

EFFECT OF ALKALINE IONS ON THE PHASE EVOLUTION, PHOTOLUMINESCENCE, AND AFTERGLOW PROPERTIES OF SrAl₂O₄: Eu²⁺, Dy³⁺ PHOSPHOR

HYUNHO SHIN, SHAFQAT ULLAH, #KWANGHYUN CHUNG

Department of Materials Engineering, Gangneung-Wonju National University,
210-702 Gangneung, Gangwon, Republic of Korea

#E-mail: stream95@hanmail.net

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A series of SrAl₂O₄: Eu²⁺, Dy³⁺ long-afterglow (LAG) phosphors with varying concentration of Li⁺, Na⁺ and K⁺, has been synthesized. The increased concentration of the three types of alkaline ions does not decrease the quantity of the total luminescent phases (SrAl₂O₄ plus Sr₄Al₁₄O₂₃), but a different set of secondary phases has been evolved for the K⁺-added series due to the failure of the incorporation of relatively large K⁺ (1.38 Å) to the Sr²⁺ (1.18 Å) site in the hosts, unlike the cases of smaller Li⁺ (0.76 Å) and Na⁺ (1.02 Å) ions. PL excitation, PL emission, and LAG luminescence, are decreased by all investigated alkaline ions, which would be due to the diminished incorporation of Eu²⁺ and Dy³⁺ activators into the luminescent hosts by the alkaline ions. For the cases of the Li⁺ and Na⁺-added series, the incorporated Li⁺ or Na⁺ to the luminescent hosts would also limit the activation of Eu²⁺ and charge trapping/detrapping of Dy³⁺ to yield the diminished PL properties and LAG luminescence. The type of defect complex formed by the addition of Li⁺ and Na⁺ ions has been deduced and compared with that formed when no alkaline ion is added.

INTRODUCTION

Strontium aluminate phosphors have attracted much attention due to their high luminescence, high quantum efficiency, long-afterglow (LAG) luminescence, and chemical stability. The photoluminescence properties of strontium aluminates phosphors are strongly dependent on the crystal structures of host material and rare earth elements doped as activator [1-2].

Matsuzawa et al. [3] reported that when Dy³⁺ was added as a co-activator, SrAl₂O₄: Eu²⁺ phosphor with a strong emission at 520 nm demonstrated a persistence time longer than 16 hours. Eu²⁺ is the main activator which excites by a 4f-5d transition. The long-afterglow (LAG) luminescence is achieved by the charge trapping/de-trapping of Dy³⁺ [3-4].

In order to improve the LAG luminescence, not only the types and concentration of activators and co-activators [5-6], but also the influence of the auxiliary components having formal charges different from Eu²⁺ has been investigated [7-9]. As for the influence of alkaline ions as auxiliary component, the addition of Na⁺ to SrAl₂O₄: Eu²⁺, Dy³⁺ phosphor was simply shown to decrease the photoluminescence (PL) emission and LAG luminescence [8-9]. Only when [Sr] in starting batch was relatively deficient than [Al], the addition of Na⁺ could yield a comparable LAG performance to the case without Na⁺ [9]. However, these reports were based

on a fixed concentration of Na⁺. Thus far, no systematic investigation about the influence of the type and concentration of alkaline ions on the LAG property has been carried out. Here, we systematically investigate the effect of the concentration of three types of alkaline ions (Li⁺, Na⁺ and K⁺) on the crystal phase evolution, PL, and LAG luminescence. Also, an appropriate defect model for the incorporation of alkaline ions into the SrAl₂O₄ host has been deduced.

EXPERIMENTAL

The base composition to which alkaline ions are to be added has been selected as Sr_{0.96}Al_{1.96}O₄: 0.04Eu²⁺, 0.04Dy³⁺ + 0.3B₂O₃^{*}, based on our preliminary effort to ensure a good LAG luminescence. B₂O₃ is generally added as a flux [3-9]. For the incorporation of alkaline ions, a series of compositions was designed as follows by considering the nominal substitution of Sr site by alkaline ions: Sr_{0.96-x}Al_{1.96}O₄: 0.04Eu²⁺, 0.04Dy³⁺ + 0.3B₂O₃ + xM (x = 0 ~ 0.04 mol), where, M is Li⁺, Na⁺ and K⁺.

The raw powders, Sr₂CO₃ (Aldrich, 99.9 %), Al₂O₃ (Dongyang Chem., 99.9 %), Eu₂O₃ (Aldrich, 99.9 %),

^{*} The starting composition in the current work (Sr_{0.96}Al_{1.96}O₄: 0.04Eu, 0.04Dy) can also be regarded as 0.96(SrAl₂O₄) + 0.02Al₂O₃ + 0.04Eu₂O₃ + 0.04Dy₂O₃ + 0.3B₂O₃.

Dy₂O₃ (Aldrich, 99.9 %), H₃BO₃ (High Purity Chem., 99.9 %), Li₂CO₃ (Junsei, 99 %), Na₂CO₃ (High Purity Chem., 99 %), and K₂CO₃ (High Purity Chem., 99 %) were weighed and ball-milled in absolute ethanol medium by zirconia balls for 12 h at 100 rpm. After drying, the powders were uniaxially pressed at 30 MPa in a mold with 22 mm in diameter, followed by calcination at 1000°C for 4 h in air. The calcined body was pulverized by mortar and pestle to pass a 75 µm sieve, and heat treated at 1350°C for 4 h under flowing 10 % H₂ + 90 % N₂ atmosphere (1 liter/min) for the synthesis of the phosphors.

Crystal structure of the synthesized specimens was analyzed by X-ray diffractometer (D/MAX-2500H, Rigaku, Tokyo, Japan). For the quantitative analysis of the crystal phases, a Rietveld refinement of the obtained XRD patterns was performed by use of the RIETAN-FP software package [10]. The crystallographic data of each phase used in the refinement was from the database of the International Centre for Diffraction Data (ICDD).

For investigating excitation and emission properties, photoluminescence (PL) spectra were measured in the wavelength range of 280 to 700 nm using PL spectrometer (F-7000, Hitachi, Tokyo, Japan). For the evaluation of afterglow luminescence property, decay curves with continuous time were measured using luminescence meter (LS100, Minolta, Osaka, Japan). A D65 lamp (40 W) was irradiated to samples for 2 min before the measurement of decay curves.

RESULTS AND DISCUSSION

Effects of alkaline ions on the phase evolution, PL, and LAG property

Figure 1 shows XRD patterns of the three series of specimens with varying concentration of alkaline ions. In order to quantify the relative ratio of crystal phases in each series of compositions, XRD patterns in Figure 1a), b), and c) were refined by Rietveld analysis using the RIETAN-FP program package [10], and an example of the result is shown in Figure 2. The dotted and solid

lines indicate measured and simulated XRD patterns, respectively, and the bottom curve denotes the difference between the experiment and simulation. Table 1 summarizes the quantified percentages of each crystal phase by Rietveld refinement. In all of the compositions, SrAl₂O₄ appeared as the main crystal phase. For the cases of Li⁺- and Na⁺-added series, Dy-containing secondary phases such as AlDyO₃, Dy₄Al₂O₄, and Dy₃Al₅O₁₂ are noted. It has been reported that the incorporation of Dy³⁺ into the luminescent host is more hardly achieved than the Eu²⁺, thereby the Dy-containing secondary phases are often observed [11], which is the same as the cases in the Li⁺ and Na⁺-added series in the present study.

In the K⁺-added series, different set of secondary phases such as, Sr₄Al₁₄O₂₅, Sr₁₂Al₁₄O₃₃, Dy₄Al₂O₄, and EuAl₁₂O₉ are noted. In particular, a notable quantity of Sr₄Al₁₄O₂₅ (10~23 wt. %) is observed which is a greenish-blue emission host (495 nm) when activators Eu²⁺ and Dy³⁺ are incorporated [12]. The radii of the cation lattices are 1.18 and 0.53 Å for Sr²⁺ and Al³⁺, respectively. Thus, Li⁺ (0.76 Å) and Na⁺ (1.02 Å) ions are able to substitute for Sr²⁺ (1.18 Å), but K⁺ with larger ionic radius (1.38 Å) may not. Since a borate glass forms in the strontium aluminate phosphor synthesized with B₂O₃ flux [13], the un-doped K⁺ is believed to join the borate glass, and the K₂O-added glass would contribute to the stabilization of a different set of the secondary phases as seen in Table 1.

In the Li⁺-added series (Table 1), the increase in x yields no apparent change in the quantity of the main host phase SrAl₂O₄. In the Na⁺- added series, the quantity of SrAl₂O₄ is maximal at x = 0.02, while the quantity at x = 0.04 is still higher than that at x = 0. Interestingly, the increase of x in K⁺- added series results in the sacrifice of the main luminescent phase SrAl₂O₄ with the increased quantity of the secondary luminescent phase Sr₄Al₁₄O₂₅. Thus, the quantity of the total luminescent phases (SrAl₂O₄ plus Sr₄Al₁₄O₂₅) is not decreased; It is maximal at x = 0.02 ~ 0.03 (97.9 wt. %), while the quantity at x = 0.04 is still higher than the that at x = 0. From these findings, it can be said that the additions of all types of the investigated alkaline ions do not diminish the quantity of the total luminescent phases. Also, it can

Table 1. Percentage (wt. %) of crystal phases in the three series of compositions, quantified by a Rietveld refinement of the XRD patterns shown in Figure 1.

Phases	x=0	a) Sr _{0.96-x} Al _{1.96} O ₄ :Eu _{0.04} Dy _{0.04} Li _x				(b) Sr _{0.96-x} Al _{1.96} O ₄ :Eu _{0.04} Dy _{0.04} Na _x				(c) Sr _{0.96-x} Al _{1.96} O ₄ :Eu _{0.04} Dy _{0.04} K _x			
		x=0.01	x=0.02	x=0.03	x=0.04	x=0.01	x=0.02	x=0.03	x=0.04	x=0.01	x=0.02	x=0.03	x=0.04
SrAl ₂ O ₄	93.62	93.48	94.3	94.82	94.27	92.91	97.17	95.89	95.24	89.22	82.95	80.58	72.85
AlDyO ₃	1.82	1.93	1.08	0.83	0.21	2.64	0.73	0.5	3.57	–	–	–	–
Dy ₄ Al ₂ O ₄	4.56	4.59	4.25	4.14	3.13	4.44	1.11	2.03	1.2	0.15	1.68	2.19	3.47
Dy ₃ Al ₅ O ₁₂	–	–	0.37	0.21	2.39	–	0.99	1.58	–	–	–	–	–
Sr ₄ Al ₁₄ O ₂₅	–	–	–	–	–	–	–	–	–	10.14	14.95	16.49	22.98
Sr ₁₂ Al ₁₄ O ₃₃	–	–	–	–	–	–	–	–	–	0.2	0.39	0.56	0.62
EuAl ₁₂ O ₁₉	–	–	–	–	–	–	–	–	–	0.01	0.04	0.19	0.08

be said that alkaline ions are not simply doped to the luminescent phases (except K^+), but also significantly influence the type and quantity of the crystalline phases (including K^+).

Photoluminescence (PL) spectra and long-afterglow (LAG) luminescence of the series of specimens

are shown in Figures 3-4. The changes in maximum PL excitation/emission intensity (Figure 3) and LAG luminescence at 15 min of decay time (Figure 4) are compared in Figure 5 as functions of the concentration of alkaline ions. In Figure 3, excitation takes place at broad wavelengths ranging from UV to visible light regime with characteristic excitation peaks at 319, 369 (maximum excitation peak), and 396 nm. Emission occurs in the wavelength range from 450 to 650 nm with maximum emission peak at 520 nm. As reported in the literature [3-4], these excitation and emission appear as a result of the $5d-4f$ transition of Eu^{2+} .

In Figure 3, no apparent peak shift in PL excitation/emission spectra is noted as the alkaline ions (Li^+ , Na^+ , and K^+) are added. This finding indicates that Eu^{2+} is the only source for excitation and emission. As for the peak intensity, however, both PL excitation (Figure 5a) and emission (Figure 5b) intensities show decreasing trends with the addition of the alkaline ions. Because the quantity of the total luminescent phase (SrAl_2O_4 plus $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$), is not decreased by the addition of the alkaline ions (Table 1), it is believed that the addition of all types of the alkaline ions is interpreted to degrade the quality of the luminescent phases in light of the incorporation of Eu^{2+} . It has been reported that the incorporation of activators to the luminescent hosts is significantly influenced by the crystal phase evolution during the synthesis of a LAG phosphor [11]. The unincorporated Eu^{2+} is believed to form the Eu -containing phase or join the borate glass. For the cases of Li^+ - and Na^+ -added series, there also

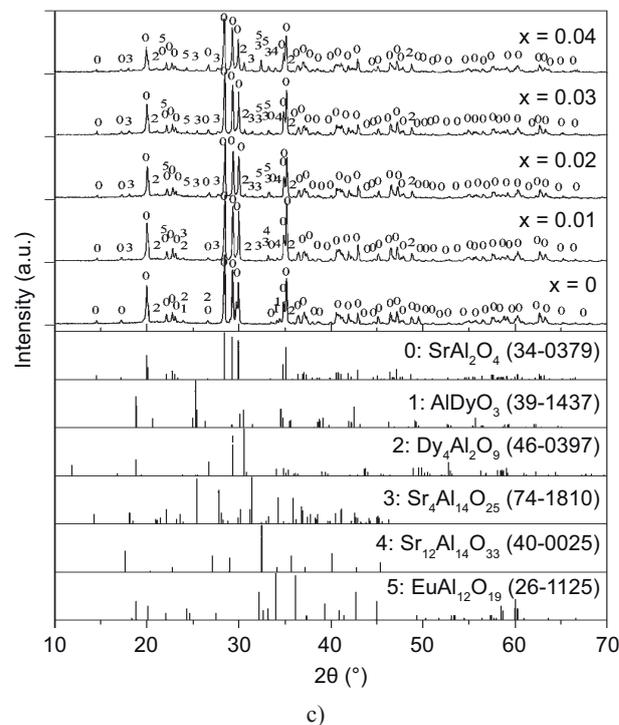
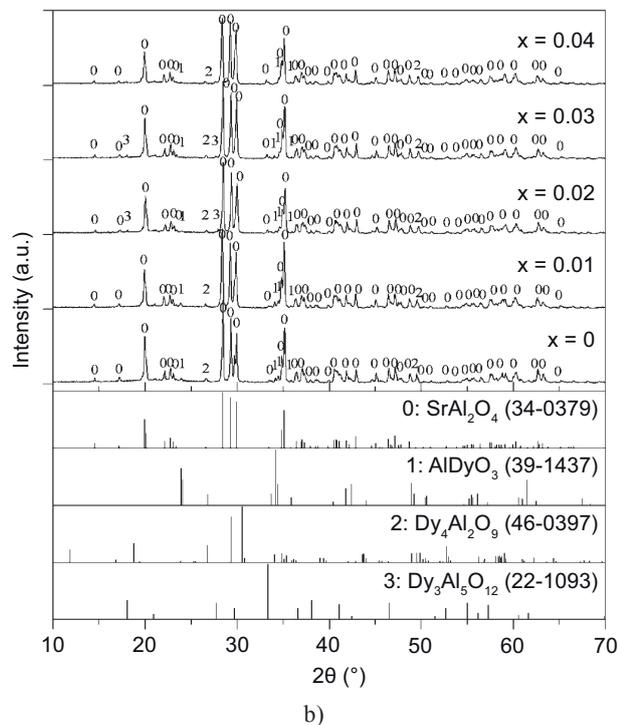
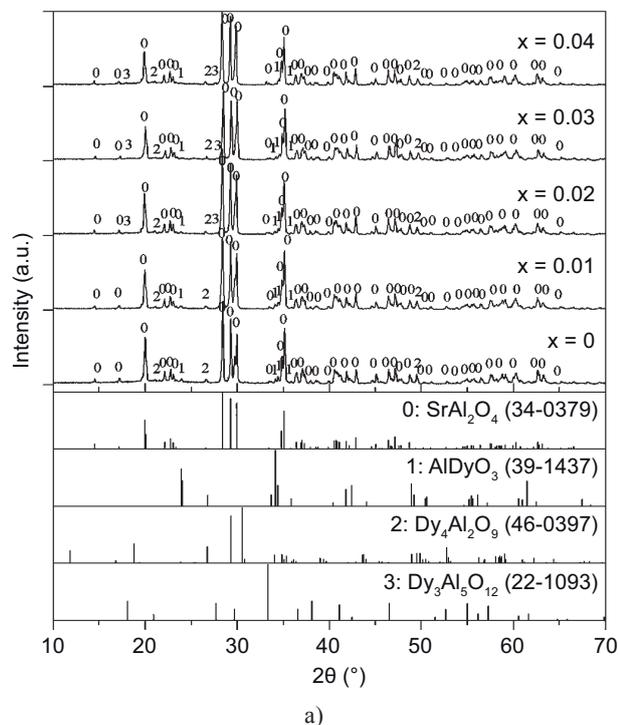


Figure 1. X-ray diffraction patterns from: a) Li^+ -added series of specimens; b) Na^+ -added series of specimens; c) K^+ -added series of specimens.

exists a possibility that the Li^+ or Na^+ incorporated to the luminescent hosts limit the functioning (activation) of Eu^{2+} to yield the diminished PL excitation and emission.

At 1 ~ 3 mol % addition, regardless of the type of the alkaline ions, the PL excitation/emission intensities are roughly similar (Figures 5a and 5b), indicating that the roles of the investigated alkaline ions in limiting the functioning/incorporation of Eu^{2+} activator are

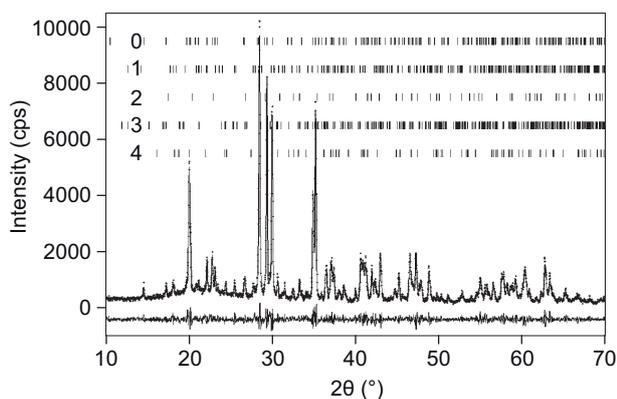


Figure 2. Result of a Rietveld refinement of XRD pattern for $\text{Sr}_{0.96-x}\text{Al}_{1.96}\text{O}_4: 0.04\text{Eu}, 0.04\text{Dy}, x\text{K}$ ($x = 0.03$) by the RIETAN-FP program package [10]. Peak positions marked at the rows of 0, 1, 2, 3 and 4 are for SrAl_2O_4 , $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, $\text{Sr}_{12}\text{Al}_{14}\text{O}_{33}$, $\text{Dy}_4\text{Al}_2\text{O}_9$, and $\text{EuAl}_{12}\text{O}_{19}$, respectively.

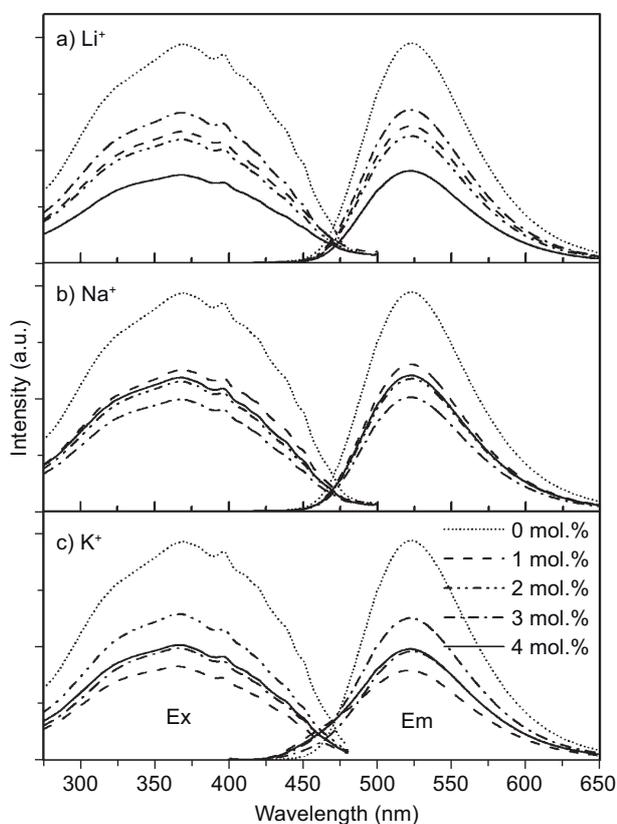


Figure 3. PL excitation and emission spectra of the investigated series of specimens: a) Li^+ , b) Na^+ , and c) K^+ .

similar. The data scatter¹ of PL excitation/emission at 4 mol % may be associated with the complicated crystal phase evolution, which influences the incorporation of activators to the luminescent hosts [11], as mentioned.

As for the LAG property, the addition of the three investigated types of the alkaline ions monotonically decreases the LAG luminescence up to 4 mol % of the alkaline ions (Figure 5c). It has been reported that long after-glow luminescence is not simply governed by the quantity of the luminescent phase but also by the quality of it, i.e., the degree of the successful activator incorporation of especially the Dy^{3+} [11]. The actually incorporated quantity of the activators into the luminescent host is believed to be far less than the nominally added quantity [11]. At 1 ~ 3 mol % additions of the alkaline ions, the PL excitation/emission intensities (which are governed mainly by the activation of Eu^{2+}) are more or less similar regardless of the type of alkaline ions (Figures 5a and 5b). However, the LAG luminescence (which is governed both by Eu^{2+} and Dy^{3+}) follows the order of the phase quantity of the main host, i.e., $\text{Na}^+ > \text{Li}^+ > \text{K}^+$ (at 1 ~ 3 mol %). Because the influence of alkaline ions is more or less similar in the excitation and incorporation process

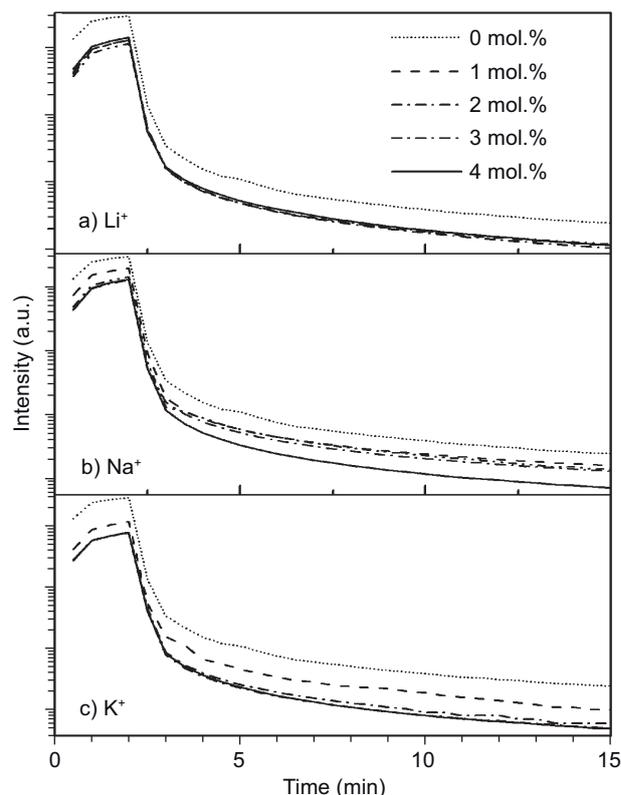


Figure 4. Afterglow properties of the investigated series of specimens: a) Li^+ , b) Na^+ , and c) K^+ .

¹ The data scatter of PL and LAG luminescence, especially the cross-over of the trend at 3 ~ 4 mol % was checked again by separate experiments, while the same trend was recorded like the case in Figure 5.

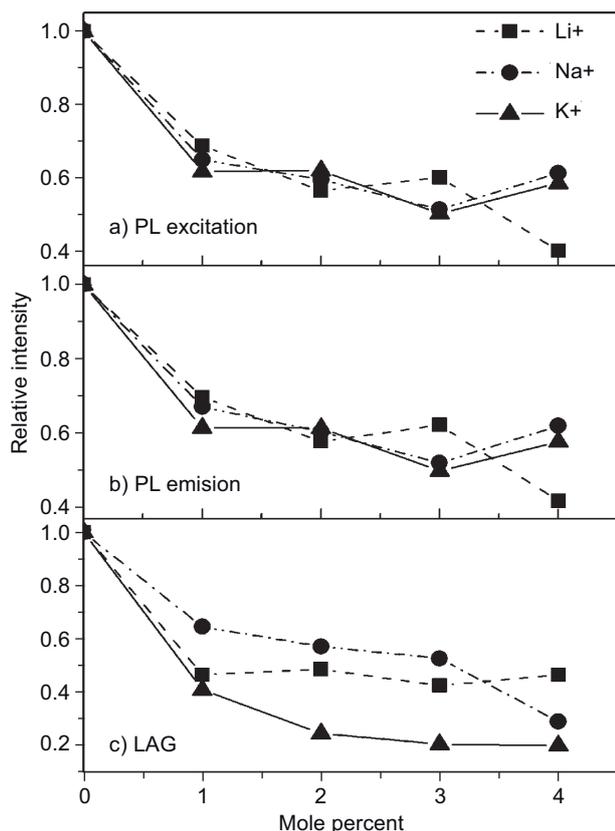


Figure 5. Change in relative intensity of the synthesized phosphors as functions of the concentration of alkaline ions. a) PL excitation, b) PL emission, and c) afterglow property at the decay time of 15 min (all data in Figure 5 are determined from Figures 3-4).

of Eu^{2+} , the degree of diminishing the functioning^{2/} incorporation of Dy^{3+} is different depending on the type of the alkaline ions; The functioning/incorporation of Dy^{3+} is most incapacitated by the addition of K^+ and least by Na^+ . In particular, since K^+ is not suitably incorporated to the luminescent host due to its ionic size, the decrease of the LAG luminescence by the K^+ addition is believed to be due to the diminished incorporation of Dy^{3+} into the luminescent phases by the K^+ addition rather than due to the de-functioning of Dy^{3+} by the incorporated K^+ .

Defects formed by the incorporation of the alkaline ions

The structure of the main host phase SrAl_2O_4 is built up of the framework of corner sharing AlO_4 tetrahedra, and the structural channels formed by the AlO_4 units are occupied by Sr^{2+} ions [13]. Although the formal charge of Dy^{3+} is the same as Al^{3+} , it may not substitute for Al^{3+} because Dy^{3+} (0.91 Å) has much larger ionic radius than Al^{3+} (0.53 Å). Instead, Dy^{3+} is believed to substitute for Sr^{2+} (1.18 Å) together with Eu^{2+} (1.17 Å) [13]. Then,

considering the charge neutrality, the incorporation of Dy^{3+} to Sr^{2+} is anticipated to accompany the formation of Sr vacancy³:



Actually, other possibilities of defect reaction are hardly imaginable at this moment considering the sizes of the ions and charge neutrality. Reaction (1) tells that V_{Sr}'' defect ($\text{Dy}_{\text{Sr}}^{\bullet} - V_{\text{Sr}}'' - \text{Dy}_{\text{Sr}}^{\bullet}$ complex) exists in the main host. From the reportedly good PL and LAG performance of the non-alkali-added compositions [13], it is believed that the energy level of V_{Sr}'' is fairly different from those of Eu^{2+} and Dy^{3+} , thereby yielding no notable interaction with the functions of Eu^{2+} (excitation) and Dy^{3+} (thermal trapping/de-trapping of charges).

When alkaline ions are present, the charge neutrality due to the addition of Dy^{3+} is proposed to be maintained by⁴



where M is the alkaline element (Li and Na). Considering the sizes of the cation lattices and alkaline ions as before, other possibilities of defect reaction are hardly imaginable at this moment. In lights of reactions (1) and (2), the incorporation of Dy^{3+} under the presence of alkaline ions avoids the formation of cation (Sr^{2+}) vacancy, but forms a new type of defect complex $\text{Dy}_{\text{Sr}}^{\bullet} - \text{M}_{\text{Sr}}'$. The detailed role of M_{Sr}' defect (M = Li and Na) in limiting the functioning the roles of Eu^{2+} (activation) and Dy^{3+} (charge trapping/detrapping) by the incorporated Li^+ and Na^+ needs further work.

CONCLUSION

A series of LAG phosphors with the following nominal composition, $\text{Sr}_{0.96-x}\text{Al}_{1.96}\text{O}_4$: 0.04Eu^{2+} , $0.04\text{Dy}^{3+} + x\text{M} + 0.3\text{B}_2\text{O}_3$ ($x = 0 \sim 0.04$), have been synthesized (M is Li^+ , Na^+ or K^+). The increased concentration of the three types of alkaline ions does not decrease the quantity of the total luminescent phases (SrAl_2O_4 plus $\text{Sr}_4\text{Al}_4\text{O}_{25}$). The K^+ -added series yields a different set of secondary phases from the cases of Li^+ and Na^+ - added series. This observation is ascribed to the fact that K^+ ion (1.38 Å) is not suitably incorporated to the Sr^{2+} site of the luminescent phase due to the much bigger ionic size of K^+ (1.38 Å) than Sr^{2+} (1.18 Å), unlike the cases of Li^+ (0.76 Å) and Na^+ (1.02 Å). The alkaline ions are not simply doped to the luminescent phases (except K^+), but also significantly influence the type and quantity of the crystalline phases (including K^+).

The additions of all types of the alkaline ions yield decreasing trends of PL excitation, PL emission, and LAG luminescence, which phenomena would be due to

² The function of Dy^{3+} is trapping and detrapping of the excited charge by Eu^{2+} , as mentioned.

³ $\text{Dy}_2\text{O}_3 \xrightarrow{3\text{SrAl}_2\text{O}_4} 2\text{Dy}_{\text{Sr}}^{\bullet} + V_{\text{Sr}}'' + 6\text{Al}_{\text{Al}} + 12\text{O}_0$

⁴ $\text{M}_2\text{O} + \text{Dy}_2\text{O}_3 \xrightarrow{4\text{SrAl}_2\text{O}_4} 2\text{Dy}_{\text{Sr}}^{\bullet} + 2\text{M}_{\text{Sr}}' + 8\text{Al}_{\text{Al}} + 16\text{O}_0$

the degraded quality of the luminescent phases in light of the incorporations of Eu^{2+} and Dy^{3+} activators into the luminescent hosts. As for the Li^+ and Na^+ - added series, the incorporated Li^+ or Na^+ into the luminescent hosts would also limit the activation of Eu^{2+} and charge trapping/detrapping of Dy^{3+} to yield the diminished PL and LAG luminescence.

At 1 ~ 3 mol % additions of the alkaline ions, the PL excitation/emission intensities (which is governed mainly by the activation of Eu^{2+}) are more or less similar regardless of the alkaline ion type, while the LAG luminescence (which is governed both by Eu^{2+} and Dy^{3+}) follows the order of $\text{Na}^+ > \text{Li}^+ > \text{K}^+$. These findings indicate that the degree of diminishing the functioning/incorporation of Eu^{2+} is more or less similar regardless of the type of the alkaline ions, while the degree for Dy^{3+} is different. By the addition of Li^+ or Na^+ , it is deduced that the defect type in the main host changes from $Dy_{Sr} \cdot -V_{Sr}'' - Dy_{Sr} \cdot$ complex to $Dy_{Sr} \cdot -M_{Sr}'$ ($M = \text{Li}$ or Na) complex.

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