I., KOUTOVOI, S.A., Effective segregation coefficient in cluster crystallization model, **Journal of Crystal Growth**, v. 303, p. 110-113, 2007.

[15] D. CURTOLO, X. ZHANG, M. ROJAS, S. FRIEDRICH AND B. FRIEDRICH, "Realization of the Zone Length Measurement during Zone Refining Process via Implementation of na Infrared Camera", **Applied Science**, vol. 8, 2018, p.1-13.

[16] M. BLANCO, N. BARELLI, A. BENEDETTI, S. FLOR, "Desenvolvimento de um dispositivo para obtenção de monocristais de ligas à base de cobre," **Química Nova**, vol. 26 ,2003, p. 757-762.

[17] SUZART, K.F., HAMADA, M.M., PEREIRA, M.C.C., MESQUITA, C.H. "Development and characterization of CsI(Tl) crystal for use as a radiation detector", **Brazilian Journal of Radiation Sciences**, The Meeting on Nuclear Applications (ENAN 2019) vol 9, 2021.

[18] GWIN, R., MURRAY, R. B., Scintillation Process in CsI (Tl). II. Emission Spectra and the Possible Role of Self-Trapped Holes, **Physical Review**, 131 (2), p 508-512, 1963.