**Relationship between Eu^{3+} substitution sites and photoluminescence
properties of $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ spinel phosphors**

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Abstract

Eu³⁺-doped SrIn₂O₄ phosphors were synthesized by the solid solution method at 1400 °C in air. The chemical composition of the phosphors was systematically changed to study the relation between the Eu³⁺ substitution site and photoluminescence (PL) properties. Under excitation of the ⁷F₀→⁵L₆ transition of Eu³⁺ at 393 nm, the SrIn₂O₄:Eu³⁺ exhibited dominant red emission peaks at 611, 616 and 623 nm, which are attributed to the electric dipole transition ⁵D₀→⁷F₂ of Eu³⁺. The results of X-ray diffraction analysis combined with PL spectroscopic analysis revealed that Eu³⁺ ions occupied two different crystallographic In³⁺ sites in the host SrIn₂O₄, while it was found to be impossible to substitute Sr²⁺ with Eu³⁺ prior to the Eu³⁺ substitution at the In³⁺ sites in the SrIn₂O₄. The intensity of the red emission peaks increased with the total amount of dopant Eu³⁺ ion at the two In³⁺ sites, and reached a maximum at 25 mol% Eu³⁺-doping (SrIn_{2-x}O₄:xEu³⁺, x=0.25). Moreover, a small amount (<10 mol%) of Eu³⁺ at the Sr²⁺ site in the SrIn_{2-x}O₄:xEu³⁺ was found to contribute to enhance the red emission peak intensity at 616 nm. As a result, the highest red emission intensity evaluated as the total emission peak intensities at the 611, 616 and 623 nm was achieved for Sr_{0.92}In_{1.75}O₄:0.33Eu³⁺ in which Eu³⁺ ion concentrations at the In³⁺ and Sr²⁺ sites were simultaneously optimized as 25 and 8 mol%, respectively (Sr_{1-y}In_{2-x}O₄:(x+y)Eu³⁺, x=0.25, y=0.08). This red emission intensity was 2.2 times higher than that of the phosphor without contribution of the Eu³⁺ at the Sr²⁺ site (SrIn_{2-x}O₄:xEu³⁺, x=0.25). The critical energy transfer distance of Eu³⁺ ion in the Sr_{0.92}In_{1.75}O₄:0.33Eu³⁺ phosphor was determined to be 0.817 nm, and the electric multipolar interaction was suggested as the dominant mechanism for concentration quenching of PL emission due to Eu³⁺ ions in the Eu³⁺-doped SrIn₂O₄ phosphors investigated in this study.

Keywords: SrIn₂O₄; Eu³⁺ substitution site; photoluminescence; red emitting; thermal quenching property.

1. Introduction

For the past decade, because of the good thermal and chemical stability, rare earth ion-doped oxide phosphors have attracted much attention as they can be used in various type of display devices, solid-state lasers, medical devices, lighting apparatus and so on [1-4]. Furthermore, the white light-emitting diodes (white LEDs) have been expected as the next generation solid-state lighting sources to replace the conventional incandescent and fluorescent lamps. The white LEDs become more and more popular owing to the favorable properties like the excellent luminescent characteristics, high energy conversion efficiency, low cost and long operation time [5, 6].

The white LEDs have been fabricated by covering blue LED chips with a yellow emitting phosphor, cerium-doped yttrium aluminum garnet (YAG:Ce³⁺) [7, 8]. However, the white LEDs fabricated in this way have drawbacks such as the low color rendering index (less than 80) and high correlated color temperature (higher than 7000 K), which restricts their wide range of applications. As one of promising approaches to overcome the drawbacks, ultraviolet (UV) or near-UV LED chip excited tri-color (blue, green and red) phosphors have been considered and studied as a better combination for white LEDs which can offer a color rendering index higher than 90 [9, 10].

However, commercially available red-emitting phosphors are sulfides such as (Ca, Sr)S:Eu³⁺ and Y₂O₂S:Eu³⁺ [11]. Due to the lower chemical stability, sulfide-based phosphors degrade in the white LED devices during operation. Therefore, it is important to develop efficient novel phosphors, particularly red-emitting phosphors that can be excited efficiently under UV or near-UV irradiation. As one of the famous red emitters in the rare earth ion-doped materials, Eu³⁺ ion primarily presents highly efficient emissions due to the large energy gap between the emitting state ⁵D₀ and the excited states ⁷F_J (J=0-5) for the contribution of the extraordinary red composition. In addition to the excellent chemical stability, wide band gap semiconducting oxides with active Eu³⁺ ion are promising red color phosphors [12, 13]. Among these oxide phosphors, indium compounds such as

75 CaIn_2O_4 [14-20] and SrIn_2O_4 [21-29] have been reported as excellent host materials
76 for rare earth metal cations doped phosphors. CaIn_2O_4 is a kind of semiconductor with
77 a reported bandgap of 3.9 eV, and belongs to ordered CaFe_2O_4 structures with the
78 $Pca2_1$ or $Pbcm$ space group and the lattice parameters of $a=0.970$ nm, $b=1.130$ nm
79 and $c=0.321$ nm for $Z=4$ [30]. Several dopant cations such as Tb^{3+} [14-16] and Pr^{3+}
80 [16] for green emission, Dy^{3+} [16] for blue-white emission and Eu^{3+} for white [17, 18],
81 yellow [18], orange [18], reddish orange [20] and red [18, 19] emissions under
82 ultraviolet (UV) and/or vacuum-ultraviolet (VUV) excitation have been investigated
83 for developing field emission displays (FEDs), cathode ray tube display (CRTs) and
84 white-LEDs. The chemical composition of these phosphors were mainly designed and
85 synthesized to occupying Ca^{2+} sites with the dopant cation in the host CaIn_2O_4 . For
86 tuning the emission colors except for red emission, the dopant concentrations in these
87 phosphors were very low and in the range of 0.12 to 0.32 mol%, while the intense red
88 emission was achieved for 15 mol% Eu^{3+} doped CaIn_2O_4 with 5 mol% Sm^{3+}
89 co-doping ($\text{Ca}_{0.8}\text{In}_2\text{O}_4:0.15\text{Eu}^{3+}, 0.05\text{Sm}^{3+}$) [19].

90 Another indium compound, SrIn_2O_4 is also a semiconductor with a reported
91 bandgap of 3.6 eV, and the red-emitting $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ has attracted much attention for
92 application to white LEDs, because SrIn_2O_4 has a strong absorption band at 396 nm,
93 which perfectly matches with the emission spectrum of GaN-based LED chips
94 [21-23]. The crystal structure of SrIn_2O_4 is an orthorhombic CaFe_2O_4 -type structure
95 with Pnam (D_{2h}^{16}) space group and the lattice parameters of $a=0.981$ nm, $b=1.145$ nm
96 and $c=0.327$ nm for $Z=4$ [24]. In the structure of SrIn_2O_4 (Fig. 1), two kinds of
97 distorted InO_6 octahedra are connected to form a network by sharing edges and
98 corners, and the In^{3+} ions are in six coordination with the ionic radii of 0.080 nm [25,
99 26]. On the other hand, Sr^{2+} ions located in the middle of the formed pentagonal prism
100 tunnel are in eight coordination with the ionic radii of 0.126 nm [24]. Baszczuk *et al.*
101 [26] reported that Eu ions can occupy all the Sr^{2+} and two different In^{3+} sites in the
102 host SrIn_2O_4 . From the results of luminescence spectroscopic analyses for
103 $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$, they concluded that Eu^{3+} ions occupy two different In^{3+} sites, while a

part of Eu^{3+} ions in the host SrIn_2O_4 could be reduced to Eu^{2+} even under non-reducing atmosphere, and the in-situ produced Eu^{2+} could occupy the Sr^{2+} site.

If dopant Eu^{3+} ion preferentially occupies the Sr^{2+} site in the host SrIn_2O_4 , the resulting charge imbalance may be compensated by formation of Sr^{2+} vacancies, which would increase the nonradiative process and result in the reduction of luminescence intensity. Because the luminescent property of phosphor arises from the complex interaction among host structure, activators, defects and interfaces. Wang *et al.* [27] reported that alkali ions are effective as a co-dopant to compensate the charge imbalance caused by the Eu^{3+} substitution at the Sr^{2+} site in the host SrIn_2O_4 , and a remarkable improvement in the PL emission intensity was achieved for $\text{Sr}_{1-x}\text{In}_2\text{O}_4:\text{xEu}^{3+}, \text{xNa}^+$ ($\text{x}=0.1$).

However, to our knowledge, there is no systematic study on the PL red-emitting properties related to the dominant Eu^{3+} occupying site, and the total concentration of Eu^{3+} ions which may occupy all the Sr^{2+} and In^{3+} sites in the host SrIn_2O_4 . In this work, we have investigated the fabrication and photoluminescence (PL) properties of $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ phosphors. The relationship between the PL emission peaks due to the dopant Eu^{3+} , the site substituted by the Eu^{3+} , oxidation state of the doped Eu^{3+} and the critical Eu^{3+} concentration in the host SrIn_2O_4 lattice were studied. Moreover, the temperature quenching effect is also measured from room temperature to 227 °C (500 K), and the results were discussed from a viewpoint to develop an efficient red-emitting phosphor for white LED applications.

2. Experimental procedures

Eu^{3+} -doped SrIn_2O_4 phosphors were synthesized by the solid solution method following the procedure reported by Lakshminarasimhan *et al.* [28]. Strontium carbonate (SrCO_3), indium oxide (In_2O_3) and europium oxide (Eu_2O_3) were used as starting materials. All the powders were purchased from Mitsuwa Chemical Company, Japan (99.99% purity). In a typical synthesis, appropriate amounts of the three starting powders (totally about 2 g) were mixed and then stirred in the 5 mL ethanol for 10

min. The mixed powder was placed into a drying furnace at 100 °C for 5 min to remove the ethanol. The dried powder was heat-treated at 1400 °C in air for 4 h. The chemical compositions of the Eu^{3+} -doped SrIn_2O_4 investigated in this study were shown in Table 1.

Room temperature X-ray diffraction (XRD; X'pert Pro $\alpha 1$, Philips) analysis was performed on the heat-treated samples using Cu $K\alpha$ radiation ($\lambda=0.15405$ nm). The morphology of the heat-treated samples was observed using scanning electron microscopy (SEM; JSN-6360LV, JEOL) at 25 kV acceleration voltages. Evaluation of oxidation state for the doped-Eu ions was performed by measurements of X-ray absorption near edge structure (XANES) spectra at the Eu LIII absorption edge with X-ray absorption spectrometer (Rigaku, R-XAS Looper). The obtained XANES spectra were analyzed by the software (Rigaku, REX2000).

PL excitation and emission spectra were recorded at room temperature using a spectrophotometer (F-7000, Hitachi) with a 150 W Xenon lamp as the excitation source. The temperature dependence of the red PL of the phosphor was evaluated under the excitation at 393 nm.

3. Results and discussion

3.1 Crystalline phases of 1400 °C heat-treated samples.

The XRD patterns for $\text{SrIn}_{2-x}\text{O}_4\cdot x\text{Eu}^{3+}$ ($x=0.005$, 0.01 and 0.1) and those for $\text{Sr}_{1-y}\text{In}_{2-(0.1-y)}\text{O}_4\cdot 0.1\text{Eu}^{3+}$ ($y=0.01$, 0.03, 0.05, 0.07, 0.09 and 0.1) are shown in Figs. 2(a) and 2(b), respectively. The diffraction peaks detected for each sample except for $\text{Sr}_{0.9}\text{In}_2\text{O}_4\cdot 0.1\text{Eu}^{3+}$ ($y=0.1$ in Fig 2(b)) were identical to those of the standard powder diffraction file for orthorhombic SrIn_2O_4 (JCPDS No. 01-072-0801, space group: Pnam (D_{2h}^{16})). As previously reported [26], no systematic shifting of XRD diffraction peaks with increasing x was observed for $\text{SrIn}_{2-x}\text{O}_4\cdot \text{Eu}^{3+}$ ($x=0.005$ and 0.01 in Fig. 2(a)), which is due to that variation of the unit cell by small amount of Eu^{3+} dopant is within the detection limit of the equipment used in this study. The lattice parameters determined for these two compositions were $a = \sim 0.982$ nm, $b = \sim 0.1148$ nm, and c

162 = ~ 0.327 nm. When x was increased to 0.1 ($x=0.1$ in Fig. 2(a)), the lattice parameter
163 in the c axis almost unchanged, while those in the a and b axes slightly increased to
164 ~ 0.985 nm and ~ 0.115 nm, respectively, which indicates that doped Eu^{3+} (0.095 nm)
165 occupied In^{3+} (0.080 nm) site as designed.

166 On the other hand, $\text{Sr}_{0.9}\text{In}_2\text{O}_4:0.1\text{Eu}^{3+}$ exhibited additional diffraction peaks
167 assigned to indium oxide (In_2O_3 , JCPDS card of No. 00-044-1087), while the rest of
168 five compositions exhibited SrIn_2O_4 single phase without formation of strontium
169 oxide (SrO) and other phases of Eu^{3+} ion, thus the doped Eu^{3+} ion was well dissolved
170 into the SrIn_2O_4 host lattice. These results indicate that Eu^{3+} ion principally occupies
171 In^{3+} site, then occupies Sr^{2+} site as a secondary substitution site in the host SrIn_2O_4 .
172 Since the size difference between In^{3+} (0.080 nm) and Eu^{3+} (0.095 nm) in six
173 coordination is 18.8%, which is rather larger than that between Sr^{2+} (0.126 nm) and
174 Eu^{3+} (0.107 nm) in eight coordination (15.1%), this order is thought to be governed by
175 the valence difference between Sr^{2+} and Eu^{3+} , which leads to the intrinsic Eu^{3+} content
176 restriction in the host SrIn_2O_4 [22, 27].

177

178 3.2 PL properties

179 As shown in Fig. 1, there are one Sr^{2+} site and two different In^{3+} sites in the host
180 SrIn_2O_4 , the dopant Eu^{3+} ion in the five compositions of $\text{Sr}_{1-y}\text{In}_{2-(0.1-y)}\text{O}_4:0.1\text{Eu}^{3+}$
181 ($y=0.01, 0.03, 0.05, 0.07, 0.09$) can be substituted in all of them. Then, their PL
182 properties were further studied. As a typical result, Fig. 3(a) presents the excitation
183 spectrum ($\lambda_{\text{em.}} = 611$ nm) and emission spectrum ($\lambda_{\text{ex.}} = 393$ nm) for
184 $\text{Sr}_{0.95}\text{In}_{1.95}\text{O}_4:0.1\text{Eu}^{3+}$ ($y=0.05$). In the excitation spectrum, a broad peak at around 345
185 nm can be observed and is ascribed to the band gap transition of SrIn_2O_4 host lattice
186 [29]. The intense excitation peaks at 393 and 464 nm can be attributed to the $^7\text{F}_0 \rightarrow ^5\text{L}_6$
187 and the $^7\text{F}_0 \rightarrow ^5\text{D}_2$ excitations, respectively [26]. In addition to its relatively higher
188 intensity, the excitation peak wavelength of 393 nm well matches with the emission
189 spectrum of GaN-based LEDs, which offers a possibility for white LED applications.
190 Thus, the excitation at 393 nm was employed for evaluating PL emission properties of

191 the phosphors investigated in this study.

192 Upon an excitation with 393 nm, the emission spectrum exhibits several peaks
193 due to the $^5D_0 \rightarrow ^7F_J$ ($J=0-4$) transitions of Eu^{3+} over the range of 570-730 nm, and the
194 main emission attributed to the $^5D_0 \rightarrow ^7F_2$ electric dipole transition are observed as
195 three peaks at 611, 616 and 623 nm (Fig. 3(b)). Thus, $\text{Sr}_{0.95}\text{In}_{1.95}\text{O}_4:0.1\text{Eu}^{3+}$ exhibits red
196 emission.

197 PL emission spectra ($\lambda_{\text{ex.}} = 393$ nm) for $\text{Sr}_{1-y}\text{In}_{2-(0.1-y)}\text{O}_4:0.1\text{Eu}^{3+}$ phosphors ($y=0$,
198 0.01, 0.03, 0.05, 0.07, 0.09 and 0.10) are shown in Fig. 4(a). All the samples exhibited
199 dominant red emission peaks at 611-623 nm. These spectra were curve-fitted and the
200 relative intensities for each emission peak centered at the 611, 616 and 623 nm were
201 evaluated and are plotted in Fig. 4(b) as a function of y , *i.e.* amount of Eu^{3+} at Sr^{2+} site
202 ($\text{Sr}_{1-y}\text{In}_{2-(0.1-y)}\text{O}_4:0.1\text{Eu}^{3+}$). Initially at $y=0$, the relative peak intensity was in the order
203 of 611 nm > 623 nm > 616 nm. However, the intensity at 616 nm significantly
204 increased with increasing y , and became highest at $y=0.05$. Then, the intensity
205 slightly increased above $y=0.05$ to reach a maximum at $y=0.09$. Conversely, the
206 relative peak intensities at 611 and 623 nm decreased with increasing y , *i.e.* with
207 decreasing amount of Eu^{3+} ions at In^{3+} site. At $y=0.1$, intensities of the three peaks
208 were lowest, which could be due to the secondary phase formation of In_2O_3 as shown
209 in Fig. 1(b). These results reveal that the emission peak intensity at 616 nm largely
210 depends on the amount of Eu^{3+} ion at Sr^{2+} site, while those at 611 and 623 nm are
211 dominantly governed by the amount of Eu^{3+} ion at the two different In^{3+} sites.

212 To investigate the possibility of the PL emission ascribed to Eu^{3+} ion at the two
213 different In^{3+} sites, further analysis of the PL emission spectrum ($\lambda_{\text{ex.}} = 393$ nm) was
214 performed on $\text{SrIn}_{1.99}\text{O}_4:0.01\text{Eu}^{3+}$, since no SrO diffraction peaks was found in the
215 XRD diffraction pattern for this composition and the doped Eu^{3+} ions was thought to
216 mainly occupy the In^{3+} sites. As shown in Fig. 5, only the characteristic f-f transition
217 peaks of Eu^{3+} can be seen in the spectrum. There are several PL emission peaks due to
218 the large energy gap between the emitting state 5D_0 and the excited states 7F_J ($J=0-2$)
219 which contribute the red emission. The details of the PL emission peaks are

220 summarized and shown in Table 2.

221 When the rare earth (RE) ion is incorporated in a host material the energy level of
222 the RE ion is generally splitted into number of sublevels due to the ligand field/
223 crystal field. These sublevels are known as the Stark sublevels, and the maximum
224 number of the f-f transition peaks due to RE ion can be given as $2J+1$ (where J is the
225 electronic angular momentum). Therefore, there should be only one peak for the 7F_0
226 level, while there are two different peaks at 578 and 584 nm due to the ${}^5D_0 \rightarrow {}^7F_0$
227 transition (Table 2). It is also well known that the maximum numbers of the Stark
228 sublevels depend on the symmetry of the crystal field surrounding RE ion [31, 32]. As
229 shown in Fig. 5, the high emission intensity achieved by the hypersensitive 5D_0 to 7F_2
230 transition reveals that the point symmetry of Eu^{3+} ion at In^{3+} site is low. Therefore,
231 there should be less than three and five peaks for the splitting of 7F_1 and 7F_2 levels,
232 respectively. However, as shown in Table 2, there are four and six peaks attributed to
233 the ${}^5D_0 \rightarrow {}^7F_1$ and the ${}^5D_0 \rightarrow {}^7F_2$ transitions, respectively. These results demonstrate that
234 the dopant Eu^{3+} ion randomly occupied the two different In^{3+} sites in the host SrIn_2O_4
235 investigated in this study.

236

237 **3.3 Optimization of PL red emission intensity**

238 To improve the performance as a red-emitting phosphor, optimization of the
239 dopant Eu^{3+} ion concentration in the host SrIn_2O_4 lattice was further investigated
240 according to the following strategy based on the results obtained shown above: (1)
241 optimizing total amount of Eu^{3+} ion at the two different In^{3+} sites, then (2) optimizing
242 the amount of Eu^{3+} ion at Sr^{2+} site for the SrIn_2O_4 with the optimized amount of Eu^{3+}
243 ions occupying the two In^{3+} sites.

244 Figure 6 shows PL emission spectra for $\text{SrIn}_{2-x}\text{O}_4:x\text{Eu}^{3+}$ ($x = 0.1, 0.15, 0.2, 0.25$
245 and 0.3) upon an excitation at 393 nm. Among the three dominant red emission peaks
246 at 611, 616 and 623 nm attributed to the ${}^5D_0 \rightarrow {}^7F_2$ transition, the most intensive one at
247 611 nm was selected, and the inset shows variation of the relative peak intensity at
248 611 nm. The intensity of the red emission peaks increased consistently with Eu^{3+}

249 concentration and reached a maximum at $x=0.25$, then became lowest at $x=0.3$. The
250 XRD analysis revealed that all the $\text{SrIn}_{2-x}\text{O}_4:\text{xEu}^{3+}$ phosphors were composed of
251 SrIn_2O_4 single phase, and the degradation at $x=0.3$ was thought to be due to the
252 concentration quenching.

253 Then, a series of $\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$ ($y=0.02, 0.04, 0.06, 0.08$ and 0.10)
254 were synthesized and characterized by comparing with $\text{SrIn}_{1.75}\text{O}_4:0.25\text{Eu}^{3+}$. As shown
255 in Fig. 7, all the phosphors exhibited the same XRD pattern identical to orthorhombic
256 SrIn_2O_4 phase. As typical morphological features, SEM images of
257 $\text{Sr}_{1-y}\text{In}_{1.75}:(y+0.25)\text{Eu}^{3+}$ ($y=0, 0.04, 0.08$ and 0.1) are shown in Fig. 8. All the
258 phosphors exhibited a similar microstructural feature, and presented crystallites
259 having a size range of about 1 to 4 μm .

260 Figure 9(a) illustrates PL emission spectra for the $\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$
261 phosphors ($y=0, 0.02, 0.04, 0.06, 0.08$ and 0.10) upon an excitation at 393 nm. The
262 variations of relative peak intensities at 611, 616 and 623 nm, and the resulting red
263 emission intensity evaluated as the total intensity of the three emission peaks due to
264 the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition are shown in Figs. 9(b) and 9(c), respectively. In this
265 optimization study, the Eu^{3+} concentration at the In^{3+} site was optimized and fixed as
266 25% prior to increasing the amount of Eu^{3+} at the Sr^{2+} site, and the relative peak
267 intensities at 611, 616 and 623 nm were found to keep the initial intensity order (611
268 nm > 623 nm > 616 nm) at all the compositions (Fig. 9(b)). The relative peak intensity
269 at 616 nm increased consistently with the amount of Eu^{3+} ion-doping, and reached a
270 maximum at $y=0.08$ to 0.1 , while those at 611 and 623 nm increased to reach a
271 maximum at $y=0.08$, then apparently decreased at $y=0.1$ (Fig. 9(b)). As a result, the
272 maximum red emission intensity ascribed to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition was achieved for
273 $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ ($y=0.08$). This intensity was 2.2 times higher than that of
274 $\text{SrIn}_{1.75}\text{O}_4:0.25\text{Eu}^{3+}$ ($y=0$) (Fig. 9(c)).

275 The oxidation state of the doped Eu ions was investigated by the XANES
276 spectroscopy. The spectrum obtained for $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ is compared with that
277 for the reference sample of Eu_2O_3 and shown in Fig. 10. Both of the two samples

278 exhibit a single band peak centered at 6988 eV assigned to Eu^{3+} [33], and thus the
 279 oxidation state of the Eu ions in the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ synthesized in this study
 280 was determined as trivalent.

281 The emission peak intensity at 616 nm increased associated with a simultaneous
 282 increase in the emission peak intensities at 611 and 623 nm, which could be due to the
 283 preferential Eu^{3+} substitution at In^{3+} sites as discussed above. Thus, a part of the
 284 additionally doped Eu^{3+} ion occupied the In^{3+} sites, and the exact Eu^{3+} ion
 285 concentration at Sr^{2+} site in the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ could be less than 8 mol%.

286 When the dopant Eu^{3+} ion occupies Sr^{2+} site, the resulting charge imbalance may
 287 be compensated by formation of Sr^{2+} vacancies as follows:

289 As previously discussed for Na^+ -codoped $\text{Sr}_{1-x}\text{In}_2\text{O}_4:x\text{Eu}^{3+}$ phosphors
 290 ($\text{Sr}_{1-x-x}\text{In}_2\text{O}_4:x\text{Eu}^{3+},x\text{Na}^+$) [27], under such a low Eu^{3+} concentration below 8 mol%,
 291 the degree of charge imbalance formed by the Eu^{3+} substitution at Sr^{2+} site could be
 292 low. Thus, the red emission intensity successfully increased without a serious
 293 reduction in the emission intensity caused by the formation of Sr^{2+} vacancies.

294 The optimized total amount of dopant Eu^{3+} ion in the host SrIn_2O_4 was
 295 determined to be 0.33, above which the red emission intensity decreased due to the
 296 concentration quenching. Since the concentration quenching is caused by energy
 297 transfer from one activator to another one, there is a critical energy transfer distance
 298 (R_c). In oxide phosphors, the R_c can be estimated by the following equation [34, 35]:

$$299 \quad R_c = 2\left(\frac{3V}{4\pi X_c N}\right)^{1/3} \quad (2)$$

300 where V is the volume of the unit cell, X_c is the critical concentration of the dopant
 301 ions and N is the number of host cation in the unit cell. By using appropriate values of
 302 V (0.376 nm^3), X_c (0.33) and N (4) [24, 36], the critical energy transfer distance of

303 Eu^{3+} ion in the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ (R_c) is determined to be 0.817 nm.

304 Park *et al.* [37] reported that the melilite structure CaYAl_3O_7 has a high Eu^{3+}
305 concentration without concentration quenching compared to other host materials, and
306 the optimized Eu^{3+} ion concentration and the R_c for the red-emitting
307 $\text{CaY}_{1-x}\text{Al}_3\text{O}_7:x\text{Eu}^{3+}$ were determined to be approximately 35 mol% ($x=0.35$) and 0.9
308 nm, respectively. The values obtained in this study are compatible with those reported
309 for the $\text{CaY}_{1-x}\text{Al}_3\text{O}_7:x\text{Eu}^{3+}$, and relatively high dopant Eu^{3+} ion concentration was
310 achieved for the $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ phosphor by the simultaneous optimizations of the Eu^{3+}
311 ion concentrations at the Sr^{2+} and In^{3+} sites, respectively.

312 The non-radiative energy transfer from one Eu^{3+} ion to another Eu^{3+} ion may
313 occur by exchange interaction, radiation reabsorption or electric multipolar interaction.
314 The exchange interaction usually occurs when the donor level has a substantial
315 overlap with the acceptor one. This overlap is responsible for the short critical
316 energy-transfer distances (R_c) less than 0.5 nm [38, 39] and makes a part of forbidden
317 transitions to be allowed one. In the present $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ phosphor, the R_c
318 value was estimated to be 0.817 nm, which reveals that the exchange interaction is not
319 the dominant mechanism for the concentration quenching observed for the present
320 $\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$ phosphors. On the other hand, the radiation reabsorption is
321 only effective when the fluorescence and absorption spectra are broadly overlapping.
322 Since such a broad spectral overlap was not observed for the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$
323 phosphor as seen in Figs. 3 and 9(a), this mechanism can be excluded in the present
324 case. Therefore, the electric multipolar interaction should be the dominant mechanism
325 for concentration quenching of PL emission due to Eu^{3+} ions in the
326 $\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$ phosphors.

327 In this study, the PL red-emitting properties related to the dominant Eu^{3+}
328 occupying site were clarified. Then, for the PL red emission, the optimized total
329 concentration of Eu^{3+} ions which occupied all the Sr^{2+} and In^{3+} sites in the host
330 SrIn_2O_4 was determined as 33%, and the Eu^{3+} substitutions in the host SrIn_2O_4 can be
331 summarized as follows: The In^{3+} site in the host SrIn_2O_4 could be selectively

substituted by Eu^{3+} ions by controlling the chemical composition as $\text{SrIn}_{(2-x)}\text{O}_4:\text{xEu}^{3+}$ (x: up to approximately 0.3), while it was impossible to replace Sr^{2+} with Eu^{3+} selectively by controlling the chemical composition as $\text{Sr}_{(1-x)}\text{In}_2\text{O}_4:\text{xEu}^{3+}$. As a result, $\text{SrIn}_{(2-x)}\text{O}_4:\text{xEu}^{3+}$ formed accompanied by the phase separation of In_2O_3 . On the other hand, the Sr^{2+} in the $\text{SrIn}_{(2-x)}\text{O}_4:\text{xEu}^{3+}$ was found to be replaced with Eu^{3+} , and the Eu^{3+} concentration at the Sr^{2+} site could be increased to 10 % ($\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$, $y=0.1$). Formation of $\text{SrIn}_{(2-x)}\text{O}_4:\text{xEu}^{3+}$ lead to the lattice expansion of the host SrIn_2O_4 , which was thought to be one of critical factors for the Eu^{3+} substitution at the Sr^{2+} site to form $\text{Sr}_{(1-y)}\text{In}_{(2-x)}\text{O}_4:(x+y)\text{Eu}^{3+}$.

Finally, to examine the potential for white-LED applications, the temperature dependence of emission intensity under excitation at 393 nm of $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ phosphor was studied. The intensities evaluated up to 500 K (227 °C) were normalized by that at room temperature and plotted as a function of temperature (Fig. 11). The PL intensity decreased slowly with increasing temperature, however the normalized PL intensities at 400 K (127 °C) and 440 K (167 °C) remained approximately 90 and 85 %, respectively. Thus, the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ was found to have a good thermal-quenching property compatible with that of $\text{CaIn}_2\text{O}_4:\text{Eu}^{3+}$ phosphor [20] at the usual LED's operating temperatures.

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351 4. Summary

In this study, $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ phosphors were synthesized by the solid solution method at 1400 °C in air. To optimize the performance as a red-emitting phosphor for white LED applications, the relation between the Eu^{3+} substitution site and photoluminescence (PL) properties was investigated. The results are summarized as follows:

- 357 (1) The dopant Eu^{3+} ions principally occupy two different crystallographic In^{3+} sites,
358 which is thought to be governed by the valence difference between Sr^{2+} and Eu^{3+} ,
359 which leads to the intrinsic Eu^{3+} content restriction in the host SrIn_2O_4 .
- 360 (2) Sr^{2+} in the $\text{SrIn}_{(2-x)}\text{O}_4:\text{xEu}^{3+}$ was found to be replaced with Eu^{3+} . The lattice

expansion induced by the Eu^{3+} substitution at the In^{3+} site was thought to be one of critical factors for the $\text{Sr}_{(1-y)}\text{In}_{(2-x)}\text{O}_4:(x+y)\text{Eu}^{3+}$ formation.

(3) Under excitation of the ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ transition of Eu^{3+} at 393 nm, the $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ exhibits dominant red emission peaks at 611, 616 and 623 nm, which are attributed to the electric dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ of Eu^{3+} .

(4) The red emission peak intensities at 611, 616 and 623 nm were dominantly governed by the total amount of Eu^{3+} ion at the two different In^{3+} sites, while a small amount (< 10 mol%) of Eu^{3+} ion at Sr^{2+} site was found to contribute to enhance the red emission peak intensity at 616 nm.

(5) The highest red emission intensity evaluated as the total emission peak intensities at the 611, 616 and 623 nm was achieved for 33 mol% Eu^{3+} -doped SrIn_2O_4 phosphor in which Eu^{3+} ion concentrations at the In^{3+} and Sr^{2+} sites were simultaneously optimized as 25 and 8 mol%, respectively ($\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$). This red emission intensity was 2.2 times higher than that of the phosphor without contribution of the Eu^{3+} at the Sr^{2+} site ($\text{SrIn}_{1.75}\text{O}_4:0.25\text{Eu}^{3+}$).

(6) The oxidation state of the doped Eu ions in the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ synthesized in this study was determined as trivalent by the XANES spectroscopic analysis.

(7) The critical energy transfer distance of Eu^{3+} ion in the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ phosphor was determined to be 0.817 nm, and the electric multipolar interaction was suggested as the dominant mechanism for concentration quenching observed for the Eu^{3+} -doped SrIn_2O_4 phosphor investigated in this study.

(8) $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ phosphor synthesized in this study exhibited a good thermal-quenching property at the usual LED's operating temperatures.

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390 of Japan.

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Figure and Table captions

Fig. 1. Crystal structure of orthorhombic SrIn_2O_4 .

Fig. 2. The XRD patterns for (a) $\text{SrIn}_{2-x}\text{O}_4:0.1\text{Eu}^{3+}$ ($x=0.005, 0.01, 0.1$), (b) $\text{Sr}_{1-y}\text{In}_{2-(0.1-y)}\text{O}_4:0.1\text{Eu}^{3+}$ ($y=0.01, 0.03, 0.05, 0.07, 0.09$ and 0.1).

Fig. 3. PL excitation spectrum ($\lambda_{\text{em.}} = 611 \text{ nm}$) and emission spectrum ($\lambda_{\text{ex.}} = 393 \text{ nm}$) for $\text{Sr}_{0.95}\text{In}_{1.95}\text{O}_4:0.1\text{Eu}^{3+}$ ($\text{Sr}_{1-y}\text{In}_{2-(0.1-y)}\text{O}_4:0.1\text{Eu}^{3+}$, $y=0.05$).

Fig. 4. (a) PL emission spectra ($\lambda_{\text{ex.}} = 393 \text{ nm}$) for $\text{Sr}_{1-y}\text{In}_{2-(0.1-y)}\text{O}_4:0.1\text{Eu}^{3+}$ phosphors ($y=0, 0.01, 0.03, 0.05, 0.07, 0.09$ and 0.10), and (b) variation of relative emission peak intensities at 611, 616, 623 nm in the spectra shown in (a).

Fig. 5. PL emission spectrum ($\lambda_{\text{ex.}} = 393 \text{ nm}$) for $\text{SrIn}_{1.99}\text{O}_4:0.01\text{Eu}^{3+}$.

Fig. 6. PL emission spectra excited at 393 nm for $\text{SrIn}_{2-x}\text{O}_4:x\text{Eu}^{3+}$ with different amount of Eu^{3+} ($x = 0.1, 0.15, 0.2, 0.25$ and 0.3). Inset shows relative intensity of the emission peak at 611 nm as a function of Eu^{3+} content.

Fig. 7. The XRD patterns for $\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$ (*: Orthorhombic SrIn_2O_4).

Fig. 8. SEM images of $\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$ ($y=0, 0.04, 0.08$ and 0.1).

Fig. 9. PL emission properties of $\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$. (a) PL spectra excited at 393 nm. Composition dependences of (b) relative emission peak intensities at 611, 616 and 623 nm and (c) the total emission intensity.

Fig. 10. XANES spectra for $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ and reference sample of Eu_2O_3 .

Fig. 11. The PL intensity of the $\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$ under excitation of 393 nm at temperatures from room temperature to 500 K (227 °C).

Table 1 Chemical composition of $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ phosphors investigated in this study.

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Fig. 5. PL emission spectrum ($\lambda_{\text{ex.}} = 393 \text{ nm}$) for SrIn_{1.99}O₄:0.01Eu³⁺.

Fig. 6. PL emission spectra excited at 393 nm for $\text{SrIn}_{2-x}\text{O}_4:x\text{Eu}^{3+}$ with different amount of Eu^{3+} ($x = 0.1, 0.15, 0.2, 0.25$ and 0.3). Inset shows relative intensity of the emission peak at 611 nm as a function of Eu^{3+} content.

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799 Table 1 Chemical composition of $\text{SrIn}_2\text{O}_4:\text{Eu}^{3+}$ phosphors investigated in this study.
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Sample				Molar ratio of starting materials		
Formula	x	y	Composition	SrCO_3	In_2O_3	Eu_2O_3
$\text{SrIn}_{2-x}\text{O}_4:x\text{Eu}^{3+}$	0.005	-	$\text{Sr}_{1.00}\text{In}_{1.995}\text{O}_4:0.005\text{Eu}^{3+}$	1	0.9975	0.0025
	0.01	-	$\text{Sr}_{1.00}\text{In}_{1.99}\text{O}_4:0.01\text{Eu}^{3+}$	1	0.995	0.005
	0.10	-	$\text{Sr}_{1.00}\text{In}_{1.90}\text{O}_4:0.10\text{Eu}^{3+}$	1	0.95	0.05
	0.15	-	$\text{Sr}_{1.00}\text{In}_{1.85}\text{O}_4:0.15\text{Eu}^{3+}$	1	0.925	0.075
	0.20	-	$\text{Sr}_{1.00}\text{In}_{1.80}\text{O}_4:0.20\text{Eu}^{3+}$	1	0.9	0.1
	0.25	-	$\text{Sr}_{1.00}\text{In}_{1.75}\text{O}_4:0.25\text{Eu}^{3+}$	1	0.875	0.125
	0.30	-	$\text{Sr}_{1.00}\text{In}_{1.70}\text{O}_4:0.30\text{Eu}^{3+}$	1	0.85	0.15
$\text{Sr}_{1-y}\text{In}_{2-x}\text{O}_4:0.1\text{Eu}^{3+}$ ($x + y = 0.1$)	0.09	0.01	$\text{Sr}_{0.99}\text{In}_{1.91}\text{O}_4:0.10\text{Eu}^{3+}$	0.99	0.955	0.05
	0.07	0.03	$\text{Sr}_{0.97}\text{In}_{1.93}\text{O}_4:0.10\text{Eu}^{3+}$	0.97	0.965	0.05
	0.05	0.05	$\text{Sr}_{0.95}\text{In}_{1.95}\text{O}_4:0.10\text{Eu}^{3+}$	0.95	0.975	0.05
	0.03	0.07	$\text{Sr}_{0.93}\text{In}_{1.97}\text{O}_4:0.10\text{Eu}^{3+}$	0.93	0.985	0.05
	0.01	0.09	$\text{Sr}_{0.91}\text{In}_{1.99}\text{O}_4:0.10\text{Eu}^{3+}$	0.91	0.995	0.05
	-	0.10	$\text{Sr}_{0.90}\text{In}_{2.00}\text{O}_4:0.10\text{Eu}^{3+}$	0.90	1	0.05
$\text{Sr}_{1-y}\text{In}_{1.75}\text{O}_4:(y+0.25)\text{Eu}^{3+}$ ($x = 0.25$)	0.25	0.02	$\text{Sr}_{0.98}\text{In}_{1.75}\text{O}_4:0.27\text{Eu}^{3+}$	0.98	0.875	0.135
	0.25	0.04	$\text{Sr}_{0.96}\text{In}_{1.75}\text{O}_4:0.29\text{Eu}^{3+}$	0.96	0.875	0.145
	0.25	0.06	$\text{Sr}_{0.94}\text{In}_{1.75}\text{O}_4:0.31\text{Eu}^{3+}$	0.94	0.875	0.155
	0.25	0.08	$\text{Sr}_{0.92}\text{In}_{1.75}\text{O}_4:0.33\text{Eu}^{3+}$	0.92	0.875	0.165
	0.25	0.10	$\text{Sr}_{0.90}\text{In}_{1.75}\text{O}_4:0.35\text{Eu}^{3+}$	0.90	0.875	0.175

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802 Table 2 PL emission peaks due to Eu^{3+} measured for $\text{SrIn}_{1.99}\text{O}_4:0.01\text{Eu}^{3+}$ under
803 excitation at 393 nm.

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Transition	Peak (nm)	Transition	Peak (nm)
$^5\text{D}_0 \rightarrow ^7\text{F}_0$	578	$^5\text{D}_0 \rightarrow ^7\text{F}_2$	611
	584		614
$^5\text{D}_0 \rightarrow ^7\text{F}_1$	586		616
	590		618
	592		624
	595		627