

Luminescent properties of (Na,M)AlSiO₄:Eu²⁺ phosphors (M = Li, K, Mg, Ca)

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A series of (Na_{1-x} or x/2M_x)AlSiO₄:0.1Eu²⁺ phosphors (M = Li⁺, K⁺, Mg²⁺, Ca²⁺) were synthesized at 1200 °C under reducing atmosphere by a liquid phase precursor (LPP) method in order to achieve new luminescent properties with the different metals in x = 0.1 ~ 0.4 concentrations. The main photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the obtained phosphors were broadly located from 320 nm to 410 nm and from 485 nm to 548 nm, respectively. These excitation spectra of Li-NAS:Eu²⁺, K-NAS:Eu²⁺, Ca-NAS:Eu²⁺ and Mg-NAS:Eu²⁺ phosphors showed a red-shift compared with the standard NaAlSiO₄:Eu²⁺ (NAS:Eu²⁺) phosphor. The main emission spectra were centered at 480 nm (blue), 544 nm (green), 548 nm (yellowish green), respectively, which suggested their prospective potential in application of near-UV pumped white light-emitting diode (n-UV WLED).

Key words: NaAlSiO₄:Eu²⁺, Metal dopant, n-UV LED, White LED, Aluminosilicate phosphor.

Introduction

The study of high efficient silicate phosphors has been receiving a lot of spotlight since the phosphor materials are playing a key role in the lighting and display. Especially it's urgent to develop high efficient phosphors fit for application in the white-light emitting diodes (WLED) which is the promising candidate for next generation solid state lighting [1-2]. A novel NaAlSiO₄:Eu²⁺ (NAS:Eu²⁺) phosphor suitable for application in WLEDs has been synthesized using a liquid phase precursor (LPP) method in our previous work [3]. Moreover, Increasing attention has been paid to the development of new phosphors that can be excited in the near-UV (370-420 nm) to enhance the efficiency of white light emitting solid-state devices [4].

A good candidate in WLEDs, NAS:Eu²⁺ phosphor exhibited a broad excitation spectrum from 230 to 450 nm and a yellowish-green emission spectrum centered at 551 nm [3]. NAS:Eu²⁺ phosphor consisted of alternative frameworks of AlO₄⁵⁻ and SiO₄⁴⁻ with alkali cations in the interstices, which occupied 8-, 9-coordination (8-, 9-cn) [5]. The sturdy framework of the NAS:Eu²⁺ phosphor caused the stable emission in the evaluation of thermal quenching properties compared with YAG:Ce³⁺ phosphor [6]. The broad wavelength excitation, good emission properties and better thermal quenching properties suggested that NAS:Eu²⁺ phosphor is a prospective candidate for application in WLEDs based on near-ultraviolet (n-UV WLEDs) chips [7].

It's also quite important to explore the potential of phosphor materials for achieving tunable emission color since the pure blue, green, and red emissions are important in n-UV WLEDs. However, the potential of NAS:Eu²⁺ phosphor has not been well studied. In order to adjust blue- or red-shift of emission, alkali and alkali earth metals are usually used for substituting the cations of the phosphor host materials. In this study, Li⁺ (8-cn: 0.92 Å), K⁺ (8-cn: 1.51 Å, 9-cn: 1.55 Å), Mg²⁺ (8-cn: 0.86 Å), and Ca²⁺ (8-cn: 1.12 Å) metal ions which have similar size with Na⁺ ion (8-cn: 1.18 Å, 9-cn: 1.24 Å) were employed in the synthesis of (Na,M)AlSiO₄:Eu²⁺ phosphors using the LPP method and the novel properties of these new phosphors under 400 nm excitation were investigated [8].

Experiment

A series of (Na_{1-x} or 2xM_x)AlSiO₄:0.1Eu²⁺ (M: Li⁺, K⁺, Mg²⁺, Ca²⁺; x = 0.1 ~ 0.4) phosphors with different concentration of doped metals were prepared by a liquid-phase precursor (LPP) method using NaCl₃ (99.8%), Al(NO₃)₃ · 9H₂O (99.5%), EuCl₃ · 6H₂O (99.5%), LiNO₃ (98%), KNO₃ (99%), Mg(NO₃)₂ · 6H₂O (98%), Ca(NO₃)₂ · 4H₂O (98%) salts, and SiO₂ sol (20.0%) as raw materials. All the raw materials were of Aldrich or chemical company grade. The Na, Al, Eu, Li, K, Mg, Ca raw materials were dissolved in deionized water at weight concentration of 30, 50, 20, 10, 10, 10, and 10 wt%, respectively. And then these solutions were mixed in terms of the targeted compositions. Subsequently the mixed solutions were impregnated into 20 μm crystalline cellulose powder (Aldrich grade). The impregnated precursors were heated at 700 °C for 2 hrs

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in air and then at 1200 °C for 3 hrs under a reducing atmosphere (N_2/H_2 -95/5%). Finally a series of $(Na,M)AlSiO_4:Eu^{2+}$ phosphors were obtained.

These phosphors were analyzed by the photoluminescence (PL) measurement at room temperature using a fluorescent spectrometer (Drasa PRO 5300, 500W, Korea) equipped with a xeno lamp as the excitation source. The influence of the varying metal ions on their luminescent properties was further studied based on these examinations.

Result and Discussion

The PLE and PL spectra of $(Na_{1-x}Li_x)AlSiO_4:0.1Eu^{2+}$ (Li-NAS:Eu²⁺) were displayed in Fig. 1. They generally shows the broad excitation and emission spectra corresponding to the $4f^7 \rightarrow 4f^65d^1(^8S_{7/2})$ transition of Eu^{2+} . Variation of the x values indicated that emission spectra slightly moved to some blue-shifts, as wavelength located at 545 nm (x = 0.1) and 548 nm (x = 0.2). The phosphors of x = 0.3 and 0.4 were sintered. Excitation region was covered from 220 to 450 nm and each emissions under 400 nm excitation were displayed as ~112.9% (x = 0.1) and ~149.5% (x = 0.2) of maximum. These red-shifting phenomena of their excitation spectra may be attributed to high crystal field splitting effect due to a strong covalent bonding of Li^+ [9].

Fig. 2 shows the PLE and PL spectra of $(Na_{1-x}K_x)AlSiO_4:0.1Eu^{2+}$ (K-NAS:Eu²⁺). While the x value was increased, the emission spectra of K-NAS:Eu²⁺ exhibited bluish-shift from 534 nm (x = 0.1) to 495 nm, 486 nm, and 486 nm (x = 0.2, 0.3, and 0.4). In the blue-emission region for x > 0.1, both the excitation and emission intensity increased with increase of K^+ ion concentration. K-NAS:Eu²⁺ phosphors had broad excitation spectra covering from 220 to 450 nm. However, the intensities under 400 nm excitation for each phosphor were not high, to ~57% green (x = 0.1), and ~28.2%, ~34.8%, and 41.8% blue (x = 0.2, 0.3, and 0.4) compared to the standard NAS:Eu²⁺ phosphor. These blue-shifting phenomena may be assigned to the fact that the low crystal-field splitting effect was enhanced since the smaller Na^+ ions were substituted by the larger K^+ ions [10].

Fig. 3 shows PLE and PL spectra of $(Na_{1-x/2}Mg_x)AlSiO_4:0.1Eu^{2+}$ (Mg-NAS:Eu²⁺). The increments of x value caused emission and excitation spectra red-shifting, as 509 nm (x = 0.05), 520 nm (x = 0.1), 529 nm (x = 0.2) and 543 nm (x = 0.3) and each intensity of the emission under 400 nm excitation were displayed as ~37.5% (x = 0.1), ~35.8% (x = 0.2), ~42.6% (x = 0.3), ~55.9% (x = 0.4), compared to the standard NAS:Eu²⁺ phosphor, respectively. These phenomena may be attributed due to smaller ion-radius of Mg^{2+} than Na^+ ion and a little of stronger covalent bonding [11].

Fig. 4 shows PLE and PL spectra of $(Na_{1-x/2}Ca_x)AlSiO_4:0.1Eu^{2+}$ (Ca-NAS:Eu²⁺). The variation of

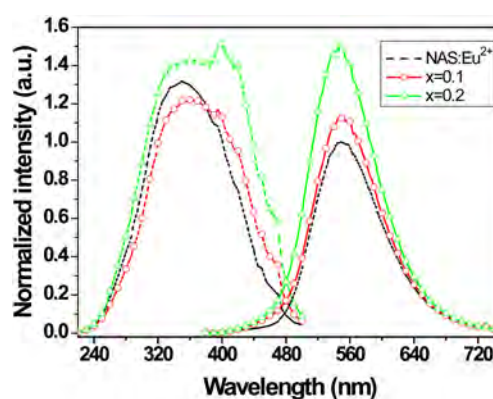


Fig. 1. PL properties of $(Na_{1-x}Li_x)AlSiO_4:0.1Eu^{2+}$ phosphors depend on x values, dotted line with symbol: excitation spectra, solid line with symbol: emission spectra and dotted line: standard NAS:Eu²⁺ phosphor (λ_{em} : 400 nm, λ_{ex} : 551 nm).

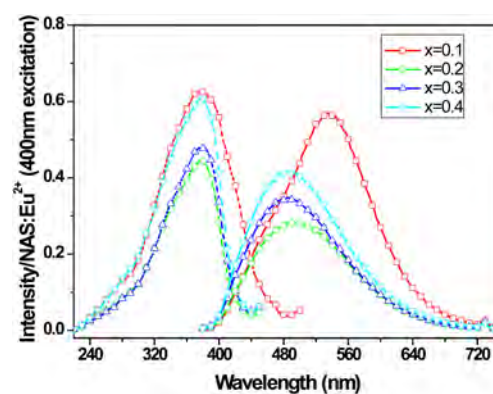


Fig. 2. PL properties of $(Na_{1-x}K_x)AlSiO_4:0.1Eu^{2+}$ phosphors, dotted line with symbol: excitation spectra and solid line with symbol: emission spectra.

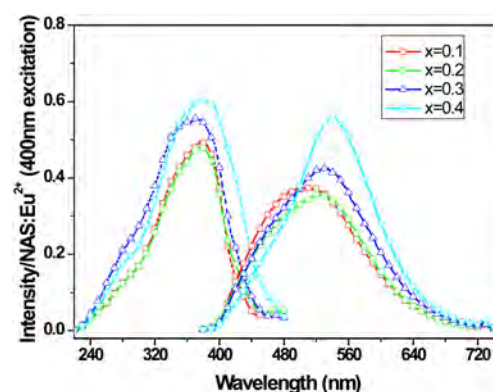


Fig. 3. PL properties of $(Na_{1-x/2}Mg_x)AlSiO_4:0.1Eu^{2+}$ phosphors depend on x values, dotted line with symbol: excitation spectra and solid line with symbol: emission spectra.

x values indicated some red-shifts of emission and excitation spectra, as 485 nm (x = 0.1), 493 nm (x = 0.2), 535 nm (x = 0.3) and 544 nm (x = 0.4) and excitation region of Ca-NAS:Eu²⁺ phosphors showed broad spectra and each emissions under 400 nm excitation were displayed as ~27.8% (x = 0.1), ~31.2% (x = 0.2), ~60.3% (x = 0.3), ~71.1% (x = 0.4) compared to the standard NAS:Eu²⁺ phosphor, respectively. These red-shifting

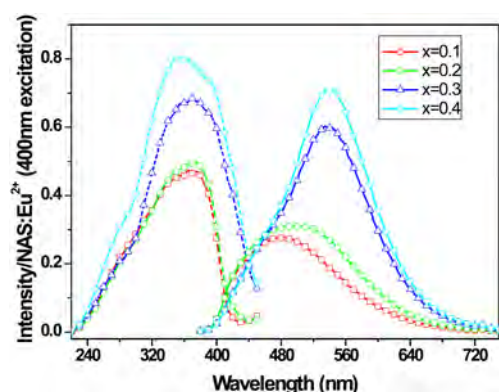


Fig. 4. PL properties of $(\text{Na}_{1-x}\text{Ca}_x)\text{AlSiO}_4:0.1\text{Eu}^{2+}$ phosphors depend on x values, dotted line with symbol: excitation spectra and solid line with symbol: emission spectra.

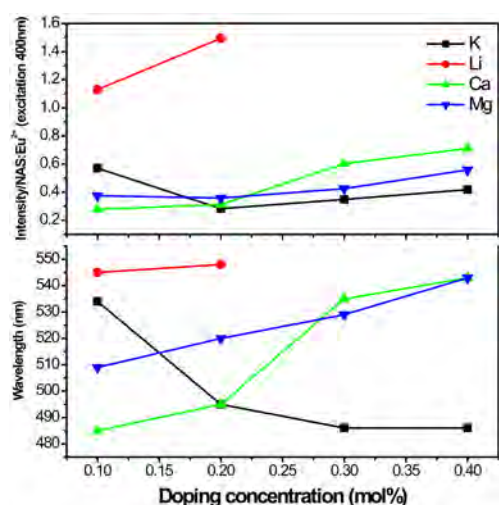


Fig. 5. PL properties under 400 nm of $(\text{Na}_{1-x}\text{ or } x/2 \text{M}_x)\text{AlSiO}_4:\text{Eu}^{2+}$ ($\text{M}: \text{Li}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}$) phosphors depend on x values compared with standard $\text{NAS}:\text{Eu}^{2+}$ phosphor (Intensity: 1.0, λ_{em} : 400 nm, λ_{ex} : 551 nm).

phenomena may be attributed due to a little of stronger covalent bonding. Whereas, high crystal-field splitting effects would be lower because ion-radiuses between Ca^{2+} and Na^+ are similar [12].

Fig. 5 is exhibited as summary of PL properties for $(\text{Na},\text{M})\text{AlSiO}_4:\text{Eu}^{2+}$ ($\text{M}: \text{Li}^+, \text{K}^+, \text{Mg}^{2+}, \text{Ca}^{2+}$) phosphors. The normalized intensity of each phosphors was compared with the standard $\text{NAS}:\text{Eu}^{2+}$ phosphor without dopant materials. According to concentration of metal dopant, intensity and emission wavelength of the phosphors was dominated. In case of $\text{Ca-NAS}:\text{Eu}^{2+}$ and $\text{Li-NAS}:\text{Eu}^{2+}$ phosphors, the intensity were gradually increased, respectively. The emission of $\text{Ca-NAS}:\text{Eu}^{2+}$ phosphor was red-shifting with increasing of x value, however, $\text{Li-NAS}:\text{Eu}^{2+}$ phosphor did not change. The intensity of $\text{K-NAS}:\text{Eu}^{2+}$ phosphor was decreased at $x = 0.2$, and the intensity was gradually increased again at $x = 0.3, 0.4$ values. The emission of $\text{K-NAS}:\text{Eu}^{2+}$

phosphor was blue-shifting as increasing x values. The emission of $\text{Mg-NAS}:\text{Eu}^{2+}$ phosphor was red-shifting as x value increased. The intensity of $\text{Mg-NAS}:\text{Eu}^{2+}$ phosphor was slightly decreased in series of $x = 0.1, 0.2$, and 0.3 values, and when x value reached at 0.4 , the intensity was increased.

Conclusions

$(\text{Na}_{1-x}\text{ or } 2x\text{M}_x)\text{AlSiO}_4:0.1\text{Eu}^{2+}$ phosphors ($\text{M} = \text{Li}^+, \text{K}^+, \text{Mg}^{2+}$ and Ca^{2+}) were synthesized at 1200°C by using a liquid phase precursor (LPP) method with the different metals in the range from $x = 0.1 \sim 0.4$ concentrations. The emission did not shift to a red light because the strong framework of $\text{NAS}:\text{Eu}^{2+}$ phosphor may prevent crystal splitting effect. However, we found the mostly potential candidate in application of white n-UV LED phosphors which was especially $\text{Li-NAS}:\text{Eu}^{2+}$ phosphor, showing 1.49 times higher intensity compared with $\text{NAS}:\text{Eu}^{2+}$ phosphor and 548 nm (yellowish green) emission spectra under 400 nm excitation.

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References

1. R.J. Xie, N. Hirosaki, M. Mitomo, K. Sakuma, and N. Kimura, *App. Phys. Lett.* 84 (2006) 2737375.
2. J.H. Seong, and J.D. Young, *App. Phys. Lett.* 90 (2007) 041906.
3. D.S. Jo, K.H. Choi, K. Toda, T. Masaki, and D.H. Yoon, *J. Ceramic. Pro. Res.* 12 (2011) s47-s50.
4. D.A. Steigerwald, J.C. Bhat, D. Collins, R.M. Fletcher, M.O. Holcomb, M.J. Ludowise, P.S. Martin, and S.L. Rudaz, *IEEE J. Sel. Top. Quantum Electron.* 8 (2002) 310-320.
5. M. Nayak, and T.R.N. Kutty, *Mater. Chem. Phys.* 57 (1998) 138-146.
6. D.S. Jo, Y.Y. Luo, K. Senthil, K. Toda, B.S. Kim, T. Masaki, and D.H. Yoon, *J. Opt. Mat.* 4 (2011) in press.
7. K. Uheda, N. Hirosaki, Y. Yamamoto, A. Naito, T. Nakajima, and H. Yamamoto, *Electrochem. Solid State Lett.* 9 (2006) H22-H25.
8. R.D. Shannon, *Acta Cryst.* A32 (1976) 751-767.
9. Y.Q. Li, N. Hirosaki, R.J. Xie, T. Takeka, and M. Mitomo, *J. Solid State Chem.* 182 (2009) 301-311.
10. A.E. Abiad, M. Mesnaoui, M. Maazaz, C. Parent, and G.L. Flem, *J. Solid State Chem.* 170 (2003) 450-457.
11. H. He, R. Fu, X. Song, D. Wang, and J. Chen, *J. Lumin.* 128 (2008) 489-493.
12. M. Hirayama, N. Sonoyama, A. Yamada, and R. Kanno, *J. Solid State Chem.* 182 (2009) 730-735.