

## Comparison of Luminescence Properties of CsI Crystals Activated with $\text{Ag}^-$ , $\text{Au}^-$ , and $\text{Tl}^+$ Ions at Room Temperature

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We have investigated the luminescence properties of CsI crystals activated with  $\text{Ag}^-$ ,  $\text{Au}^-$ , and  $\text{Tl}^+$  ions at room temperature. When the activated CsI crystals are irradiated by light with a wavelength shorter than the absorption edge of CsI bulk crystals, luminescence bands related to the activated centers are observed in the visible wavelength region, in addition to intrinsic luminescence bands due to self-trapped excitons. In CsI: $\text{Au}^-$  and CsI: $\text{Tl}^+$ , the visible luminescence bands exhibit decay profiles with a decay time of about 1  $\mu\text{s}$ . On the other hand, the visible luminescence band in CsI: $\text{Ag}^-$  consists of two luminescence components with decay times of 25 and 250  $\mu\text{s}$ . Their luminescence properties are discussed from the viewpoint of their application as a scintillator material. © 2013 The Japan Society of Applied Physics

### 1. Introduction

CsI crystals have been widely used as scintillator materials for  $\gamma$ -rays because of their high stopping power for  $\gamma$ -rays due to the relatively high density of 4.51 g/cm<sup>3</sup> and the large atomic number of CsI.<sup>1–4</sup> To improve luminescence efficiency, CsI crystals are usually activated with impurity ions such as  $\text{Na}^+$  and  $\text{Tl}^+$ . Therefore, CsI: $\text{Tl}^+$  and CsI:Na crystals have also been used as a scintillator material for  $\gamma$ -rays. From the sensitive wavelength of optoelectronic devices such as amorphous silicon detectors, CsI: $\text{Tl}^+$  crystals have been applied as a scintillator material for nondestructive testing and medicine. Although it is easy to handle CsI: $\text{Tl}^+$  in comparison with CsI:Na owing to the low deliquescence of CsI: $\text{Tl}^+$ , the scintillator material contains a  $\text{Tl}^+$  ion, which is a heavy metal ion with toxicity. Recently, the use of products containing toxic heavy metals such as thallium (Tl) and lead (Pb) has been avoided owing to a surge of environmental awareness. Therefore, CsI crystals activated with ions with no toxicity are demanded as a new scintillator material.

$\text{Ag}^-$  and  $\text{Au}^-$  anions are potential candidates for activated metal ions with no toxicity, because these anions have the outermost  $s^2$  electronic configuration and belong to the family of  $\text{TI}^+$ -type ions.<sup>5,6</sup> CsI crystals doped with these anions exhibit several absorption bands formed by intraionic transitions from the  $s^2$ -to- $sp$  electronic configuration and intense luminescence bands in the energy region below the band edge of the CsI host crystal. The luminescence properties of CsI: $\text{Ag}^-$  and CsI: $\text{Au}^-$  crystals have been investigated mainly at low temperatures and under excitation in the energy region below the band edge of CsI.<sup>7–11</sup> In this study, we have investigated the luminescence properties of CsI: $\text{Ag}^-$  and CsI: $\text{Au}^-$  under excitation in the energy region above the band edge of CsI at room temperature (RT). The luminescence properties of CsI: $\text{Ag}^-$  and CsI: $\text{Au}^-$  are evaluated and compared with those of CsI: $\text{Tl}^+$ .

### 2. Experimental Procedure

Since  $\text{Ag}^-$  and  $\text{Au}^-$  ions are not naturally present in alkali halide crystals, a special treatment is needed to produce

$\text{Ag}^-$  and  $\text{Au}^-$  ions in such crystals. First, the  $\text{Ag}^+$  or  $\text{Au}^+$  ions were added into pure single CsI crystals purchased from Union Materials Inc. (Japan) by a diffusion reaction of noble-metal halide powders with the crystals. Second, the noble metal cations were converted to anions by heating the crystals in potassium vapor or an electrolytic coloration technique. Third, in order to remove F centers and isolate impurity ions, the samples were wrapped in an aluminum foil and heated to about 600 °C for several minutes and subsequently quenched to RT. CsI: $\text{Tl}^+$  crystals were grown by the Bridgman method from CsI powder with a  $\text{TlI}$  concentration of  $4 \times 10^{-2}$  mol %, which corresponds to a  $\text{Tl}^+$  ion concentration of  $4 \times 10^{18}$  number/cm<sup>3</sup> in the crystals.

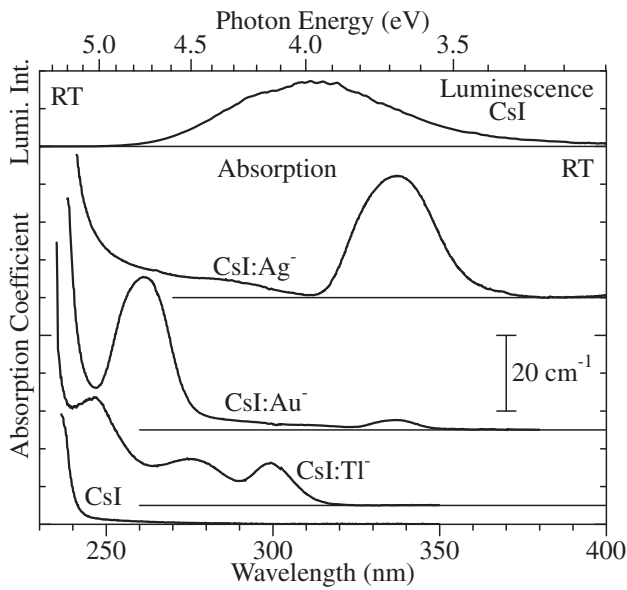
Optical measurements up to the vacuum ultraviolet wavelength region were performed at the BL-1B line of UVSOR (Institute for Molecular Science, Okazaki, Japan). The synchrotron radiation from a 750 MeV electron storage ring was monochromatized through a 1 m Seya-Namioka-type monochromator for sample excitation. Photoluminescence spectra were measured using a grating monochromator (Action SpectraPro-300i) equipped with a CCD camera (Roper Scientific LN/CCD-100EB-GI). Excitation spectra were measured using an optical detection system composed of the grating monochromator and a photomultiplier (Hamamatsu R636-01). The intensity of excitation light was corrected using the excitation spectrum of sodium salicylate.

To measure temporal profiles of the luminescence intensity, an ArF excimer laser (Lambda Physik COMPex 102) was used as the excitation light source in our laboratory. The time-resolved luminescence spectra were measured using a detection system (ORIEL Instruments INSTASPEC™ V) consisting of a monochromator (MS257™) and an intensified CCD detector (Model 77193). The ArF excimer laser has a wavelength of 193 nm and a pulse duration of about 15 ns. Temporal profiles of the luminescence intensity at a specific wavelength were obtained from the time-resolved luminescence spectra at various delay times after the laser excitation. All the measurements were performed at RT.

### 3. Results and Discussion

Figure 1 shows the absorption spectra of CsI crystals

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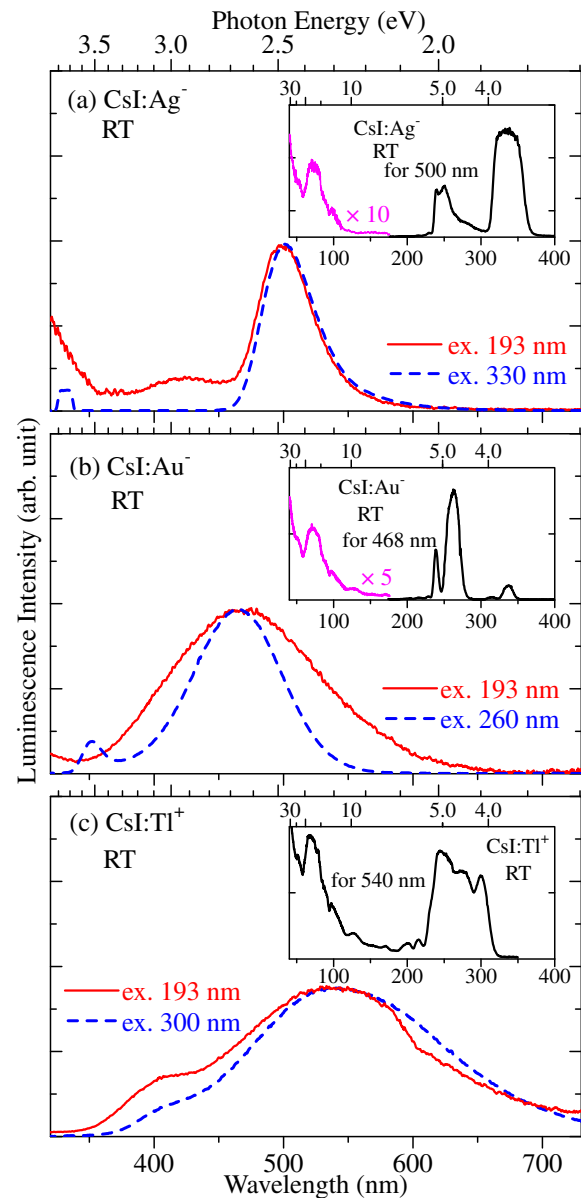


**Fig. 1.** Absorption spectra of CsI:Ag<sup>-</sup>, CsI:Au<sup>-</sup>, and CsI:Tl<sup>+</sup> crystals at RT. The top and bottom spectra are the luminescence and absorption spectra of nondoped CsI crystals, respectively.

activated with Ag<sup>-</sup>, Au<sup>-</sup>, and Tl<sup>+</sup> ions, the luminescence properties of which are compared later in this section. The luminescence and absorption spectra of nondoped CsI crystals are also shown in the top and bottom of Fig. 1, respectively. The nondoped CsI crystals exhibit no absorption band at a wavelength longer than 235 nm, which corresponds to the fundamental absorption edge of CsI. In the activated CsI crystals, the absorption bands due to the activated centers are observed at a wavelength longer than 235 nm. The pronounced absorption bands peaking at 340 nm for CsI:Ag<sup>-</sup> and at 265 nm for CsI:Au<sup>-</sup> correspond to the C absorption band formed by the intraionic transitions from the <sup>1</sup>S<sub>1</sub> ground state to the <sup>1</sup>P<sub>1</sub> excited state in activated ions.<sup>7-11</sup> From the intensities of the C absorption bands, the concentrations of Au<sup>-</sup> and Ag<sup>-</sup> ions in the crystals were estimated to be on the order of 1 × 10<sup>17</sup>/cm<sup>3</sup> using the Smakula–Dexter formula.<sup>12,13</sup>

The A absorption band formed by the intraionic transition from the <sup>1</sup>S<sub>1</sub> ground state to the <sup>3</sup>P<sub>1</sub> excited state is observed with a peak at 380 nm for CsI:Au<sup>-</sup> and at 300 nm for CsI:Tl<sup>+</sup>. In CsI:Tl<sup>+</sup>, the absorption bands observed at a wavelength shorter than the A absorption band are also related to the Tl<sup>+</sup> ions. Although various models of the absorption bands have been proposed, there has been no definitive model. We assigned these absorption bands to the charge transfer or perturbed exciton bands from the spectral changes of the absorption bands in CsBr<sub>1-x</sub>I<sub>x</sub> mixed crystals.<sup>14</sup> It should be noted that the absorption bands due to the activated centers are covered with a broad luminescence band due to self-trapped excitons (STEs) in nondoped CsI crystals, which is shown in the top of Fig. 1. This finding implies that activated centers can reabsorb the STE luminescence of CsI bulk crystals.

Figure 2 shows the luminescence spectra of the CsI crystals activated with Ag<sup>-</sup>, Au<sup>-</sup>, and Tl<sup>+</sup> ions in the visible wavelength region at RT. The broken and solid lines correspond to the spectra under excitation at 193 nm and at



**Fig. 2.** (Color online) Luminescence spectra of the (a) CsI:Ag<sup>-</sup>, (b) CsI:Au<sup>-</sup>, and (c) CsI:Tl<sup>+</sup> crystals at RT. The solid and broken lines correspond to luminescence spectra under excitation at 193 nm by an ArF excimer laser and at the absorption bands due to the activated centers, respectively. The insets show excitation spectra for luminescence bands due to activated centers in the CsI:Ag<sup>-</sup>, CsI:Au<sup>-</sup>, and CsI:Tl<sup>+</sup> crystals in the vacuum ultraviolet wavelength region at RT.

the absorption band due to activated centers, respectively. Broad luminescence bands peaking at 540, 500, and 450 nm are observed in CsI:Tl<sup>+</sup>, CsI:Ag<sup>-</sup>, and CsI:Au<sup>-</sup>, respectively. The 500 nm luminescence band in CsI:Ag<sup>-</sup> is attributed to the radiative transition from the relaxed excited state of <sup>3</sup>P<sub>1</sub> and called the A' luminescence band.<sup>8,9</sup> The 560 nm luminescence band in CsI:Tl<sup>+</sup> is attributed to the STE perturbed by a Tl<sup>+</sup> ion<sup>15-17</sup> and/or the radiative recombination of an electron in a Tl<sup>0</sup> center with a neighboring V<sub>K</sub> center.<sup>18,19</sup> The origin of the 450 nm luminescence band in CsI:Au<sup>-</sup> is unknown. However, we consider the origin to be the radiative transition from the relaxed excited states of the Au<sup>-</sup> ion located at the off-center position in the lattice site.<sup>10</sup>

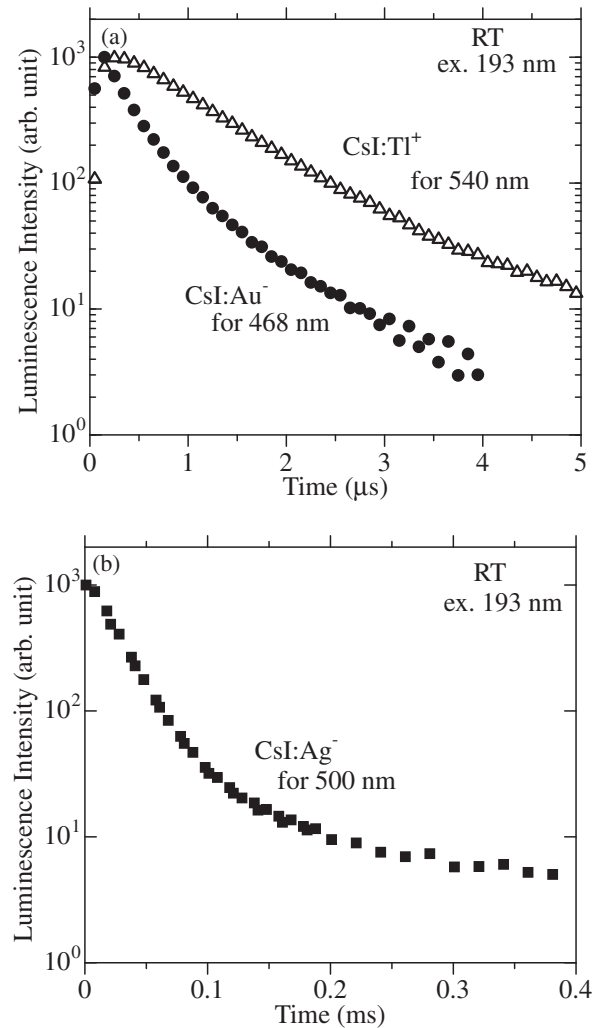
The luminescence spectra under excitation at 193 nm, which is shorter than the band gap of CsI, are not identical to those under excitation at the absorption bands due to the activated centers. Excitation in the wavelength region of the band-to-band transition of CsI could bring about luminescence bands due to other impurity ions and/or defects in addition to activated centers. Nevertheless, visible luminescence bands associated with activated centers dominate even under excitation at 193 nm. This finding implies that activated centers play an important role as luminescence centers.

The excitation spectra for the visible luminescence bands in the CsI:TI<sup>+</sup>, CsI:Ag<sup>-</sup>, and CsI:Au<sup>-</sup> crystals are shown in the inset of Fig. 2. The excitation bands observed at a wavelength longer than 235 nm originate from the absorption bands due to the activated centers. The excitation spectra at a wavelength below 235 nm exhibit no distinct difference among CsI:TI<sup>+</sup>, CsI:Ag<sup>-</sup>, and CsI:Au<sup>-</sup>. Since the CsI crystals have a larger absorption coefficient than 10<sup>5</sup> cm<sup>-1</sup> in the wavelength region of the band-to-band transition, the penetration depth of the incident light is limited to the surface region, which is comparable to that in the case of the bulk crystal. Therefore, the number of activated centers excited directly by the incident light is extremely small compared with that under excitation at the absorption bands due to the activated centers. Nevertheless, visible luminescence bands are observed even under excitation in the wavelength region of the band-to-band transition. This finding implies an efficient energy transfer process from CsI host crystals to activated centers.

Figure 3 shows the temporal profiles of the luminescence bands due to the activated centers in the CsI crystals at RT. In CsI:TI<sup>+</sup>, the temporal behavior of the visible luminescence band, which is shown by open triangles in Fig. 3(a), exhibits a slight increase in the early state and a single exponential decay. The decay time of 940 ns is obtained from the slope of the single exponential decay. This value coincides with those reported previously.<sup>3,4,16</sup> The increase in temporal behavior is caused by the recombination of electrons, which are thermally released from isolated TI<sup>0</sup> centers, with TI<sup>+</sup>-V<sub>k</sub> complex centers.<sup>18</sup> The temporal behavior of the visible luminescence band in CsI:Au<sup>-</sup>, which is shown by filled circles in Fig. 3(a), is slightly faster than that in CsI:TI<sup>+</sup>. The decay profile consists of two decay components having decay times of about 280 and 960 ns, respectively.

As shown by filled squares in Fig. 3(b), excitation at 193 nm on the CsI:Ag<sup>-</sup> crystal induces the temporal profiles with decay times of 25 and 250 μs. In general, the decay time constant of the A' luminescence band of Ag<sup>-</sup> centers in alkali halides is a few tens of μs at RT, reflecting the radiative transition probability of the <sup>3</sup>P<sub>1</sub> excited state.<sup>20,21</sup> Therefore, the 25 μs decay component in CsI:Ag<sup>-</sup> is attributed to the radiative transition from the <sup>3</sup>P<sub>1</sub> state. The 250 μs decay component might be associated with nearby defects created by excitation above the band gap of CsI.

Lastly, we would like to evaluate the CsI:Ag<sup>-</sup> and CsI:Au<sup>-</sup> crystals from the standpoint of their application as a new scintillator material. The visible luminescence from



**Fig. 3.** Temporal profiles of the luminescence bands in the CsI:TI<sup>+</sup>, CsI:Au<sup>-</sup>, and CsI:Ag<sup>-</sup> crystals at RT. Results of the CsI:TI<sup>+</sup> and CsI:Au<sup>-</sup> crystals are shown by open triangles and filled circles in (a), respectively. Data of the CsI:Ag<sup>-</sup> crystal are shown by filled squares in (b). The filled squares correspond to the excitation at 193 nm by the ArF excimer laser.

scintillator materials under the X-ray excitation is converted to an electric signal using popular amorphous silicon detectors. Amorphous silicon detectors have spectral sensitivity to light of visible wavelength and are particularly sensitive to light with a wavelength range from 550 to 600 nm. The wavelength region is a good fit for the visible luminescence in the CsI:TI<sup>+</sup> crystals. Although the visible luminescence bands in the CsI:Ag<sup>-</sup> and CsI:Au<sup>-</sup> crystals are located at a wavelength shorter than that in CsI:TI<sup>+</sup>, the spectral sensitivity of amorphous silicon detectors covers the visible luminescence bands in the CsI:Ag<sup>-</sup> and CsI:Au<sup>-</sup> crystals. Therefore, the CsI:Ag<sup>-</sup> and CsI:Au<sup>-</sup> crystals are not severely flawed as scintillator materials. Under excitation at 193 nm, the visible luminescence in CsI:Ag<sup>-</sup> has a decay time of several hundreds of μs. This finding implies that the CsI:Ag<sup>-</sup> crystal is not an adequate scintillator material for the radiation detector to achieve a fast response. Since the decay of the visible luminescence band in CsI:Au<sup>-</sup> is slightly faster than that in CsI:TI<sup>+</sup>, the CsI:Au<sup>-</sup> crystals might be preferred as a new scintillator material.

#### 4. Conclusions

We have investigated the luminescence properties of the CsI crystals activated with  $\text{Ag}^-$ ,  $\text{Au}^-$ , and  $\text{Tl}^+$  ions at RT. Under excitation above the band gap of CsI crystals, the  $\text{CsI:Ag}^-$ ,  $\text{CsI:Au}^-$ , and  $\text{CsI:Tl}^+$  crystals exhibit visible luminescence bands peaking at 500, 450, and 540 nm, respectively. The temporal profiles of the visible luminescence bands in  $\text{CsI:Au}^-$  and  $\text{CsI:Tl}^+$  have a decay time constant of about 1  $\mu\text{s}$ . The visible luminescence band in  $\text{CsI:Au}^-$  decays slightly faster than that in  $\text{CsI:Tl}^+$ . On the other hand, the visible luminescence band in  $\text{CsI:Ag}^-$  exhibits a 25  $\mu\text{s}$  decay component arising from the radiative transition probability from the  $^3\text{P}_1$  excited state and a 250  $\mu\text{s}$  decay component associated with nearby defects. The existence of the slow decay components implies that the  $\text{CsI:Ag}^-$  crystals are inferior to the  $\text{CsI:Tl}^+$  and  $\text{CsI:Au}^-$  crystals in terms of quality as a scintillator material.

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