Evaluation of photoluminescence and scintillation properties of Yb\(^{2+}\)-doped SrCl\(_2\)-xBr\(_x\) crystals

Kohei MIZOI\(^1\), Miki ARAI\(^1\), Yutaka FUJIMOTO\(^1\), Daisuke NAKAUCHI\(^2\), Masanori KOSHIMIZU\(^1\), Takayuki YANAGIDA\(^2\) and Keisuke ASA\(^1\)

\(^1\)Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6–6–07 Aoba, Aramaki, Aoba-ku, Sendai 980–8579, Japan
\(^2\)Division of Materials Science, Nara Institute of Science and Technology, 8916–5 Takayama-Cho, Ikoma, Nara 630–0192, Japan

Photoluminescence and scintillation properties are reported for SrCl\(_2\)-xBr\(_x\):Yb\(^{2+}\) (x = 0, 0.3, 1.4, 1.6, and 2.0) crystals grown by a self-seeding solidification method. SrCl\(_2\)-xBr\(_x\) have been reported to crystallize in some structural types with different local site symmetries depending on the Cl/Br ratio. Taking advantage of this property, we can control the crystal structure and the local Yb\(^{2+}\) site symmetry of SrCl\(_2\)-xBr\(_x\):Yb\(^{2+}\) by changing the compositions and investigate the behaviors of the spin-allowed and spin-forbidden transitions dependent on the local site symmetry. For photoluminescence and scintillation, both spin-allowed and spin-forbidden Yb\(^{2+}\) 5d–4f transitions were observed for SrCl\(_2\)-Yb\(^{2+}\) with local O\(_h\) symmetry and SrCl\(_{0.4}\)Br\(_{1.6}\):Yb\(^{2+}\) and SrBr\(_2\)-Yb\(^{2+}\) with local C\(_{4h}\) symmetry, whereas only spin-forbidden Yb\(^{2+}\) 5d–4f transition was observed for SrCl\(_{1.7}\)Br\(_{0.3}\):Yb\(^{2+}\) and SrCl\(_{0.6}\)Br\(_{1.4}\):Yb\(^{2+}\) with local D\(_{2h}\) symmetry. The spin-allowed transitions were observed in crystals with higher local site symmetry. Light yields of SrCl\(_{2-x}\)Br\(_x\):Yb\(^{2+}\) (x = 0, 0.3, 1.4, 1.6, and 2.0) were (21000 to 71000) photons/MeV. Crystals with higher local site symmetry, which showed the spin-allowed transitions, had relatively high light yields. Among them, SrCl\(_{0.6}\)Br\(_{1.4}\):Yb\(^{2+}\) showed a light yield of 71000 photons/MeV, which is higher than those of previously reported Yb\(^{2+}\)-doped scintillators, for example, SrI\(_2\):Yb\(^{2+}\) (56000 photons/MeV) and CsBaI\(_3\):Yb\(^{2+}\) (54000 photons/MeV).

Key-words : Scintillators, Yb\(^{2+}\) ion, 5d–4f transition, Mixed-anion compounds

1. Introduction

Scintillators are materials that emit light by converting the energy of incident ionizing radiation and used in various fields, such as diagnostic imaging equipments\(^1\) and security inspection systems.\(^2\) For scintillators for X-ray and gamma ray detection, various properties, such as fast decays, high light yields, and high effective atomic numbers (Z\(_{\text{eff}}\)), are required depending on the applications. However, there are no commercial scintillators which satisfy all of these requirements. Hence, new scintillators with improved performance have been under development. Compared with organic scintillators, inorganic scintillators generally have high light yields and high sensitivity to X-rays and gamma rays due to their high effective atomic numbers. There are halide- and oxide-based inorganic scintillators among commercially available ones, and they exhibit different characteristics. Halide-based materials have a relatively narrower bandgap than oxide-based ones, and thus have high light yields and good energy resolution,\(^3\) although they have some difficulties of application to scintillators due to its high deliquescence. Over the past decades, inorganic scintillator research has focused on both improving the characteristics of conventional scintillators and exploring new host compounds. One promising way for improving the performance of inorganic scintillators is addition of rare-earth elements, such as Eu\(^{3+}\) or Ce\(^{3+}\), as luminescence centers to halide crystals because they exhibit bright luminescence owing to 5d–4f emission. For example, SrI\(_2\):Eu\(^{3+}\)(4,5) BaBr\(_2\):Eu\(^{2+}\)(6,7) CsBaI\(_3\):Eu\(^{2+}\)(7) KSrI\(_2\):Eu\(^{2+}\)(8) and LaBr\(_3\):Ce\(^{3+}\)(9) have been reported to show high light yields. Among the rare-earth elements as the luminescence centers, there are many reports about Eu\(^{2+}\) as the luminescence centers for scintillators, because it shows efficient luminescence within UV and visible range due to its spin-allowed 4f\(^7\)–4f\(^6\)5d transition. For example, Eu\(^{2+}\)-doped SrI\(_2\) has favorable properties, such as high light yield (~80000 photons/MeV) and high energy resolution (~4%) at 662 keV owing to 4f\(^7\)–4f\(^6\)5d transition of the Eu\(^{2+}\) ions.\(^3,4\) Similar luminescence behavior can be expected for Yb\(^{2+}\) because Yb\(^{2+}\) has...
closed-shell 4f$^{14}$ configuration whereas Eu$^{2+}$ has half-shell 4f$^7$ configuration. Ytterbium is a rare-earth element that has been primarily explored as a dopant for laser applications in, e.g., YAG:Yb$^{10}$ and in its trivalent state (Yb$^{3+}$). Yb$^{3+}$ ion exhibits charge transfer transition-based luminescence.$^{11}$ Although there are many studies on ytterbium-activated scintillators such as YAG:Yb,$^{12}$ LuAG:Yb,$^{12}$ and Lu$_2$O$_3$:Yb,$^{13}$ their focus is on Yb$^{3+}$ as the luminescence center, whereas there are few reports on the scintillation properties of Yb$^{2+}$. In contrast to the scintillation properties, many reports have been published on the optical properties of Yb$^{2+}$-doped crystals. In the previous reports, Yb$^{2+}$ shows broad-band 5d→4f luminescence which can be tuned within UV and visible range by choice of the host compound. Emission wavelength of Yb$^{2+}$ is reported to vary depending on hosts in a range of (350 to 550) nm, such as 377 nm for CaSO$_4$:Yb$^{2+}$ and 525 nm for BaFCl:Yb$^{2+}$ and this matches the wavelength region of high sensitivity for conventional photon detectors. Scintillation properties of Yb$^{2+}$-doped halide crystals have been reported for SrCl$_2$:Yb$^{2+}$,$^{14}$ SrI$_2$:Yb$^{2+}$,$^{17}$ CsBa$_2$I$_5$:Yb$^{2+}$,$^{18}$ and Cs$_2$SrI$_6$:Yb$^{2+}$,$^{18}$ whose light yields are (54000, 56000, 43000 and 40000) photons/MeV, respectively. We have developed ACaCl$_2$: Yb$^{2+}$ (A = Cs, Rb, and K) crystalline scintillators with light yields of (59,000 to 75,000) photons/MeV.$^{19}$ Eu$^{2+}$-doped halide scintillators have shown higher light yields than Yb$^{2+}$-doped ones. For example, SrI$_2$:Eu$^{2+}$,$^{3,4}$ and CsBaI$_2$:Eu$^{2+}$,$^{6}$ have light yields of (80000 and 97000) photons/MeV, respectively, whereas SrI$_2$:Yb$^{2+}$,$^{17}$ and CsBaI$_2$:Yb$^{2+}$,$^{17}$ doped halide scintillators have shown higher light yields of Yb$^{2+}$-doped ones. For example, SrI$_2$:Eu$^{2+}$,$^{3,4}$ and CsBaI$_2$:Eu$^{2+}$,$^{6}$ have light yields of (80000 and 97000) photons/MeV, respectively, whereas SrI$_2$:Yb$^{2+}$,$^{17}$ and CsBaI$_2$:Yb$^{2+}$,$^{17}$ have light yields of (56000 and 54000) photons/MeV, respectively. On the other hand, there are some contrary results, for example, Yb$^{2+}$-doped SrCl$_2$ (56000 photons/MeV)$^{10}$ and CsCaCl$_3$ (75000 photons/MeV)$^{19}$ have higher light yields than Eu$^{2+}$-doped SrCl$_2$ (120000 photons/MeV)$^{20}$ and CsCaCl$_3$ (18000 photons/MeV)$^{21}$). Thus, Yb$^{2+}$-doped halide scintillators have the potential to show superior scintillation performance to Eu$^{2+}$-doped materials. Therefore, further development of efficient Yb$^{2+}$-doped scintillators needs to be explored.

A simplified energy level scheme of Yb$^{2+}$ is shown in Fig. 1(a). The Yb$^{2+}$ 4f$^{13}$5d$^1$ excited state splits into several levels owing to crystal field splitting of the 5d levels of Yb$^{2+}$ and spin–orbit split 4f$^{13}$ core.$^{22,23}$ Yb$^{2+}$ shows 5d→4f emission due to the transitions from the 4f$^{13}$5d excited states to the 4f$^{14}$ ground state. It is reported that the 4f$^{14}$-4f$^{13}$5d emission band of Yb$^{2+}$ has a similar energy (±0.3 eV) to the 4f$^2$-4f$^5$5d emission band of Eu$^{2+}$ in the same site of the same host compound.$^{24}$ Thus, Yb$^{2+}$ is expected to show efficient luminescence owing to its 4f$^{12}$-4f$^{13}$5d transitions similar to Eu$^{2+}$. Yb$^{2+}$ shows two emission bands from a lower-energy high-spin (HS) state and a higher-energy low-spin state. The radiative transitions from the former and the latter states are spin-forbidden and spin-allowed, respectively. A simplified energy level scheme of Yb$^{2+}$ spin-allowed and spin-forbidden transitions is shown in Fig. 1(b). The spin-allowed transition has often been observed in MgF$_2$, KMF$_2$, NaMgF$_3$, SrB$_4$O$_7$, MFX (M = Ca, Sr, X = Cl, Br), MSO$_4$:Yb$^{2+}$ (M = Ca, Ba),$^{14}$ M$_2$(PO$_4$)$_3$:Cl:Yb$^{2+}$ (M = Ca, Sr, Ba)$^{29}$ with decay time constants of (500, 30, 140, 44, 20–85, 400, 16–58) µs, respectively. There are some examples of the spin-allowed transition at room temperature in SrCl$_2$:Yb$^{2+}$,$^{10}$ SrI$_2$:Yb$^{2+}$,$^{17}$ CsBa$_2$I$_5$:Yb$^{2+}$,$^{17}$ CsMX$_3$:Yb$^{2+}$ (M = Ca, Sr, X = Cl, Br, I)$^{30,31}$ Cs$_2$CaCl$_6$:Yb$^{2+}$,$^{18}$ and Cs$_2$SrI$_6$:Yb$^{2+}$,$^{18}$ with decay time constants of (0.50, 0.74, 0.87, 0.09–1.19, 1.46, and 1.50) µs, respectively. The spin-allowed transition is desirable for scintillators used in pulse counting mode detectors because of its relatively fast decay time. It is reported that spin-allowed transition are often observed in hosts with heavy anions or high local site symmetries,$^{30,31}$ however, it has not been clarified which factor is more important in the occurrence of the spin-allowed transition.

In this work, we synthesized SrCl$_2$_Br$_x$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) crystals and investigated the photoluminescence (PL) and scintillation properties.
et al. reported that SrCl$_2$ and SrBr$_2$ are fully miscible over the whole range of compositions and that the resulting solid solutions crystallize in cubic with the local O$_h$ symmetry for composition of $x = 0$, orthorhombic with the local D$_{2h}$ symmetry for compositions of $0.30 \leq x \leq 0.50$ and $0.70 \leq x \leq 1.40$, and tetragonal with the local C$_{4h}$ symmetry for compositions of $1.60 \leq x \leq 2.0$. Taking advantage of this property, it is possible to control the crystal structure and the local Yb$^{3+}$ site symmetry of SrCl$_{2-x}$Br$_x$Yb$_2$ by changing the compositions and investigate the behavior of spin-allowed and spin-forbidden transitions that depend on local site symmetry. Moreover, mixed-anion compounds have been reported to be suitable host materials for phosphors due to their unique properties such as electronic structures and local site symmetries. Some mixed-halide scintillators have been reported to show higher light yields than single-halide scintillators, for example, BaBr$_2$:Eu$^{2+}$ and BaF$_2$:Eu$^{2+}$ (32000 photons/MeV) and Br$_2$:Eu$^{2+}$ (32000 photons/MeV)$.^{33}$ Thus, SrCl$_{1-x}$Br$_x$Yb$_2$ crystals have potential to show high light yields. Previously, we reported the PL and scintillation properties of SrCl$_2$:Yb$^{2+}$, SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$, and SrBr$_2$:Yb$^{2+}$. In this work, we added SrCl$_{1-x}$Br$_x$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$, and investigated the relationship between PL and scintillation properties and the local site symmetry of SrCl$_{1-x}$Br$_x$Yb$_2$ ($x = 0, 0.3, 1.4, 1.6, 2.0$). The excitation and emission spectra, X-ray-excited radioluminescence (XRL) spectra, PL and scintillation decay profiles, and light yields of SrCl$_{1-x}$Br$_x$Yb$_2$ ($x = 0, 0.3, 1.4, 1.6, 2.0$) crystals are studied.

2. Experimental

The SrCl$_{2-x}$Br$_x$:Yb$^{2+}$ crystals were fabricated using a solidification method.$^{34}$ Powders of SrCl$_2$ (99.99 %, Rare Metallic Co. Ltd.), SrBr$_2$:6H$_2$O (99.9 %, Mitsuo Chemical Co. Ltd.) and YbCl$_3$:6H$_2$O (99.9 %, Mitsuo Chemical Co. Ltd.) were mixed in the stoichiometric ratios of the end products. The $x$ values representing the Br/Cl proportion are $0, 0.3, 1.4, 1.6,$ and $2.0$. YbCl$_3$ powders were mixed in a molar ratio of 0.5 mol % to Sr. The mixed powders were loaded into quartz ampules and heated at 350 K in vacuum for 1 d to remove water. Subsequently, the dried mixtures were sealed under vacuum (ca. 80 Pa). The ampules were placed in a tabular furnace and heated up to 900°C and maintained at that temperature for a period of 10 h, and subsequently cooled down to room temperature in 85 h. After the crystal growth, a part of the as-grown crystals was cut and polished. The surface of the SrCl$_2$:Yb$^{2+}$ and SrBr$_2$:Yb$^{2+}$ crystals became wet and was partially dissolved in air for several days owing to their deliquescence. On the contrary, the surface of the SrCl$_{2-x}$Br$_x$:Yb$^{2+}$ ($x = 0.3, 1.4, 1.6$) crystals only became cloudy. This suggests that mixed-halide crystals had relatively lower deliquescence than single halide crystals.

The X-ray diffraction (XRD) patterns were recorded using a Rigaku Ultima IV-PXS diffractometer with Cu-Kα radiation in the continuous scan mode at $2\theta = 10–80^\circ$ at a sampling interval of 0.02° and scan rate of 2° min$^{-1}$. PL spectra were measured from (200 to 500) nm using a fluorescence spectrophotometer (Hitachi High-Tech F-7000) at room temperature, and a 150 W Xe lamp was used as the excitation source. The PL quantum efficiencies (QEs) were estimated using a Quantaurus-QY (Hamamatsu Photonics C11347-01) spectrophotometer. The PL decay curves were obtained using a Delta Flex 3000U-TMK2 (Horiba) instrument at room temperature. The XRL spectra were measured using a SILVER-Nova multi-channel spectrometer (StellarNet Inc.) at room temperature. The X-ray source was an X-ray generator equipped with a Cu anode target (Rigaku RINT2200) with power settings of 40 kV and 40 mA. Temporal scintillation decay profiles were recorded using a pulsed X-ray beam, which was obtained through the combination of a pulsed LED light source and an X-ray tube. A detailed description of this setup can be found in our previous report.$^{35}$

3. Results and discussion

Figure 2 shows the XRD patterns of SrCl$_{2-x}$Br$_x$:Yb$^{2+}$ ($x = 0, 0.3, 1.4, 1.6,$ and $2.0$) crystals. In SrCl$_2$:Yb$^{2+}$, all peaks are attributed to those of SrCl$_2$ (ICSD No: 00-006-0537). SrCl$_2$:Yb$^{2+}$ was confirmed to be in a single cubic phase with the local O$_h$ symmetry at the Sr$^{2+}$ site. In SrCl$_{1-x}$Br$_x$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$, most peaks are attributed to those of SrCl$_2$:Br$_3$ (ICSD No: 00-036-0586) and SrCl$_{0.6}$Br$_{1.4}$ (ICSD No: 01-076-0990), respectively, and the peaks which did not correspond to SrCl$_{1.7}$Br$_{0.3}$ and SrCl$_{0.6}$Br$_{1.4}$ were confirmed to be in almost single orthorhombic phase with the local D$_{2h}$ symmetry. The phase of SrCl$_2$:2H$_2$O was observed for SrCl$_{1.5}$Br$_{0.5}$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ due to their deliquescence during the measurements. In SrCl$_{0.6}$Br$_{1.6}$:Yb$^{2+}$, most peaks are attributed to those of SrCl$_{0.6}$Br$_{1.6}$ (ICSD No: 01-076-0989), and the peaks of another phase which does not correspond to SrCl$_{0.6}$Br$_{1.6}$ may be attributed to SrCl$_{0.6}$Br$_{1.4}$ (ICSD No: 01-076-0990). In SrBr$_2$:Yb$^{2+}$, all peaks are attributed to those of SrBr$_2$ (ICSD No: 01-074-0463). SrCl$_{0.6}$Br$_{1.6}$:Yb$^{2+}$ and SrBr$_2$:Yb$^{2+}$ were confirmed to be in almost single tetragonal phase with the local C$_{4h}$ symmetry. The crystal structure of SrCl$_{2-x}$Br$_x$:Yb$^{2+}$ ($x = 0, 0.3, 1.4, 1.6,$ and $2.0$) crystals corresponded to those in a previous report.$^{32}$ Thus, we succeeded in controlling the crystal structure by changing compositions.

Figures 3–7 show the PL excitation and emission spectra for SrCl$_{2-x}$Br$_x$:Yb$^{2+}$ ($x = 0, 0.3, 1.4, 1.6,$ and $2.0$), respectively, at room temperature. Six excitation peaks and

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shoulders for SrCl$_2$:Yb$^{2+}$ can be observed. It was reported that the excitation spectra of Yb$^{2+}$-doped crystals split into several bands, in particular, 6 bands in SrCl$_2$:Yb$^{2+}$ and SrI$_2$:Yb$^{2+}$.

The most likely cause of the separation is crystal field splitting of the 5d levels of Yb$^{2+}$ and spin–orbit split 4f$^{13}$ core, which have been discussed in detail in previous papers.19,34 For crystal field splitting, the 5d electronic level splits in a crystal field into $e_g$ and $t_{2g}$ levels. The...
excitation peaks of each sample were classified into four groups as shown in Figs. 3–7. The excitation energy of the group is defined as the average energy of the peaks in the group. The energy differences between groups (A) and (C) and between groups (B) and (D) were (0.5 to 0.7) eV for all samples as shown in Table 1, which were similar to the energy difference between \( ^2F_{5/2} \) and \( ^2F_{7/2} \) in the previous reports (\(-0.8 \text{ eV}\)) for SrCl\(_2\):Yb\(_{2+}\)\(^{21,22}\). Thus, groups (A) and (C) and groups (B) and (D) could be assigned to \( ^2F_{5/2} \) and \( ^2F_{7/2} \) states, respectively. For spin–orbit coupling, both \( \epsilon_g \) and \( \epsilon_u \) levels split into two states according to the 4f\(^{13}5d^1\) configuration of Yb\(^{2+}\) with the 5d electron coupled to a spin–orbit split 4f\(^{13}\) core, which has \( ^2F_{5/2} \) and \( ^2F_{7/2} \) states with an energy difference of \( \sim 1.2 \text{ eV} \) for SrCl\(_2\):Yb\(_{2+}\)\(^{16}\) and SrI\(_2\):Yb\(_{2+}\)\(^{17}\).

The energy differences between the groups (A) and (C) and (B) to (D) were (1.2 to 1.5) eV for all samples as shown in Table 1, which were similar to the energy difference between \( ^2F_{5/2} \) and \( ^2F_{7/2} \) of the previous reports (\(-1.2 \text{ eV}\)). Thus, groups (A) and (B) and groups (C) and (D) could be assigned to \( ^2F_{5/2} \) and \( ^2F_{7/2} \) states, respectively. Finally, the groups of excitation peaks of groups (A), (B), (C), and (D) were assigned to \( ^2F_{5/2} (t_{2g}), ^2F_{5/2} (e_g), ^2F_{7/2} (t_{2g}), \) and \( ^2F_{7/2} (e_g) \), respectively. Two excitation peaks were observed in one group such as the groups (B) and (D) for SrCl\(_2\):Yb\(_{2+}\), SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\), and SrBr\(_2\):Yb\(_{2+}\), and the groups (B) and (C) for SrCl\(_1\):Br\(_{0.3}\):Yb\(_{2+}\) and SrCl\(_0\):Br\(_{1.4}\):Yb\(_{2+}\). The most likely cause of the further separation is the lowering of the crystal field symmetry from \( \text{Oh} \) to \( D_{2h} \) or \( C_{2h} \) due to the Jahn–Teller effect on the exited 5d states. A similar split was reported for MgF\(_2\):Yb\(_{2+}\)\(^{23}\).

In the PL emission spectra, two emission peaks were observed for SrCl\(_2\):Yb\(_{2+}\), SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\), and SrBr\(_2\):Yb\(_{2+}\) crystals whereas one emission peak was observed for SrCl\(_1\):Br\(_{0.3}\):Yb\(_{2+}\) and SrCl\(_0\):Br\(_{1.4}\):Yb\(_{2+}\). Two emission peaks were observed around (385 and 408) nm for SrCl\(_2\):Yb\(_{2+}\), (390 and 410) nm for SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\), and (395 and 420) nm for SrBr\(_2\):Yb\(_{2+}\) as shown in Figs. 3, 6, and 7, respectively. A single emission peak was observed around 415 nm for SrCl\(_1\):Br\(_{0.3}\):Yb\(_{2+}\) and 417 nm for SrCl\(_0\):Br\(_{1.4}\):Yb\(_{2+}\) as shown in Figs. 4 and 5 respectively. The PL decay profiles for all samples are shown in Fig. 8. The PL decay behavior of all samples was approximated using a single exponential function, and the estimated PL decay constants of SrCl\(_2\):Yb\(_{2+}\) (\( x = 0, 0.3, 1.4, 1.6, \) and 2.0) crystals are shown in Table 2. Both short and long components were observed for SrCl\(_2\):Yb\(_{2+}\), SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\), and SrBr\(_2\):Yb\(_{2+}\) whereas only long components were observed for SrCl\(_1\):Br\(_{0.3}\):Yb\(_{2+}\) and SrCl\(_0\):Br\(_{1.4}\):Yb\(_{2+}\). The PL decay time constants of spin-allowed Yb\(^{2+}\) 4f\(^{13}\)5d\(^1\) \( \rightarrow \) 4f\(^1\) transitions have been reported to be \( \sim 500 \text{ ns} \) for SrCl\(_2\):Yb\(_{2+}\)\(^{16}\) and \( \sim 700 \text{ ns} \) for SrI\(_2\):Yb\(_{2+}\)\(^{17}\). The decay time constants of the fast components of SrCl\(_2\):Yb\(_{2+}\) (480 ns), SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\) (470 ns), and SrBr\(_2\):Yb\(_{2+}\) (300 ns) were similar to those reported values, and thus the peaks around 385 nm for SrCl\(_2\):Yb\(_{2+}\), 390 nm for SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\), and 395 nm for SrBr\(_2\):Yb\(_{2+}\) are all assigned to the spin-allowed Yb\(_{2+}\) 4f\(^1\)5d\(^1\) \( \rightarrow \) 4f\(^1\) transition. On the other hand, the PL decay time constants of spin-forbidden Yb\(_{2+}\) 4f\(^1\)5d\(^1\) \( \rightarrow \) 4f\(^1\)4d\(^1\) transition have been reported to be \( \sim 550 \mu\text{s} \) for SrCl\(_2\):Yb\(_{2+}\)\(^{16}\) and 20–85 \mu\text{s} for MFX (M = Ca, Sr; X = Cl, Br):Yb\(_{2+}\)\(^{28}\). The decay time constants of the long component of SrCl\(_2\):Yb\(_{2+}\) (580 \mu\text{s}) corresponded to that of a previous report (\(-550 \mu\text{s}\))\(^{16}\) and those of SrCl\(_1\):Br\(_{0.3}\):Yb\(_{2+}\) (65 \mu\text{s}), SrCl\(_0\):Br\(_{1.4}\):Yb\(_{2+}\) (72 \mu\text{s}), SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\) (61 \mu\text{s}), and SrBr\(_2\):Yb\(_{2+}\) (45 \mu\text{s}) were all similar to those of MFX (M = Ca, Sr; X = Cl, Br):Yb\(_{2+}\) (20–85 \mu\text{s})\(^{28}\). Thus, peaks around 408 nm for SrCl\(_2\):Yb\(_{2+}\), 415 nm for SrCl\(_1\):Br\(_{0.3}\):Yb\(_{2+}\), 417 nm for SrCl\(_0\):Br\(_{1.4}\):Yb\(_{2+}\), 410 nm for SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\) and SrBr\(_2\):Yb\(_{2+}\) are all assigned to the spin-allowed Yb\(_{2+}\) 4f\(^1\)5d\(^1\) \( \rightarrow \) 4f\(^1\) transition. In SrCl\(_0\):Br\(_{1.6}\):Yb\(_{2+}\), different phase of SrCl\(_0\):Br\(_{1.4}\):Yb\(_{2+}\) was observed as shown in Fig. 2(d). The phase does not seemed to contribute to the emission peak and the decay
time constants of spin-allowed transition of SrCl$_2$:Yb$^{2+}$ showed only the spin-
forbidden transition.

Both spin-allowed and spin-forbidden transitions were observed for SrCl$_2$:Yb$^{2+}$ with local $O_h$ symmetry, SrCl$_{0.4}$Br$_{1.6}$:Yb$^{2+}$ and SrBr$_2$:Yb$^{2+}$ with local $C_{4v}$ symmetry, whereas only spin-forbidden transitions were observed for SrCl$_1$:Br$_{0.3}$:Yb$^{2+}$ and SrCl$_{0.8}$Br$_{1.4}$:Yb$^{2+}$ with local $D_{2d}$ symmetry. It is reported that spin-allowed transition is often observed in hosts with heavy anions or high local site symmetries.$^{30,31}$ In CsMX$_3$:Yb$^{2+}$ (M = Ca, Sr, X = Cl, Br), spin-allowed transition has been observed for CsCaBr$_3$:Yb$^{2+}$ with local $O_h$ symmetry, whereas no spin-allowed transition has been observed for CsCaCl$_3$:Yb$^{2+}$ with local $O_h$ symmetry. The occurrence of spin-allowed transition has been related to the variation of the anions rather than local site symmetry for CsMX$_3$:Yb$^{2+}$ (M = Ca, Sr, X = Cl, Br).$^{30,31}$ On the other hand, in this work for SrCl$_{1-x}$Br$_x$:Yb$^{2+}$ ($x = 0, 0.3, 1.4, 1.6$, and $2.0$), spin-
allowed transition was observed for both SrCl$_2$:Yb$^{2+}$ and SrBr$_2$:Yb$^{2+}$ in spite of their different anions. Moreover, no spin-allowed transition was observed for SrCl$_1$:Br$_{0.3}$: Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ with lower local site symmetry ($D_{2h}$). Considering the results, the occurrence of spin-
allowed transition seems to be related to the local site sym-
metry rather than the variation of the anion for SrCl$_{2-x}$Br$_x$:Yb$^{2+}$ ($x = 0, 0.3, 1.4, 1.6$, and $2.0$).

The decay time constants of the spin-forbidden transition of SrCl$_2$:Yb$^{2+}$ ($\approx580$ ns) were longer than those of other samples, ($61$ to $72$) ns, which may be related to the effect of local site symmetry. According to previous reports for CsMX$_3$:Yb$^{2+}$ (M = Ca, Sr, X = Cl, Br, I)$^{30,31}$ in $O_h$ symmetry, transitions from HS states to the ground state are symmetry-forbidden, and thus, the decay time of the excited HS states are particularly long. However, lower symmetry weakens the forbidden character of the transition from the HS state to the ground state and hence reduces the decay time. For instance, it is reported that decay time constant of spin-forbidden transition of CsCaCl$_3$:Yb$^{2+}$ (280 ns) with local $O_h$ symmetry was longer than that of CsSrCl$_3$:Yb$^{2+}$ (160 ns) with local $C_{4v}$ symmetry, which was also observed in this work for SrCl$_2$:Yb$^{2+}$ (580 ns) with local $O_h$ symmetry and SrCl$_{1.2}$Br$_{0.4}$:Yb$^{2+}$ ($x = 0, 0.3, 1.4, 1.6$, and $2.0$) ($61$ to $72$) ns with local $D_{2h}$ and $C_{4h}$ symmetry.

The PL QEs of SrCl$_2$:Yb$^{2+}$, SrCl$_{0.4}$Br$_{1.6}$:Yb$^{2+}$, SrCl$_1$:Br$_{0.3}$:Yb$^{2+}$, SrCl$_{0.8}$Br$_{1.4}$:Yb$^{2+}$ and SrBr$_2$:Yb$^{2+}$ were $56$, $87$, $85$, $93$, and $69\%$, respectively. The possible cause of high QE values of mixed-halide crystals is their unique coordination structure and crystal structure; however, the mechanism is unclear.

The XRL spectra of SrCl$_{2-x}$Br$_x$:Yb$^{2+}$ ($x = 0, 0.3, 1.4, 1.6$, and $2.0$) crystals were shown in Figs. 9(a) and 9(b). Two emission peaks were observed for SrCl$_2$:Yb$^{2+}$, SrCl$_{0.8}$Br$_{1.6}$:Yb$^{2+}$, and SrBr$_2$:Yb$^{2+}$, whereas only single emission peak was observed for SrCl$_1$:Br$_{0.3}$:Yb$^{2+}$ and SrCl$_{0.8}$Br$_{1.4}$:Yb$^{2+}$. Two emission peaks were observed around ($383$ and $406$) nm for SrCl$_2$:Yb$^{2+}$ ($390$ and $410$) nm for SrCl$_{0.4}$Br$_{1.6}$:Yb$^{2+}$, and ($390$ and $415$) nm for SrBr$_2$:Yb$^{2+}$, as shown in Fig. 9(a). The single emission peak was observed around $410$ nm for SrCl$_{1.7}$Br$_{0.3}$:Yb$^{2+}$ and $417$ nm

![Fig. 8. PL decay profiles of SrCl$_{2-x}$Br$_x$:Yb$^{2+}$.](image-url)
for SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ as shown in Fig. 9(b). These wavelengths were all similar to those observed in the PL emission spectra shown in Figs. 3−7. Therefore, XRL spectra of SrCl$_{2−x}$Br$_x$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) crystals can be attributed to the same origin as the PL emission spectra.

Figure 10 shows the scintillation decay time profiles of SrCl$_{2−x}$Br$_x$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) crystals at room temperature. Two components were observed for SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ at (0 to 20) µs and (20 to 1000) µs. The former component is owing to the detection of the scattered X-rays. The latter component was approximated using a single exponential function. Those of SrCl$_{1.7}$Br$_{0.3}$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) were approximated using a single exponential function and the scintillation decay time constants of all samples are shown in Table 3.

The scintillation decay time constants of SrCl$_2$:Yb$^{2+}$, SrCl$_{0.4}$Br$_{1.6}$:Yb$^{2+}$, and SrBr$_2$:Yb$^{2+}$ were estimated to be (470, 430 and 320) ns, respectively, and are similar to the PL decay time constants of the spin-allowed transition. Those of SrCl$_{1.7}$Br$_{0.3}$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ were estimated to be (69 and 68) µs, respectively, and are similar to the PL decay time constants of the spin-forbidden transition. Thus, the obtained decay time constants of SrCl$_{2−x}$Br$_x$:Yb$^{2+}$ can be attributed to the spin-allowed transition, and those of SrCl$_{1.7}$Br$_{0.3}$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ can be attributed to the spin-forbidden transition. No scintillation components of spin-allowed transition were observed for SrCl$_{1.7}$Br$_{0.3}$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ with local D$_{2h}$ symmetry, which is consistent with the PL decay behavior.

Table 3. Scintillation decay time constants for SrCl$_{2−x}$Br$_x$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) crystals and their local site symmetries

| Material                  | Decay time constants [µs] | Symmetry |
|---------------------------|---------------------------|----------|
| SrCl$_2$:Yb$^{2+}$        | 0.47                      | O$_h$    |
| SrCl$_{0.4}$Br$_{1.6}$:Yb$^{2+}$ | 69                        | D$_{2h}$ |
| SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ | 68                        | D$_{2h}$ |
| SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ | 0.43                      | C$_{4h}$ |
| SrBr$_2$:Yb$^{2+}$        | 0.32                      | C$_{4h}$ |

Fig. 11 shows the pulse height spectra of SrCl$_{2−x}$Br$_x$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) crystals and a NaI:Tl commercial scintillator (OKEN) irradiated with 662 keV.
gamma rays from a $^{137}$Cs source. The amplifier gain was the same for all samples, and the shaping time was 10 μs for SrCl$_2$–Br$_2$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) and 2 μs for NaI:Tl. Photoelectric absorption peaks were observed at approximately 570 channels for SrCl$_2$:Yb$^{2+}$, 180 channels for SrCl$_2$:Br$_2$:Yb$^{2+}$, 230 channels for SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$, 830 channels for SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$, 620 channels for SrBr$_2$:Yb$^{2+}$, and 470 channels for NaI:Tl. The scintillation light yields are shown in Table 4 assuming that the light yield of NaI:Tl was 40000 photons/MeV. Light yields of SrCl$_2$:Yb$^{2+}$, SrCl$_2$:Br$_2$:Yb$^{2+}$, SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$, SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$, and SrBr$_2$:Yb$^{2+}$ are estimated to be (49000, 21000, 23000, 71000, and 53000) photons/MeV, respectively. The light yields of SrCl$_2$:Yb$^{2+}$, SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$, and SrBr$_2$:Yb$^{2+}$ are higher than those of previously reported Yb$^{2+}$-doped scintillators, for example, SrI$_2$:Yb$^{2+}$ (56000 photons/MeV) and CsBa$_2$I$_5$:Yb$^{2+}$ (54000 photons/MeV). Considering its high light yield and relatively fast decay time constant (430 ns), SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$ crystals are suitable for use in pulse counting mode such as survey meters for gamma ray detection. The light yields of SrCl$_2$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ were lower than those of SrCl$_2$:Yb$^{2+}$, SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$, and SrBr$_2$:Yb$^{2+}$. The most likely reason of their lower light yields is that they were partial light yields rather than total owing to the shaping time of 10 μs in spite of their long decay time (~70 μs), and thus, precise light yields could not be estimated.

### Table 4. Scintillation light yields of SrCl$_2$:Br$_2$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) crystals and NaI:Tl and their local site symmetries

| Materials       | Channel | Light yields [photons/MeV] | Symmetry |
|-----------------|---------|---------------------------|----------|
| SrCl$_2$:Yb$^{2+}$ | 570     | 49000                     | O$_h$    |
| SrCl$_2$:Br$_2$:Yb$^{2+}$ | 180     | 21000                     | D$_{2h}$ |
| SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ | 270     | 23000                     | D$_{2h}$ |
| SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$ | 830     | 71000                     | C$_{1h}$ |
| SrBr$_2$:Yb$^{2+}$ | 620     | 53000                     | C$_{1h}$ |
| NaI:Tl          | 470     | 40000                     | —        |

4. Conclusions

The PL and scintillation properties of SrCl$_2$:Br$_2$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) were investigated. The crystal structure and the local Yb$^{2+}$ site symmetry of SrCl$_2$:Br$_2$:Yb$^{2+}$ could be controlled by changing the Cl/Br ratio that allowed investigation of the behavior of spin-allowed and spin-forbidden transitions dependent on local site symmetry. SrCl$_2$:Yb$^{2+}$ was confirmed to be in single cubic phase with the local O$_h$ symmetry. SrCl$_2$:Br$_2$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ were confirmed to be in almost single orthorhombic phase with the local D$_{2h}$ symmetry. SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$ and SrBr$_2$:Yb$^{2+}$ were confirmed to be in almost single tetragonal phase with the local C$_{4h}$ symmetry. Both spin-allowed and spin-forbidden Yb$^{2+}$ 5d–4f transitions were observed for SrCl$_2$:Yb$^{2+}$, SrCl$_{0.8}$Br$_{1.2}$:Yb$^{2+}$, and SrBr$_2$:Yb$^{2+}$, whereas only spin-forbidden Yb$^{2+}$ 5d–4f transition was observed for SrCl$_2$:Br$_2$:Yb$^{2+}$ and SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ for PL and scintillation. The spin-allowed transition was observed in crystals with higher local site symmetry. The PL decay time constants of the spin-allowed transition were (300 to 480) ns and those of spin-forbidden transition were (60 to 580) μs. SrCl$_2$:Br$_2$:Yb$^{2+}$ (x = 0, 0.3, 1.4, 1.6, and 2.0) had light yields of (21000 to 71000) photons/MeV. Crystals with high local site symmetry, which showed the spin-allowed transition, had relatively high light yields. Among them, SrCl$_{0.6}$Br$_{1.4}$:Yb$^{2+}$ had the highest light yield of 71000 photons/MeV, which was higher than that of previously reported Yb$^{2+}$-doped scintillators, such as SrI$_2$:Yb$^{2+}$ (~56,000 photons/MeV) and CsBa$_2$I$_5$:Yb$^{2+}$ (~54,000 photons/MeV).

Acknowledgments

This research was supported by a Grant-in-Aid for Scientific Research (A) (No. 18H03890, 2018–2021) funded by the Japan Society for the Promotion of Science. This research was partially involved in the Cooperative Research Project of the Research Center for Biomedical Engineering, Ministry of Education, Culture, Sports, Science and Technology.

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