Optical properties of CsI:Tl crystals grown using different precursors purities

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Abstract. CsI doped with Tl (CsI:Tl) is a scintillator material used for radiation detector applications. CsI:Tl was crystalized by a modified homemade Bridgman-Stockbarger technique using different precursor purities. The purpose is to verify effects of precursor purity on optical properties of Cs:Tl crystals by UV-VIS and X-ray luminescence spectroscopy. A type and concentration of impurities in the precursor are directly related the optical properties of CsI:Tl crystals. The CsI:Tl crystals were grown in two levels of CsI and TlI reactant materials, i.e., having as a very high purity of 99.999%, showing a colorless crystal and a high purity of 99.9% showing an orange crystal. Absorption coefficient determined by transmittance and reflectance spectra was used to find an optical gap in the CsI:Tl crystals. For the colorless crystal, optical gaps of the Tl-related state and the CsI bandgap were observed at 3.82 eV and 5.14 eV, respectively. On the other hand, a merging of the Tl-related state and the CsI bandgap was observed for the orange crystal to form a virtual single bandgap at 3.51 eV. These results indicated the effects of precursor purity on optical gap of the CsI:Tl crystals. Also, X-ray luminescence spectra centred at 2.07 – 2.25 eV, which are corresponding to that of the absorption edge, showed a red shift of 160 meV for the orange CsI:Tl crystal.

1. Introduction

Cesium iodide (CsI) is considered as a leading candidate scintillator material for widely used in nuclear engineering, nuclear physics and medical imaging for gamma ray detectors, particle detectors and X-ray imaging [1-3]. Emission of CsI crystal is in a range of ultraviolet to visible. It is known that CsI doped with Tl (CsI:Tl) makes the emission shifted to the visible range. Further, CsI:Tl exhibits a high stopping power of gamma rays due to a high atomic number of Tl. This property empowers the material in a use of gamma ray detection. It also has good mechanical and hygroscopic properties compared to NaI:Tl scintillator and exhibit good pulse shape discrimination to different particle energies [4, 5]. It is known that perfection and purity of the crystals were found to effect on the scintillation characteristics [6]. Therefore, it is important to study a behavior of the present impurities in the CsI:Tl crystals to predict an efficiency of gamma ray detection.

In past work, we have demonstrated the growth of CsI:Tl crystals to develop the gamma ray detectors [7] using the low-cost raw materials. The impact of impurity on their radiation detection was reported. However, an optical properties of such CsI:Tl crystals, which is directly affected on an efficiency of the detection, is need further investigation. Thus, in this work, two CsI:Tl ingots grown using CsI precursors

with different purities of 99.999% and 99.9% (a low-cost raw material) were investigated by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD), UV-VIS spectroscopy. Optical gap, which relates to the energy states of the impurities in the CsI:Tl crystals, was systematically studied. X-ray luminescence spectra was demonstrated an effect of the impurities in the CsI:Tl crystals. Moreover, a performance of radiation detectors, which depends on precursor purity, was also discussed.

2. Experiment

The CsI:Tl crystals used in this study were grown by a modified homemade Bridgman-Stockbarger technique. The CsI precursors with purities of 99.999% and 99.9% were used to obtain crystals with different impurity levels [7]. The same amount of Tl in form powder of thallium iodide (TlI) of 0.355%wt was used. To verify a homogeneous, the CsI:Tl crystals were divided into three samples, which are the top, middle and bottom parts. Diameter and thickness of the samples were about 14 mm and about 4 mm, respectively. The samples were polished by polishing machine to make a smooth and an appropriate surface for examination with various techniques. A JEOL JSM-7610F field emission scanning electron microscope (FE-SEM) and a Bruker AXS Model D8 Discover X-ray diffractometer (XRD) were performed to analyze morphology and crystalline quality. Optical properties were investigated by a UV-3600 SHIMADZU UV-VIS spectroscopy and X-ray luminescence spectroscopy. Absorption coefficient determined by transmittance and reflectance spectra was used to find the optical gap of both the CsI:Tl crystals. Besides, emissions related to the impurities in the CsI:Tl crystals were examined by X-ray luminescence spectroscopy using a Cu target X-ray generator operating at 50 kV and 30 mA. Finally, both the CsI:Tl crystals were coupled with a Hamamatzu H5783 photomultiplier tube (PMT) to evaluate the detection efficiency (radiation efficiency and energy resolution) at 122 keV gamma-ray spectroscopy of Co-57.

3. Results and discussion

Figure 1 shows typical FE-SEM images of the CsI:Tl crystals grown using (a) the 99.999% and (b) 99.9% CsI precursors, which was exhibited in colorless and orange crystals, respectively. The result confirms a smoothness and uniform surface. No void or hole was observed in the crystals. There is no significant difference between both of crystals. A circular domain observed in the figure is due to a corrosion during a polishing process. Figure 2 illustrates XRD profiles of (a) the colorless and (b) orange CsI:Tl crystals. The samples were scanned using 2θ-scan mode over the range of 10° to 80° with a scanning step of 0.02°. Diffraction profiles in log-scale were represented to clarify all preferred diffraction peaks. The diffraction with the (110), (200), (211), (220), (310), and (321) reflections was observed for both crystals. This indicates that CsI:Tl crystalized in a cubic lattice, which is verified to be a body-centered-cubic (bcc) structure [8]. Noted that an intensity of the (110) reflection is strongest compared to other preferred orientations. A lattice constant calculated from the (110) reflection from the colorless and orange CsI:Tl crystals was 0.453±0.002 and 0.455± 0.002 nm, respectively. While, for the orange CsI:Tl crystal, a broad diffraction centered at 2θ = 40° was clearly observed in figure 2(b).
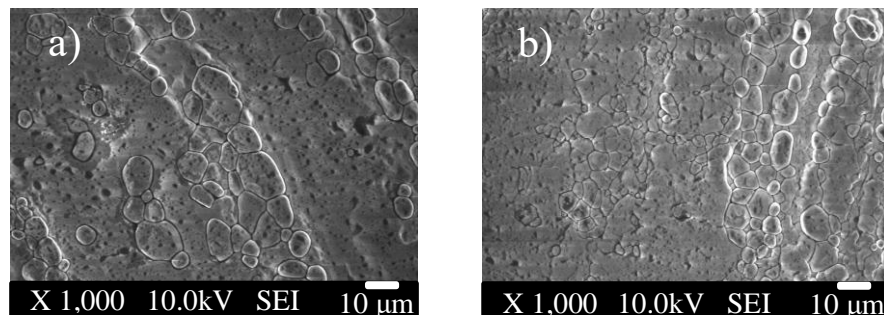

Figure 1. FE-SEM images of the CsI:Tl crystals grown with (a) the 99.999% and (b) 99.9% CsI precursors, exhibited in colorless and orange crystals, respectively.
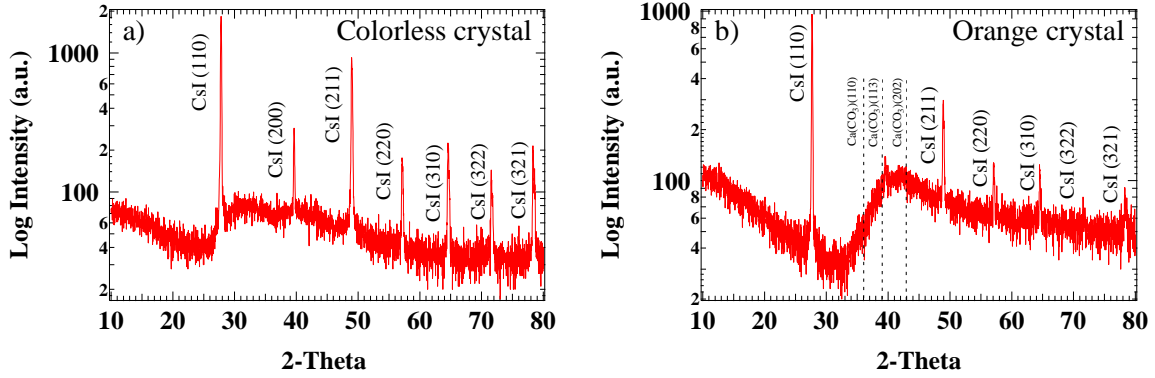
Figure 2. X-ray diffraction profiles of (a) the colorless and (b) the orange CsI:Tl crystals, which were grown using the 99.999% and 99.9% CsI precursors, respectively.

This might be due to a presence of the (110), (113) and (202) reflections related to the calcite ($CaCO_3$) [7], which might incorporate slightly in the orange crystal due to a higher impurity level of the low-cost CsI precursor.

Optical bandgap of CsI:Tl crystals is parameter determining performance used for a scintillation detector. Since, it is important to know a range of emission during an operation. The optical bandgap is known to directly affect to the range of emission of the CsI:Tl crystals. The optical bandgap, which was determined using absorption spectra, which can be calculated by the Tauc relation, as expressed in equation (1) [9, 10],

$$\left(\alpha h\nu\right)^n = A\left(h\nu - E_g\right),\tag{1}$$

where A is a characteristic parameter, h is Planck's constant, ν is the frequency, $h\nu$ is photon energy, α is an absorption coefficient, E_g is bandgap. n indicates a type of transition, which is either $n = 2$ for direct band transitions or $n = 1/2$ for indirect band transitions [11].

For the CsI:Tl crystals was confirmed by many research groups [12, 13] to have a direct band transitions. Thus, the value of n = 2 was used in this work. On the other hand, to calculate the absorption coefficient (α), both the transmittance and reflectance spectra observed from the CsI:Tl crystals were combined using the relation in equation (2) [14],
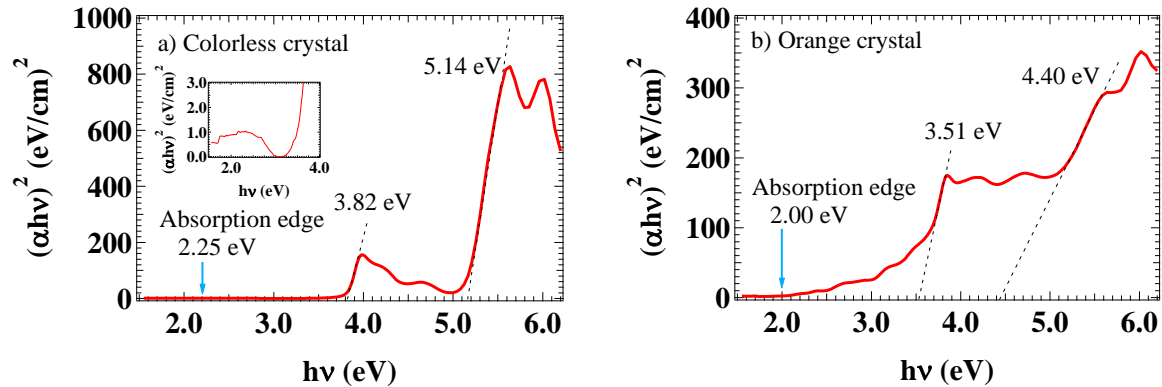

Figure 3. Absorption spectra obtained from (a) colorless and (b) orange CsI:Tl crystals, which were grown using the 99.999% and 99.9% CsI precursors, respectively. The inset shows a magnified absorption spectrum around an absorption edge for the colorless crystal.

$$\alpha = \frac{1}{d} \ln \left\{ \frac{\left[\left(1-R\right)^4 + 4T^2 R^2 \right]^{\frac{1}{2}} - \left(1-R\right)^2}{2TR^2} \right\}, \qquad (2)$$

where d is the thickness of crystal, T is transmittance and R is reflectance of the crystals. Spectra of T and R were investigated by UV-VIS spectroscopy.

With a combination of equation (1) and equation (2), figure 3 shows a plot between $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) for the CsI:Tl crystals grown using (a) the 99.999% CsI precursor (colorless crystal) and (b) 99.9% CsI precursor (orange crystal). It is clearly seen the optical gaps related to the Tl-doped state and the bandgap of CsI as well as the absorption edge. As seen in figure 3(a), the colorless CsI:Tl crystal exhibited optical gaps at 3.82 and 5.14 eV, which attributed to the Tl-doped state [15] and the bandgap of CsI [12, 13], respectively. In addition, a low absorption, which attributed to the absorption edge, located around 2.25 eV was also observed as shown in an inset. While, for the orange CsI:Tl crystal, the absorption edge, the Tl-doped state, the bandgap of CsI were observed at 2.00, 3.51 and 4.40 eV, respectively. This indicates a lowering of all the optical gaps, which is due to a higher impurity level in the CsI:Tl crystal. It is also evidenced that the absorption between the Tl-doped state and the bandgap of CsI becomes stronger and, then merged together.

It is known that the emission of CO_3-doped CsI scintillator are located about 410 and 550 nm (3.02 and 2.25 eV) [16]. Consequently, an existence of $CaCO_3$ is expected to induce a formation of the band tail observed in the absorption spectrum in a range of 2.00 to 3.51 eV for the orange crystal. Such band tail is probably caused by the presence of $(CO_3)^{2-}$, as therefore, a substitution of $(CO_3)^{2-}$ in the CsI:Tl crystal lattice causes the band tail dragged down from Tl-doped state to about 2.00 eV. Also, a red shift of an absorption edge was observed from 2.25 eV for the colorless crystal to 2.00 eV for the orange crystal, respectively. This might effect on the emission of the CsI:Tl crystals observed by X-ray luminescence. Furthermore, a reduction of CsI bandgap from 5.14 eV to 4.40 eV for the colorless and the orange crystals, respectively, is consistent with the calculated bandgap of $CsCaI_3$, about 4.02 eV [17]. This suggests that, the present of $CaCO_3$ also resulted in an incorporation of $(Ca)^{3+}$ in the CsI crystal, which exhibited a decrease of the bandgap of CsI down to 4.40 eV and merging with the Tl-doped state. As a result, with a use of CsI precursor with purity of 99.9% demonstrated an incorporation of the unintended impurities, such as $(Ca)^{3+}$ and $(CO_3)^{2-}$, which created states between the Tl-doped state and bandgap of CsI and band tail, respectively. This also exhibits a formation of a virtual single bandgap at around 3.51 eV for the calcite contained CsI:Tl crystal (the orange CsI:Tl crystal).
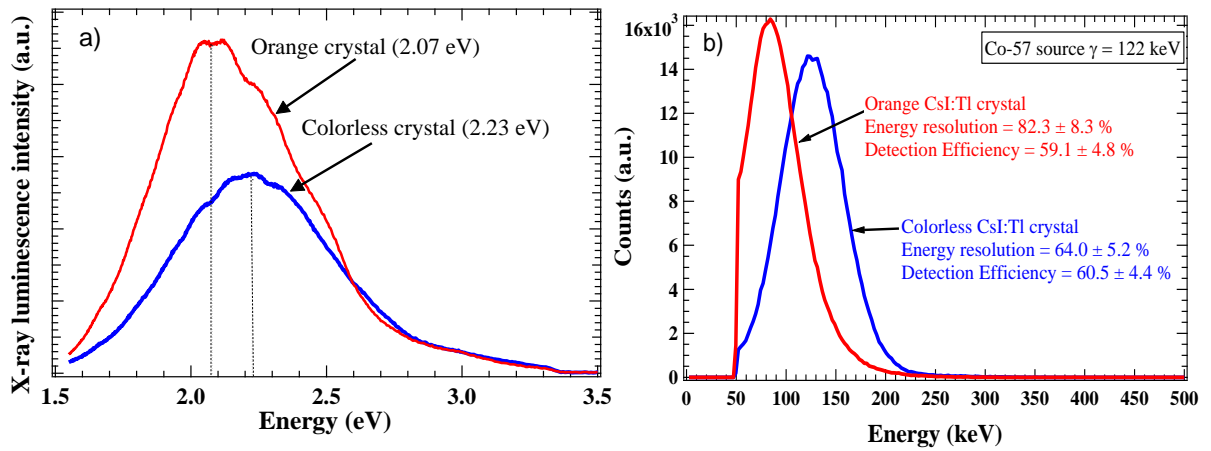

Figure 4. (a) X-ray luminescence spectra and (b) energy spectrum of Co-57 source for the colorless and the orange CsI:Tl crystals.

Figure 4(a) shows an emission from both the CsI:Tl crystals, which were investigated by X-ray luminescence spectroscopy. A Cu Target X-ray generator with X-ray source operating at 50 kV and 30 mA was used as an excitation. The colorless and orange CsI:Tl crystals show a broad emission centered at 2.23 and 2.07 eV, respectively. A red shift of about 160 meV was observed when the CsI:Tl crystal grown with the 99.9% CsI precursor. In addition, an emission intensity of the orange CsI:Tl crystal exhibited stronger than that of the colorless crystal. It is known that such broad emission is suggestively contributed to the impurity states. A higher concentration of impurities is found to result in a higher intensity of emission, which is expected to increase the detection efficiency of the scintillators. Noted that, the difference in energy of the peak position of X-ray luminescence spectra, as seen in figure 4(a), is due to a different type of impurities incorporated in the CsI:Tl crystals.

Since, the absorption is attributed to the transition of electrons from the valence band to the doping states or to the conduction band or to other higher excited states in an electronic structure. Then, bandgap of CsI host crystal, Tl-related doping states and absorption edge were observed in an absorption spectrum as shown in figure 3. On the other hand, the luminescence was observed when the excited electrons release their energy and, then, transition from the excited states down to the ground states. In case of CsI:Tl, it has a mid-gap states, due to an incorporation Tl atom or other impurities from the raw precursor materials, located between the valence and conduction bands of CsI. Particularly, the luminescence obtained from CsI:Tl not directly represents the bandgap of CsI:Tl. However, it represents the gap between the impurity related states, which are located at the energy lower than the Tl-doping states in our case, and valence band. As a result, the luminescence is typically used to indicate the impurity related states and the luminescence peak position is usually observed at the energy equivalent to that of an absorption edge. Thus, the optical gap energy obtained in figure 3 represents the bandgap energy and indicates the doping-related states. On the other hand, the peak position of luminescence spectrum shown in figure 4(a) represents the energy of electron released from the impurity-related states, which is corresponding to the absorption edge.

To investigate the detection efficiency of the scintillators, both CsI:Tl crystals were cut into the cylindrical shapes of a diameter of 10 mm and thickness around 3-4 mm. Both the CsI:Tl crystals were coupled with a photomultiplier tube (PMT) with black Teflon and then connected to electronic parts to detect gamma radiations at 122 keV of Co-57. Figure 4(b) shows a similar detection efficiency for the colorless and the orange CsI:Tl scintillators, which were respectively estimated to be 60.5±4.4% and 59.1±4.8%. In addition, the colorless CsI:Tl scintillator gives energy resolution about 64.0±5.2%, while the orange CsI:Tl scintillator showed the energy resolution about 82.3±8.3%. Noted that, the electronic conditions and amplifications were maintained for both scintillators. The colorless scintillator with higher purity CsI:Tl crystal showed a higher energy resolution compared to that of the orange scintillator with lower purity CsI:Tl crystal, although they had similar the detection efficiency. However, the peak sensibility energy of PMT used in this study is 2.95 eV (420 nm) and nearly constant sensibility in a range of 2.76 to 3.54 eV (350 to 450 nm) and a steeply deceasing sensibility of 1.90-2.76 eV (450-650 nm). We would expect that if we use a new PMT with a wavelength response of 2.0-2.5 eV (500-600 nm) for coupling with both CsI:Tl scintillators, it can improve the response to the wavelengths that are suitable for the light emission of crystals. Thus, a use of low-cost CsI precursor as a low material for the growth of CsI:Tl crystal is a one of the promising approaches to develop the high efficient and low-cost radiation detectors.

4. Conclusion
Optical properties of CsI:Tl crystals grown with different purities of the CsI precursors were systematically investigated. It is found that the orange CsI:Tl crystal grown by the low-cost CsI precursor with purity of 99.9% was slightly contaminated with a few amount of calcite or other impurities, which directly modified the optical gaps of this material. Based on our results, the CsI:Tl crystal with lower impurities (colorless crystal) exhibited the optical gaps of the absorption edge, the Tl-doped state and the bandgap of CsI at 2.25, 3.82 and 5.14 eV, respectively. While, as an existence of $CaCO_3$, the CsI:Tl crystal showed a modification of the CsI bandgap from 5.14 eV to 4.40 eV, due to

an incorporation of $(Ca)^{3+}$ to the CsI host crystal. Consequently, a coalescence of the Tl-doped state and the bandgap, resulting in a modification of optical gap to form a virtual single bandgap at around 3.51 eV, was demonstrated for the orange CsI:Tl crystal. The X-ray luminescence peak observed at 2.07 eV is equivalent to the absorption edge, indicating an emission related the impurity related states not band-to-band transition. Further, the absorption edge and the luminescence peak were red-shifted for the orange CsI:Tl crystal, which is probably caused a higher impurity level, especially an incorporation of $(CO_3)^{2-}$ in the CsI:Tl crystal due to a present of $CaCO_3$. This also effects on the luminescence intensity, which is increased for the orange CsI:Tl crystal. However, both the CsI:Tl scintillator represented the similar detection efficiency. Although the energy resolution of the orange CsI:Tl scintillator was lower than that of the colorless CsI:Tl scintillator. Based on our results, the optical gap and the luminescence intensity of CsI:Tl were significantly depended on the unintended impurities in the raw precursor materials, which may enhance a performance of radiation detector. Thus, a use of low-cost CsI precursor with low purity of 99.9% could be one of the promising approaches to achieve the high efficient and low-cost radiation detectors with further optimization of detection efficiency measurement conditions.

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