



# Scintillation response of Europium and Indium-co-doped CsI(Na) single crystal under the exposure of gamma-ray

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## ABSTRACT

The traditional CsI(Na) single crystal scintillator was studied to improve its scintillation properties, by co-doping Sodium with Europium and Indium ions. The growth was done by the Czochralski technique. Inductively coupled plasma optical emission spectroscopy and UV spectra including the absorption, excitation, and photoluminescence of the cut ingots were obtained in the region of 200 to 800 nm. The results show that the luminescence intensity of Europium-co-doped CsI(Na) is significantly increased compared to CsI(Na) single crystal, however Indium co-dopant has reduced the CsI(Na) luminescence intensity. Eu's high quantum emission efficiency due to its  $4f \rightarrow 5d$  internal transitions and the radiative energy transfer between  $\text{Na}^+$  and  $\text{Eu}^{2+}$  centers are the possible reason for this enhancement. While decreasing the CsI(Na) luminescence intensity, by adding the In co-dopant, is probably due to non-constructive spectral overlap between emission transition of  $\text{In}^+$  and absorption transition of  $\text{Na}^+$  which results in non-radiative energy transfer between  $\text{Na}^+$  and  $\text{In}^+$ .

In this regard, the pulse height spectrum of these crystals was determined under the excitation of the gamma-ray sources. It is observed that Eu co-dopant strongly increases the scintillation light yield of the conventional CsI(Na) detector and improves its energy resolution, however In co-doped CsI(Na) reduces scintillation yield.

## 1. Introduction

The CsI(Na) crystal is known as one of the efficient scintillators. In most cases, the physical parameters of CsI(Na) are identical to CsI(Tl). The scintillation light output of CsI(Na) is high but is less than NaI(Tl). It has the mass attenuation coefficient greater than NaI(Tl) and its relatively high physical density ( $4.53 \text{ g/cm}^3$ ) and the atomic number increase the X and Y-ray stopping power. The CsI(Na) is moderately hygroscopic, but it is easy to handle with simple precautions. The light output of this scintillator is not self-absorbed, and its blue emission characterization at 420 nm has a good spectral match with photo detectors [1,2]. Most existing scintillators suffer from poor energy resolution and light yield which limit the accuracy of their functional capacity, like medical imaging. Therefore, it is very timely and desirable to either invent new scintillators which have superior the energy resolution and light yield or improve the existing ones or both. The co-doping of traditional scintillation material with a convenient sensing impurity can be an effective way to improve them [3–5]. At present, this research is a study of the co-doping  $\text{Na}^+$  with  $\text{Eu}^{2+}$  and  $\text{In}^+$  in CsI single crystals and the differences in created sub-levels of various elements in the host lattice. The Eu's high quantum efficiency due to its  $4f \rightarrow 5d$  internal transitions has led this lanthanide ion to be considered by researchers.

For excitation at 240 nm, CsI(Eu), has a broad emission band (around 410–480 nm) at room temperature (RT) [6,7]. On the other hand, the  $ns^2$  configuration of the  $\text{In}^+$  ion as a dopant to improve the function of CsI scintillator has been considered in the past. For a free ion, In, the electronic configuration is characterized by singlet ground state  $^1S$ , singlet and triplet excited states  $^1P$ , and  $^3P$ . The latter in result of the spin-orbit coupling is split into three excited electron levels:  $^3P_0$ ,  $^3P_1$ , and  $^3P_2$ . The electronic transitions,  $^1S_0 \rightarrow ^1P_1$ ,  $^1S_0 \rightarrow ^3P_1$ , and  $^1S_0 \rightarrow ^3P_2$ , are often observed in the absorption spectrum. There is an excitation at 230–260 nm for CsI(In), at RT, which its origin is less clear. At RT, The radiative emission of  $^3P_1 \rightarrow ^1S_0$  (at 550 nm) is dominant [8,9]. Therefore, inspired by the performance of these two ions, in this research, we studied the effect of their corporation, by considering the UV-absorption and luminescence spectra and also their response to gamma-ray excitation.

## 2. Experimental

### 2.1. Crystal growth procedure

A CsI(Na), CsI(Na,Eu) and CsI(Na,In) single crystals were grown, using the Czochralski method. The raw materials for these growths

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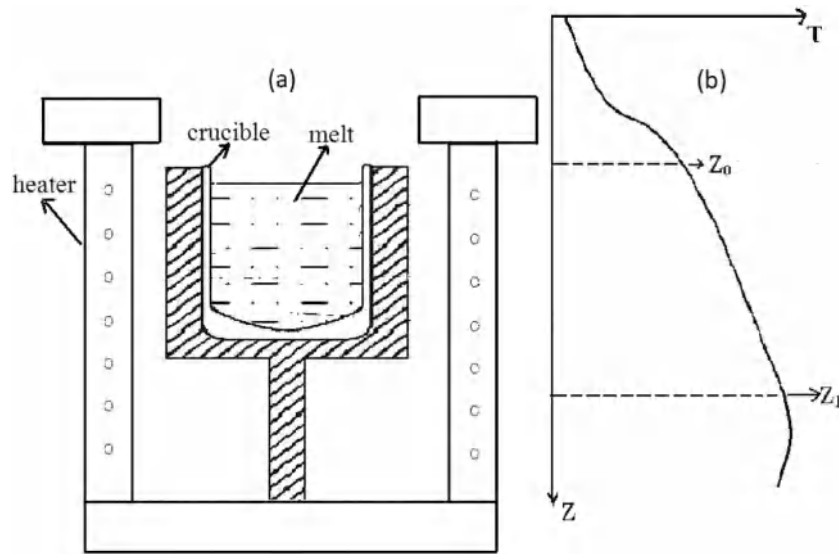


Fig. 1. (a) The schematic diagram of Czochralski furnace and crucible, (b) The temperature gradient curve.

were synthesized by the melted-state reaction. The 600 g of CsI powder (99.999%, Sigma-Aldrich), the 0.12 g (0.02 mol%) of NaI powder (99.999%, Sigma-Aldrich), 0.006 g (0.001 mol%) of  $\text{Eu}_2$  powder (99.999%, Sigma-Aldrich) and 0.006 g (0.001 mol%) of InI (99.999%, Sigma-Aldrich) were mixed for chemicals to grow these crystals, in a platinum crucible with the diameter of 30 mm, was located in a furnace with the resistant heating system.

To create a convenient thermal gradient and reduce the crystal cracks, the furnace thermocouples in  $T_0$  and  $T_1$  zones were regulated in 700 °C and 770 °C, respectively. The melt was located between  $Z_0$  and  $Z_1$  levels. The proper thermal gradient of furnace causes to a flatness of the solidification front surface. A schematic view of the furnace and crucible of the Czochralski system as well as the temperature gradient curve were displayed in Fig. 1.

The growing process was performed in the Ar-gas atmosphere, with the pulling rate of 3 mm/h and the rotation rate of 20 rpm. The crystal growth time was about 36 h. The annealing process was done, for 12 h at 550 °C and eventually, the crystal was cooled to room temperature, at a rate of 25 °C/h. The length of the crystal is about 10 cm, and its diameter is about 2.5 cm and weighs about 260 g. Fig. 2 shows one of the grown single crystals. Then, all the ingots were divided to the three equal parts, part A is the top of the ingot: 0–3 mm, part B is the center of the ingot: 3–6 mm and part C is the bottom of the ingot: 6–9 mm. Fig. 3 indicates three parts of the cutting ingots.

## 2.2. Measurements of UV and photoluminescence spectra

The UV-Vis analysis was performed using Perkin-Elmer UV-Vis spectrometer. Photoluminescence and UV-excitation spectra were recorded in the wavelength region 200–800 nm in the Varian Cary Eclipse model at RT. Inductively coupled plasma-optical emission spectroscopy (ICP-OES; Model 730-ES, Varian), in the wavelength region 167–785 nm, with CCD detector was used to detect of Na, Eu, and In concentrations in the crystals. The instrument detection limit was 1 ppb. To measure the dopant and co-dopant concentrations in the crystals by ICP(OES) method, the system requires a piece of crystal to be dissolved in a suitable liquid. Since CsI(Na) is a type of an alkali halide salt, it can be solve in water. To avoid the impurities reaction, the deionized water was used.

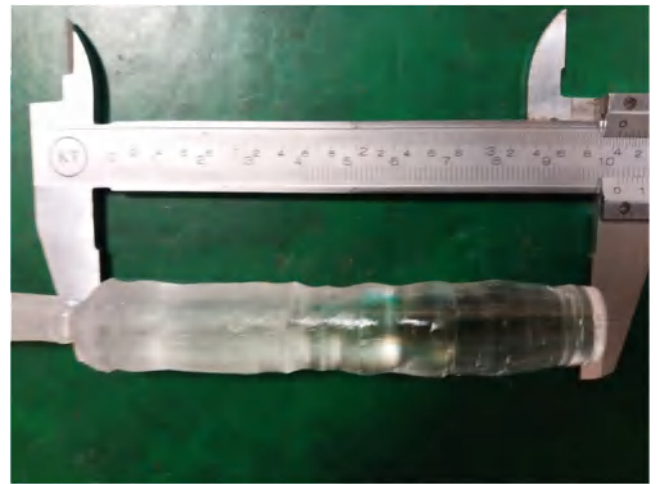


Fig. 2. The 10 cm-CsI(Na) grown single crystal.

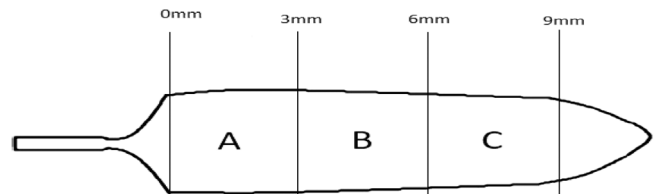


Fig. 3. The three parts of the cutting crystal (part A: 0–3 mm, part B: 3–6 mm, part C: 6–9 mm).

## 2.3. Pulse height spectrum

Three zones selected (A, B, C) of each doped samples with the same dimensions of  $\varnothing 1'' \times 1''$  were tested, to increase the accuracy of scintillation test. In order to have resolution good enough for the response measurements, the polishing of the all parts of the crystal surfaces using polisher system, through mixed  $\text{Al}_2\text{O}_3$  powder (grain size of 3–5  $\mu\text{m}$ ) in ethanol, was found to be essential.

The lateral and a cross-sectional surface of these crystals were covered by Teflon reflective layer, as shown in Fig. 4. The other end of the samples was optically coupled to a photomultiplier tube using



Fig. 4. The covered surfaces of the crystal by Teflon and the silicon grease.

silicone grease. Teflon reflective layer and silicone grease layer are used to reflect scintillation photon back into the crystals, to improve the scintillation efficiency. All of these considerations to prevent the photon lost, formed by gamma and crystal interaction, are photon management.

The pulse height spectrum of these crystals was measured under the excitation with two sources simultaneously, i.e. a  $^{137}\text{Cs}$  source with 662 keV and a  $^{60}\text{Co}$  source with 1170 and 1330 keV collimated gamma rays, with an activity of 58  $\mu\text{Ci}$  for both sources, to observe their energy peak discrimination by crystals. The scintillation photons were detected by a photomultiplier (PMT; Model FEU31, Russia). The sources were located along the cylindrical axis of the scintillator and the PMT at a 10 cm distance from the surface of the sample crystal. The nuclear electronic system consisted of a high voltage supply (Model CC228 01Y BEIJING Hamamatsu, China), preamplifier (Model IAP 3001, Iran), amplifier (Model IAP 3600, Iran), multichannel analyzer (Model HVMCA NT-124), and a data acquisition system. NTMCA software was used to analyze the integrated spectrum.

### 3. Results and discussion

#### 3.1. UV absorption and excitation spectrum

The concentration of  $\text{Na}^+$ ,  $\text{Eu}^{2+}$  and  $\text{In}^+$  ions in the selected specimens was measured using ICP (OES). Its data in Table 1 shows that the ratio of the concentrations in the middle parts (B) of these crystals remains relatively constant in comparison with that found in the melt, therefore, the optical tests are done on these parts. The co-dopant concentration cannot be dramatically altered according to the reference [10].

Observations from the UV absorption and excitation spectra of crystals in Fig. 5 indicate that main peaks, in the wavelength region of 200–400 nm, are located near 245–250 nm. According to these spectra,

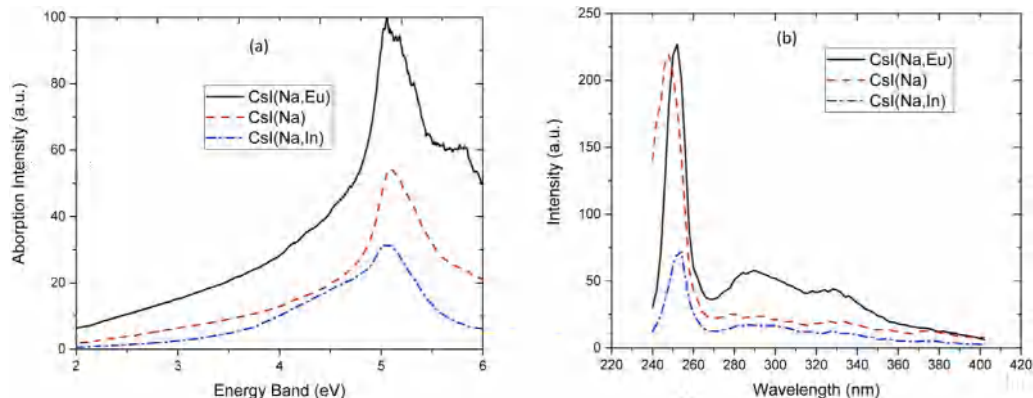


Fig. 5. (a) The UV absorption spectrum and (b) the UV excitation spectrum of single crystals.

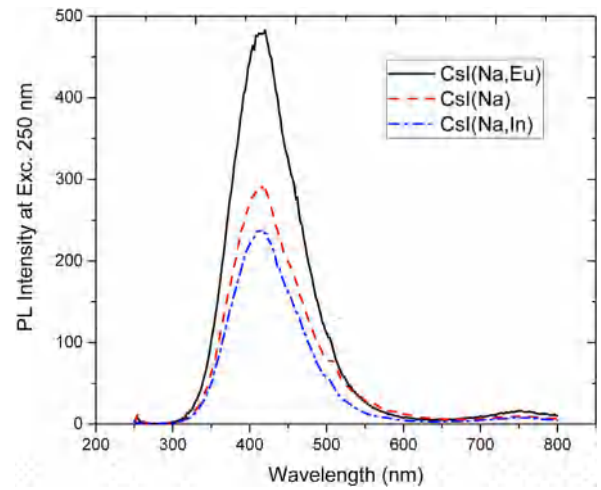


Fig. 6. The photoluminescence peak of the single crystals near 420 nm at Exc. 250 nm.

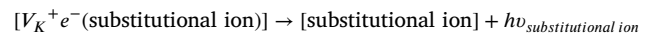
the addition of a co-dopant to  $\text{CsI}(\text{Na})$  single crystal has an effect on the wavelength red-shift. The existence of additional peaks in  $\text{CsI}(\text{Na},\text{Eu})$  and  $\text{CsI}(\text{Na},\text{In})$  absorption spectra, in Fig. 5a, is probably associated with co-dopant presence. The excitation band of  $\text{CsI}(\text{Na})$  single crystals has the main peaks at the first and gradually disappear at the end, Fig. 5b.

#### 3.2. Photoluminescence spectrum

The blue emission spectrum of the  $\text{CsI}(\text{Na})$ ,  $\text{CsI}(\text{Na},\text{Eu})$ ,  $\text{CsI}(\text{Na},\text{In})$  single crystals, as shown in Fig. 6, is involved the main peak near 420 nm.

The substitutional ion including the dopant (and co-dopant) ion perturbed the host crystal field by the complex formation of exciton and substitutional ion, during the excitation in the (host lattice, substitutional ion) system. The configuration of a self-trapped hole (STH) ( $V_K$ -center) near substitutional ion in the host lattice likely results in the emission with its related released energy.

As expected, the recombination energy for substitutional ion localized in the host lattice is summarized as follows:



Therefore, the luminescence characteristic of  $\text{Na}^+$  dopant perturbation is the blue emission at 420 nm, with  $h\nu_{\text{Na}^+} \approx 2.95$  eV released energy, in the host lattice.

$\text{Eu}^{2+}$ -co-doping is accompanied by a vacancy as a charge compensator. Therefore, the recombination energy of electrons with STH is

expected near the (vacancy—Eu<sup>2+</sup>) dipole, in the region of  $h\nu_{Eu^{2+}} \approx 2.75$  eV–2.95 eV, with the wavelengths of 420–450 nm. By co-doping In<sup>+</sup>, at RT, it is expected the dominant released wavelength at 550 nm with  $h\nu_{In^+} \approx 2.25$  eV energy, which is associated with the recombinant energy of capturing e<sup>-</sup> in the STH near In<sup>+</sup> localized center.

Although no new emission wavelength can be observed in the photoluminescence spectrum of CsI(Na, Eu) and CsI(Na, In), compared to CsI(Na), by co-doping Eu<sup>2+</sup> and In<sup>+</sup>, their luminescence intensity are varied. Whether this luminescence decreases or increases, depends on the co-dopant luminescence quantum efficiency and energy transferring between dopant and co-dopant.

The luminescence quantum efficiency,  $Q_E$ , is proportional to  $(k_r/k_r + k_{nr})$ , Where  $(k_r)$  contains the relative rate constant of the radiational recombination processes which increases the luminescence quantum efficiency; and  $(k_{nr})$  is the relative rate constant of the non-radiant recombination which decreases the luminescence quantum efficiency [11].

The energy transfer between a dopant and a co-dopant occurs if there is a suitable interaction and energy difference between both system. In fact, by co-doping, the part of the co-dopant excitation energy are transmitted to the neighboring dopant ion.

The probability of energy transfer is proportional to the exchange interaction [12,13]. The exchange interaction between emission transition of co-dopant and absorption transition of dopant is represented their spectral overlap, which is proportional to

$$\int g_{co-dopant}(E)g_{dopant}(E) dE;$$

By doping Eu ion into CsI(Na) single crystal, which is in the lanthanide group, the radiative energy transfer will probably occurs as follows. Eu<sup>2+</sup> as a co-dopant, absorbs the excitation energy efficiently, and also has a high quantum emission yield, due to 4f → 5d transitions. Na<sup>+</sup> neighboring ion as a dopant, has an absorption bandwidth that overlaps the Eu<sup>2+</sup> emission bandwidth. Photons emitted by Eu<sup>2+</sup> will be re-absorbed by Na<sup>+</sup>, and consequently, the scintillator light yield will be enhanced.

By doping In ion into CsI(Na) single crystal, with ns<sup>2</sup> electronic configuration, it seems that the non-radiative energy transfer is more likely. At RT, Na<sup>+</sup>, as a dopant ion, is excited into a metastable level,  $E_m$ . Its adjacent In<sup>+</sup>, as a co-dopant, has probable emission transition from the sub-level  $^3P_1$  to  $^1S_0$  with a wavelength peak at 550 nm, at RT. It has no luminescence (or a small emission quantum yield) from a level lying close to  $E_m$ . However, Na<sup>+</sup> has absorption bands within In<sup>+</sup> absorption bands, In<sup>+</sup> has no or very small emission in the emission spectral range of the Na<sup>+</sup>. As a result, a reduction in the overall emission occurs. Thus, by co-doping In<sup>+</sup> and Na<sup>+</sup>, the non-radiant recombination ( $k_{nr}$ ) between Na<sup>+</sup> and In<sup>+</sup> is created, and  $Q_E$  is diminished. Hence, the reduced CsI(Na, In) light yield expect compared to the CsI(Na) light yield.

The effect of co-dopant on CsI(Na) scintillation properties is studied by examining the response of the samples to gamma rays and determining the energy resolution and light yield.

### 3.3. Pulse height spectrum

The energy spectrum of all three single crystals, in their three zones (A, B, C), was obtained under the gamma-ray sources of <sup>137</sup>Cs with 662 keV and <sup>60</sup>Co with 1170 and 1330 keV energy, as displayed in Fig. 7. The presence of three peaks in the pulse height spectrum remarks energy peak discrimination by crystals.

The crystal was arranged in an optical contact on the photocathode of the photomultiplier. The energy resolution,  $\Delta E/E$ , was measured on the full energy peak of their pulse height spectrum, for Cs  $\gamma$ -peak.

The light yield was obtained using the number of photoelectrons reached to the crystal surface from the source by the method of comparison. In this method, comparison of signal amplitudes from the tested detector, and reference detector with known light yield is carried

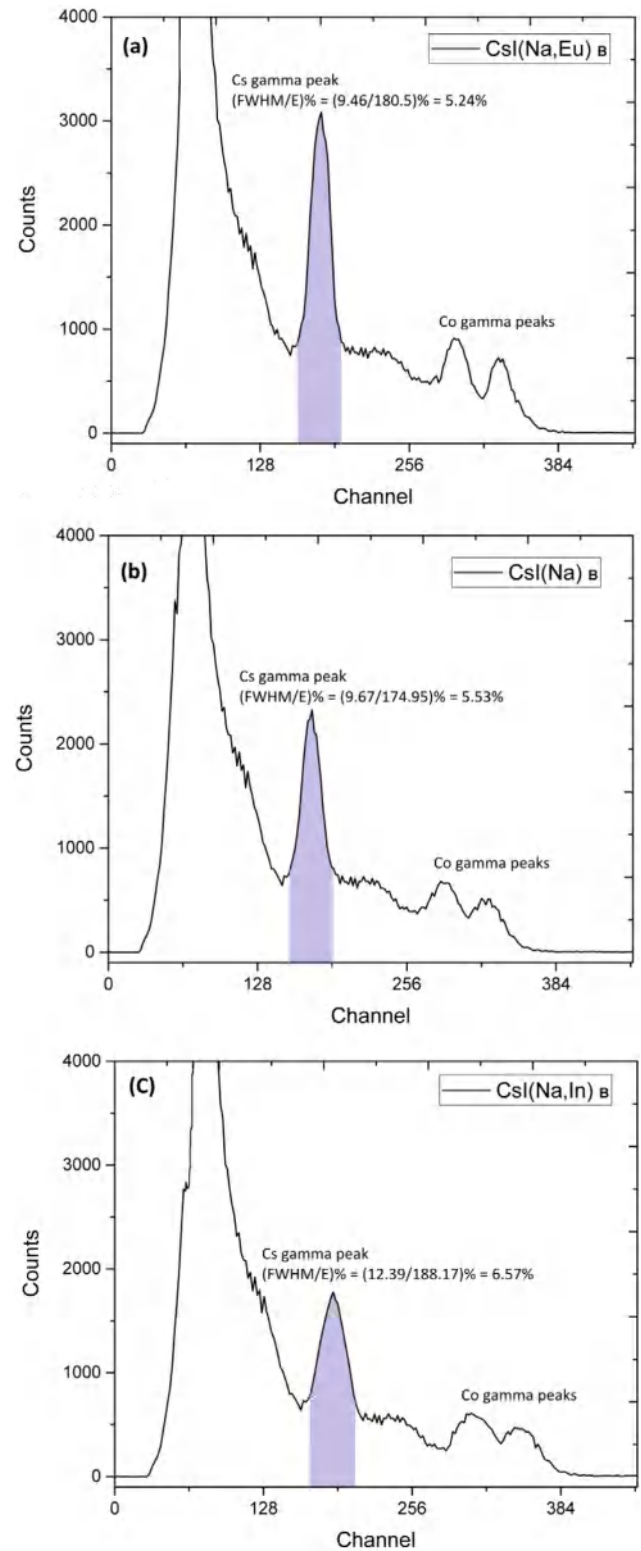


Fig. 7. The pulse height spectra of (a) CsI(Na, Eu), (b) CsI(Na), and (c) CsI(Na, In) single crystals under the gamma-ray sources of <sup>137</sup>Cs and <sup>60</sup>Co.

out [14]. NaI(Tl) in the same condition of tested detectors, with the light yield (100%), is taken as the reference detector [2].

The average energy resolution ( $\overline{\Delta E/E}$ ) of CsI(Na) is 5.6% and for co-doped CsI(Na, Eu) scintillator, it decreases to 5.35%. This quantity for CsI(Na, In) raises to 6.57%. Moreover, the effect of co-doping Eu<sup>2+</sup> and

**Table 1**  
Summary of results to improve CsI(Na) scintillator.

| Crystal scintillator | Na (mol%) | Eu (mol%) | In (mol%) | Emission wavelength (nm) | Light yield (LY%) | Energy resolution $\Delta E/E$ (%) |
|----------------------|-----------|-----------|-----------|--------------------------|-------------------|------------------------------------|
| $CsI(Na)_A$          | 0.016     | –         | –         | 420                      | 84                | 5.69                               |
| $CsI(Na)_B$          | 0.0217    | –         | –         | 420                      | 86                | 5.53                               |
| $CsI(Na)_C$          | 0.027     | –         | –         | 421                      | 84                | 5.58                               |
| $CsI(Na, Eu)_A$      | 0.0145    | 0.001     | –         | 419                      | 96                | 5.39                               |
| $CsI(Na, Eu)_B$      | 0.0208    | 0.001     | –         | 420                      | 99                | 5.24                               |
| $CsI(Na, Eu)_C$      | 0.028     | 0.001     | –         | 423                      | 98                | 5.43                               |
| $CsI(Na, In)_B$      | 0.022     | –         | 0.001     | 420                      | 70                | 6.57                               |

$Na^+$  on improving average light yield ( $\overline{LY}$ ) is about 12.5% more than CsI(Na) light yield and it is remarkable, despite a decrease of about 15% in the average light yield of co-doping  $In^+$  and  $Na^+$ , which its reason was investigated in Section 3.2. The results of the studies on the middle parts of these scintillators are summarized in Table 1.

#### 4. Conclusion

To improve the scintillation properties of CsI(Na) single crystal, this material was sensitized with  $Eu^{2+}$  and  $In^+$  ions. This co-doped was applied to the crystal by the growth of The Czochralski method. The optical properties of the crystals were examined through the ICP, UV, and PL spectra. Then, the scintillation response of the crystals was investigated under the cesium and cobalt gamma rays via a pulse height spectrum.

This is explained with adding different impurities, according to their ionic configuration and the possibility of creating new sub-levels in the host lattice, the radiative or non-radiative energy transfer occurs that leads to a decrease or increase in the luminescence intensity and the scintillation light yield.

The results indicate that despite the proper optical quality of all crystals after co-doped, only the Eu lanthanide plays a special role in enhancing the photoluminescence intensity and light yield of the traditional CsI(Na) scintillator and improves its energy resolution. Eu's high quantum efficiency, relying on its  $4f^6 5d \rightarrow 4f^7$  internal transitions, and its energy transfer, due to the large overlapping between  $Eu^* \rightarrow Eu$  emission transition and  $Na \rightarrow Na^*$  absorption transition are the reasons for this improvement.

In spite of the fact that quenching sub-levels originate from co-doping In and Na. Accordingly, there is a non-constructive spectral overlap between  $In^* \rightarrow In$  emission transition and  $Na \rightarrow Na^*$  absorption transition which ultimately reduces the luminescence intensity of the blue and scintillator light yield, and increase the energy resolution.

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