Comparative study of nondoped and Eu-doped SrI₂ scintillator

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Optical and scintillation properties of nondoped and Eu 3% doped SrI₂ crystals grown by the Vertical Bridgman method were investigated. Eu-doped crystal showed an intense single band emission at 430 nm due to the Eu²⁺-5d-4f transitions in both photoluminescence and scintillation while the nondoped crystal had a complex spectral shape. The latter emission consists of mainly four bands: 360 nm, 540 nm, 410 nm and 430 nm. The origins of 360 nm and 540 nm were self-trapped exciton and unexpected impurity, respectively. The origins of 410 and 430 nm lines were ascribed to F center in different I sites. Under 137Cs γ-rays, both crystals showed a clear photoabsorption peak. The scintillation light yields of the nondoped and Eu-doped SrI₂ resulted 33,000 ph/MeV and 82,000 ph/MeV, respectively. The energy resolution at 662 keV of Eu-doped was 4% while that of the non-doped SrI₂ was 8%.

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1. Introduction

Scintillating materials are a type of phosphors which convert absorbed energy of ionizing radiation to UV–Vis photons immediately [1–4]. There are a lot of application fields of radiation detectors using scintillators such as medical imaging [5,6], security [7,8], environmental monitoring [9,10] and high energy physics [11,12]. Especially, many efforts have been paid to develop inorganic scintillators for X-ray and γ-ray detectors since mid-20th. Detection efficiency for these high energy photons depends on the density and effective atomic number of materials. Common inorganic scintillators consist of insulator (sometimes semiconductor) host material and emission centres which are very commonly rare earth ions or transitional metal ions. Generally, rare earth ions such as Ce³⁺ [13,14], Pr³⁺ [15,16], and Eu²⁺ [17,18] are selected as a dopant since they show intense luminescence due to 5d-4f parity and spin allowed transition. Among these dopants, Eu²⁺ has attracted much attention because of observations of very high light yield scintillation from Eu²⁺-doped scintillators historically [19,20].

In recent years, Eu²⁺-doped SrI₂ scintillator has been very intensely investigated. Eu-doped SrI₂ was, in fact, invented around mid-20th [21], but no one had paid a continuous attention on this material possibly due to its featureless properties. However, owing to recent progress of crystal growth technology, dramatically improved scintillation properties (eg. scintillation light yield, energy resolution and decay time) have been discovered in Eu-doped SrI₂ crystals [22–33]. Eu-doped SrI₂ showed high light yield of 120000 ph/MeV (maximum value was reported in Ref. [25]), typically 3% energy resolution at 662 keV (the best value of 2.6% was achieved in Ref. [28]), and typically decay time of 1–2 µs depending on the Eu concentration. Although most studies have been done by doping with Eu, in a view point of condensed matter physics, investigation of nondoped SrI₂ is also an important research in order to gain a knowledge of such excellent scintillation response when doped with Eu ions. In earlier papers [29,31], nondoped SrI₂ was studied and it showed a very complicated scintillation spectrum. The band gap energy was reported as ~5.5 eV, and non-equivalent I sites was suggested [23]. Therefore, discussion of the nature of scintillation from nondoped SrI₂ is still an interesting topic. In this work, we have comparatively characterized optical and scintillation properties of Eu-doped and nondoped SrI₂ crystals.

2. Experimental procedures

Eu 3% doped and nondoped SrI₂ crystals were prepared by Oxide Corporation, 1747-1 Makihara, Mukawa-cho, Hokuto-shi, Yamanashi 408-0302, Japan.

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Corps., Yamanashi, Japan, using the Vertical Bridgman technique. The sample size were 0.5 inch\(\times\)0.5 inch-high and encapsulated since SrI\(_2\) showed a strong hygroscopicity. The cylindrical surface was fine-polished for optical and scintillation characterizations. Although most the investigations were done with the encapsulated samples, the temperature dependence measurements (mentioned below) were carried out with smaller (-10 \(\times\) 10 \(\times\) 2 mm\(^2\)) samples because of the limited space allowed in the cryostat. Fig. 1 shows a photograph of nondoped and Eu-doped SrI\(_2\) crystal samples. Under UV exposure (254 nm), the samples showed violet and green luminescence for Eu-doped and nondoped samples, respectively.

Characterizations of optical and scintillation properties were carried out at Nara Institute of Science and Technology (NAIST), Nara, Japan. The basic optical characterizations including photoluminescence (PL) and PL decay time profiles were studied. The X-ray induced radioluminescence (RL) spectrum (the basic setup is shown in Ref. [34]) at various temperatures, and scintillation decay time and afterglow profiles at room temperature (setup is presented in Ref. [35]) were also evaluated. In the former measurements, an ordinary X-ray generator was used as an irradiation source, which was supplied with 80 kV bias voltage and 2.5 mA tube current. Once X-rays were absorbed by the scintillator placed in the cryostat (Pascal-OP-S101AD, Pascal Co., Ltd.), emission photons were fed into SR163 monochromator (Andor) and then Andor DU-420-BU2 CCD via 3 m optical fiber. The measurement temperature range was from 10 to 300 K. The detailed setup and geometry of the temperature dependence measurement can be found in the literature [36]. For the scintillation decay time characterizations, the excitation source was a pulse X-ray tube, and the timing resolution of the total system was around 1 ns. \(\gamma\)-ray induced detector properties including pulse height spectrum, the relation between the pulse height and \(\gamma\)-ray energy, and energy resolution were investigated by using a laboratory-constructed setup which consists of R7600-U200 PMT, ORTEC 113 pre-amplifier, ORTEC572 shaping amplifier and Amptek 8000A multichannel analyzer. A typical setup was described previously [37], and the shaping time of 3 \(\mu\)s was applied. Radioisotopes used as \(\gamma\)-ray source were \(^{22}\)Na, \(^{57}\)Co, \(^{133}\)Ba, \(^{137}\)Cs, \(^{152}\)Eu, and \(^{241}\)Am.

![Figure 1](image.png)  
**Fig. 1.** Picture of Eu-doped and nondoped SrI\(_2\) crystalline scintillators. The inset shows typical luminescence under UV lamp excitation.

### 3. Experimental results and discussion

#### 3.1. Optical properties

Fig. 2 represents PL emission map of Eu-doped SrI\(_2\). Intense emission due to Eu\(^{2+}\) 5d-4f transition appeared around 430 nm under UV excitation. On the other hand, we could not observe a clear emission signal from the nondoped SrI\(_2\). The absolute PL quantum yield of encapsulated Eu-doped SrI\(_2\) was only a few %. As it is well known, Eu-doped SrI\(_2\) shows bright luminescence, but the encapsulation affects largely to the PL quantum yield. In the inset of Fig. 2, PL decay time profile of Eu-doped SrI\(_2\) is shown. Primary decay time component was around 1.3 \(\mu\)s, and it was a typical PL decay time of Eu\(^{2+}\) emission.

Fig. 3 shows PL decay time profiles of the nondoped SrI\(_2\) under 340 and 365 nm excitation. Although we could not observe a clear emission map from the nondoped SrI\(_2\), we were able to measure very clear scintillation spectrum (shown later), and we determined two emission bands peaking around 385 and 420 nm. PL decay times of these emissions at 385 and 420 nm were 326 and 370 ns, respectively. Compared with Eu\(^{2+}\) 5d-4f emission, these decay times were much faster. Since these two decay times were similar, the same origin is suggested for these two emission bands.

#### 3.2. X-ray induced scintillation properties

X-ray induced RL spectra at different temperatures are shown in Fig. 4. An intense emission peak appeared at 430 nm in the Eu-doped sample due to Eu\(^{2+}\) 5d-4f transition, and the spectral shape was same with that of PL. Although Eu\(^{3+}\) 4f-4f emission generally appears around 600 nm, such emission lines were not observed. When compared with the nondoped sample, the broad emission was suppressed by the Eu-doping. The scintillation light yield monotonically increased with decreasing the temperature, and the emission intensity saturated below 100 K. The other hand, in the non-doped SrI\(_2\), the spectral shape was complicated and some emission bands around 360, 410, 430, and 540 nm were observed. 360 nm emission did not appear at high temperature, and it appeared clearly at temperature below 200 K. 410 and 430 nm emission bands were not resolved clearly at room temperature, but they showed similar temperature dependence. To our knowledge, this is the first time to resolve 410 and 430 nm emission bands clearly, and these were considered to be one emission in the previous study (e.g., [29]). Their emission intensities increased to 100 K and saturated below 75 K. Similar temperature dependence of the scintillation and PL decay time suggested the same origin for these two emission bands. The emission intensity of the broad band at 540 nm monotonically increased when the temperature decreased.

Taking into account of optical and scintillation properties obtained in this work, a valid scenario of emissions at 360, 410, 430, and 540 nm are considered as follows:

- **360 nm:** In the former study [23], this band was assigned to the self-trapped exciton (STE) based on results that the excitation bands started around 5.2 eV, and the emission appeared around low temperature (90 K). We agree this interpretation.
- **410 nm:** Although some papers assign the origin of this emission as the STE (e.g., [29]) without experimental or logical basis, we consider the origin is F-center since this emission appears in common PL.
- **430 nm:** The origin would be the same as that of the 410 nm band. In previous work [23], at least two non-equivalent I sites were reported, and 410 and 430 nm emissions would be assigned to these I sites (F-center).
- **540 nm:** In the former study, it was blamed that this emission is
due to some impurities (e.g., [29]), the STE (e.g., [32]) or some hydrates (e.g., [23]). At least we disagree the scenario of the STE [32] because the emission was observed when the excitation energy was lower than the bandgap [23]. Therefore, we basically agree with this interpretation that the origin would be due to unexpected impurities. One of the possible candidate of the impurities are transitional metal (TM) ions since they show a broad luminescence band. This possibility is declined by the scintillation decay time described later since TM ions show typically a decay time on the order of ms. By spectral shapes and decay profiles, the contamination of unexpected rare earth ions are also denied. In addition, we conducted ICP measurement, and we confirmed at least alkali, alkali metal, and Pb ions are included with the detection limit level (< a few ppt). In the cation, remaining possibility will be ns²-ions except for Pb²⁺. On the other hand, the most recent work about SrI₂ suggests that the origin of the green emission of the non-doped sample is blamed for anions such as O₂⁻, OH⁻ or halogen vacancy [33], and we cannot exclude these possibilities.

Fig. 3 demonstrates X-ray induced scintillation decay and afterglow time profiles. In the scintillation decay curve, the 5d-4f emission of Eu²⁺ was dominant, and the decay time constant was 1.3 μs. The time constant was much smaller (450 ns) without Eu-doping. These decay times were similar with those observed in PL evaluations, and it was suggested that the energy migration process from the host to emission centers worked smoothly.

Compared with the previous result of Eu 3% doped SrI₂ [28] which showed 3.9 μs scintillation decay, the scintillation decay time was faster and this results suggested the crystalline quality of the present sample was high. On the other hand, the previous study reported that scintillation decay times of the nondoped sample were ~100 and ~500 ns [29] and we could not observe the faster (~100 ns) component in our sample. In the afterglow profile, Eu-doped sample showed the normalized intensity of ~0.1% at several tens of milliseconds after X-ray excitation was cut off. The inset shows a thermally stimulated luminescence spectrum at room temperature which equals to the luminescence spectrum of the afterglow. This long afterglow is mainly caused by Eu²⁺ emission and may partially affected by the emission of Eu³⁺ due to the 4f-4f transitions, though it was not observed clearly in the scintillation spectrum. The charge imbalance of Eu³⁺ and Sr²⁺ would create some defects, and such defects would affect the afterglow. On the other hand, afterglow of the nondoped SrI₂ was better at least one digit than Eu-doped SrI₂, and the afterglow was similar level with that of Tl-doped CsI [35]. Therefore, at the present stage, Eu-doped and the nondoped SrI₂ should not be considered for the X-ray detectors which are generally integrated-type detectors and require high emissivity, low afterglow and low cost.

3.3. γ-ray induced scintillation properties

In order to evaluate the scintillation detector properties, Fig. 6 compares 137Cs pulse height spectra of non-doped and Eu-doped SrI₂. In order to determine the light yield, the non-doped and Eu-doped samples were compared with Tl-doped CsI (Saint Gobain in Japan) and Tl-doped NaI (product of Neutron Co. Ltd., Tokyo, Japan), respectively. The light yield of Tl-doped CsI was ~43000 ph/MeV calibrated with Si-APD and 55Fe 5.9 keV X-ray peak. The detailed methodology for the calibration can be found in our previous work [38]. The light yield of the reference Tl-doped NaI was ~45000 ph/MeV. This value was obtained by the comparison with the light yield calibrated Ce-doped Gd₂SiO₅ scintillator [39] since the size of NaI was too large to attach on Si-APD. In all samples, clear photoabsorption peak and Compton edge were observed. By the comparison with reference materials, the scintillation light yield of Eu-doped SrI₂ was around 82000 ph/MeV. This result was consistent with previous works. On the other hand, the light yield...
of nondoped SrI₂ was ~33000 ph/MeV. The light yield of non-doped SrI₂ has turned out to be much higher than the previously reported value [23]. As a result, the nondoped SrI₂ has a high scintillation light yield with relatively fast scintillation decay of 450 ns in the longer wavelength (~540 nm), and it is applicable for Si semiconductor readout. The relation between the photoabsorption peak channel and the γ-ray energy is displayed in Fig. 7. Although most work reported a similar plot namely light yield nonproportionality, the present work focused on the detector property and we presented a linearity plot. From 32.2 keV (137mBa) to 1408 keV (152Eu), linear responses were observed in both scintillators. Then, the energy resolution is plotted against γ-ray energies as shown in Fig. 8. In both samples, the energy resolution was in proportional to $E^{1/2}$ where $E$ denoted the γ-ray energy. In Eu-doped and nondoped SrI₂, photon statistics was a dominant factor in the energy resolution. At 662 keV, energy resolutions Eu-doped and non-doped SrI₂ were 4% and 8%, respectively. In the past study, the energy resolution of Eu 3% doped SrI₂ was around 3%, and it was slightly better than our sample. One possible reason for this difference would be blamed for the encapsulating technique and the reflector since we did not use the reflector when they were encapsulated. Therefore, higher energy resolution would be possible to establish the fabrication methodology by using the reflector.

4. Conclusion

Eu 3% doped and nondoped SrI₂ crystalline scintillators were prepared by the Vertical Bridgman method. In PL and scintillation spectra, Eu²⁺ 5d-4f emission was observed in Eu-doped sample while complicated spectrum was observed in the nondoped sample. Temperature dependence of scintillation spectra was evaluated, and the study showed scintillation intensity increased at low temperature range. In the nondoped sample, four emission bands at 360, 410, 430 and 540 nm were detected. The origin of the 360 nm emission was ascribed to the STE. The 410 and 430 nm emissions were ascribed to different F-centers due to non-equivalent I sites. The determination of the origin of 540 nm...
emission will require further study and one possibility is unexpected impurities. Scintillation detector performance such as the light yield, linearity and the energy resolution were evaluated. Scintillation light yields of Eu-doped and nondoped SrI$_2$ resulted 82000 and 33000 ph/MeV, respectively. The energy resolutions at 662 keV of Eu-doped and nondoped SrI$_2$ were 4 and 8%, respectively.

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