Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 38S (2012) S563–S566

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis and luminescent properties of Al_2O_3–SiO_2 phosphors

Jun Seong Lee, Young Jin Kim *

Department of Materials Science and Engineering, Kyonggi University, Suwon 443-760, Republic of Korea

Abstract

$3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders were prepared at various temperatures of 1100–1600 °C under H_2 atmosphere. XRD data showed that three phases of α-Al_2O_3, quartz, and amorphous SiO_2 were produced at 1100–1400 °C, exhibiting strong greenish-blue emissions around 475–485 nm. With the increase in the temperature the red-shift in PLE spectra was observed and also two discrete peaks apparently appeared. Mullite single phase could be achieved at 1500–1600 °C, and it exhibited similar luminescent spectra to that of the mixed phase at 1100–1400 °C. The firing atmosphere affected the emission and excitation properties of Eu^{2+} doped mullite powders.

Keywords: A. Powders: solid state reaction; C. Optical properties; D. Mullite; E. Functional applications

1. Introduction

Eu^{2+}/Eu^{3+} ions doped aluminum silicates systems (xAl_2O_3–$ySiO_2$) such as mullite have been investigated as phosphors for fluorescent lamps and white light emitting diodes (LEDs).

The representative composition of aluminum silicates is Al_2SiO_5, which has three polymorphs: sillimanite, andalusite, and kyanite [1]. Mullite can be synthesized by using these materials as precursors, and has been recognized as a promising candidate for the structural and functional applications due to its low thermal expansion, low thermal capacity, and high creep resistance [2]. The composition of mullite is very wide, ranging from $3Al_2O_3$–$2SiO_2$ to $2Al_2O_3$–SiO_2, which are referred to as 3/2- and 2/1-mullite, respectively. In mullite, the Al sites occupy either octahedral or tetrahedral sites, while Si is tetrahedrally coordinated in the same manner with sillimanite. However, the tetrahedral cation sites are occupied partially by Al or Si [3–7]. Previous works reported that the photoluminescence (PL) spectra of Eu^{2+} doped mullite exhibited the blue emission, of which peak wavelengths depended on the Al/Si ratios [3,8]. Kutty and Nayak [3] demonstrated that Eu^{2+} ion preferred the structural cavity rather than 6- or 4-coordinated regular lattice sites because of its large ionic radius, and the increase in the SiO_2 content caused the red-shift due to the enhanced covalency (nephelauxetic effect). Wechtel [9] widely examined the blue emission properties of $(1-x)Al_2O_3$–$xSiO_2$:Eu^{2+}, and concluded that Eu^{2+} ions were located between mullite and the second phase (amorphous SiO_2 or α-Al_2O_3). Besides mullite system, PL properties of Eu^{2+} doped Al_2O_3–SiO_2 glasses [10,11] and Eu^{3+}/Eu^{2+} doped α(γ)-Al_2O_3 powders [12–14] were also studied. They all showed blue emissions by doping Eu^{2+} ions.

Eu^{2+} doped phosphors usually generate broad absorption and emission spectra because of the energy transitions between $4f^7$ and $4f^65d^1$ configurations, which are dipole-allowed and strongly depend on the crystal field surrounding Eu^{2+} ions. Consequently, the luminescent properties closely rely on the host materials. Most of the Eu^{2+} activated aluminum silicates, for instance, exhibit blue emissions. Meanwhile, the excitation spectra of Eu^{3+} ions consist of sharp peaks due to f–f energy transition, leading to the narrow red emission band due to $^5D_0$–^7F_J transition in most cases.

In spite of many works on the luminescent properties of xAl_2O_3–$ySiO_2$, a correlation between the created phases and emission characteristics is not clear so far. In this experiment, Eu ions doped $3Al_2O_3$–$2SiO_2$ mixtures were fired at the various temperatures, and we investigated the creation of various phases and their contribution to the luminescence.

2. Experimental

Al_2O_3 (High Purity Chemicals, 99.99%), SiO_2 (High Purity Chemicals, 99.9%) and Eu_2O_3 powder (United International

---

* Corresponding author. Tel.: +82 31 249 9766; fax: +82 31 244 6300.
E-mail address: yjkim@kyonggi.ac.kr (Y.J. Kim).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.05.098

Inc., 99.99%) were used as starting materials. The mixture of $3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders were ball-milled for 24 h with Teflon balls, and then fired at various temperatures of 1100–1600 °C introducing 5% H_2 (95% N_2) gas by 50 sccm in an electric tube furnace for the reduction process $Eu^{3+} \rightarrow Eu^{2+}$ [14]. The crystalline phases of prepared powders were determined by X-ray diffractometer (XRD, Rigaku Miniflex 2) using CuK_α radiation (λ = 1.5406 Å). Photoluminescence (PL) properties were measured by PL system (PSI Darsa-5000) with a xenon lamp as an excitation source at the room temperature.

3. Results and discussion

XRD patterns of $3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders (3/2-mullite composition) prepared at various temperatures of 1100–1600 °C under H_2 atmosphere are shown in Fig. 1. At 1100–1400 °C, both α-Al_2O_3 and quartz peaks dominantly appeared. With increasing the temperature up to 1400 °C, α-Al_2O_3 peaks did not change, whereas quartz peaks gradually decreased, indicating that amorphous SiO_2 phase was produced more. At 1400 °C, cristobalite phase appeared, but its amount was negligible. At 1500–1600 °C, the crystal structure was drastically transformed to 3/2-mullite single phase, while an insignificant amount of α-Al_2O_3 remained un-reacted.

Corresponding PL excitation (PLE) spectra are shown in Fig. 2. With increasing the temperature up to 1400 °C, PLE intensity gradually increased and two excitation peaks (~ 325 and ~360 nm) became more apparent. PLE spectra at 1500–1600 °C were similar to those at 1100–1400 °C, but they generated from the distinctive activation mechanism of Eu^{2+} ions because of the different host crystal structure. Related PL spectra show greenish-blue emissions around 470–490 nm in all samples (Fig. 3). These results are closely related to the synthesized host crystal structures. The samples prepared at 1100–1400 °C were composed of α-Al_2O_3, quartz, and amorphous SiO_2 phase as described in Fig. 1. The greenish-blue emission of Eu^{2+} doped α-Al_2O_3 + quartz + amorphous SiO_2 phases has not been reported yet, but the luminescence obviously generated from Eu^{2+} ions incorporated in these mixed phases. We cannot verify the luminescent mechanism of Eu^{2+} doped these mixed phases including the location of Eu^{2+} ions and the role of each phase at present. But a couple of possible luminescent mechanisms could be considered based on the previous works as follows.

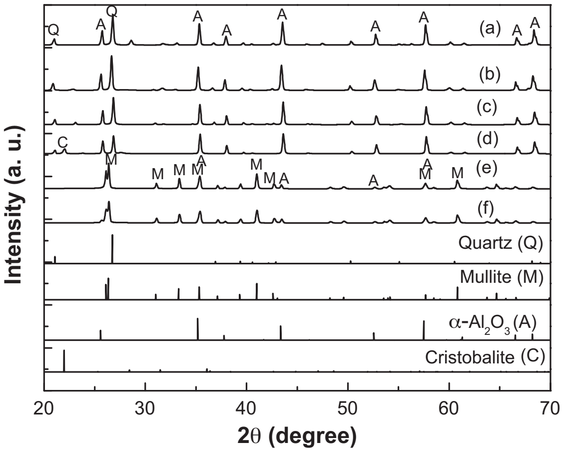

Fig. 1. XRD patterns of $3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders prepared at various temperatures. (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C, (e) 1500 °C, and (f) 1600 °C.

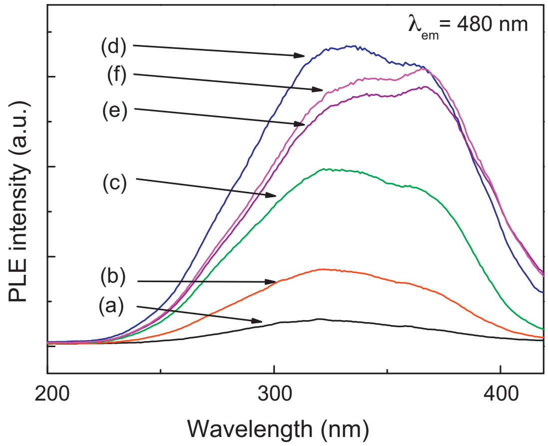

Fig. 2. PLE of $3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders prepared at various temperatures. (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C, (e) 1500 °C, and (f) 1600 °C.

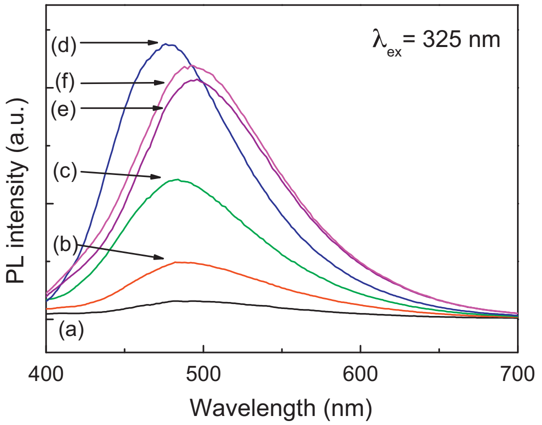

Fig. 3. PL spectra of $3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders prepared at various temperatures. (a) 1100 °C, (b) 1200 °C, (c) 1300 °C, (d) 1400 °C, (e) 1500 °C, and (f) 1600 °C.

It was reported that Eu^{3+} and Eu^{2+} ions could be incorporated into Al sites in $\alpha(\gamma)$-Al_2O_3 prepared by well-defined combustion synthesis technique in spite of the large distinction in the ionic radii of Eu^{3+} (~0.9 Å)/Eu^{2+} (~1.09 Å) and Al^{3+} (~0.5 Å), leading to the red and green emission, respectively [12–14]. On the other hand, in our experiment it was confirmed that Eu^{2+} doped respective α-Al_2O_3 and quartz single phase powders obtained at 1400 °C actually did not show any luminescence. To verify the effects of amorphous SiO_2 phase, Eu^{2+} doped α-Al_2O_3 single phase containing amorphous SiO_2 could be intentionally made by using B_2O_3 as shown in the inset of Fig. 4. Unlike Eu^{2+} doped α-Al_2O_3 without amorphous SiO_2 phase, its PLE spectra exhibited a strong absorption peak at 320 nm as shown in Fig. 4. This demonstrated that Eu^{2+} ions

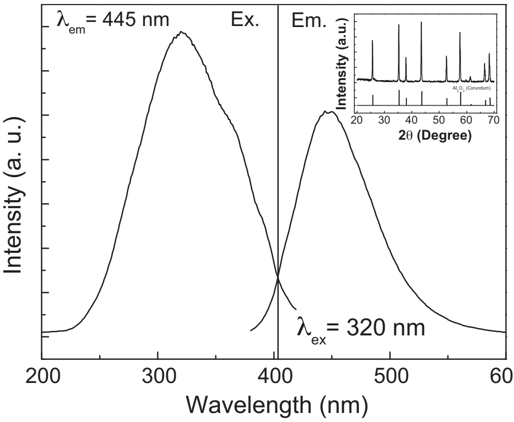

Fig. 4. PL and PLE of $0.662Al_2O_3$–$0.335SiO_2$–$0.003Eu_2O_3$–H_3BO_3 (5 wt%).

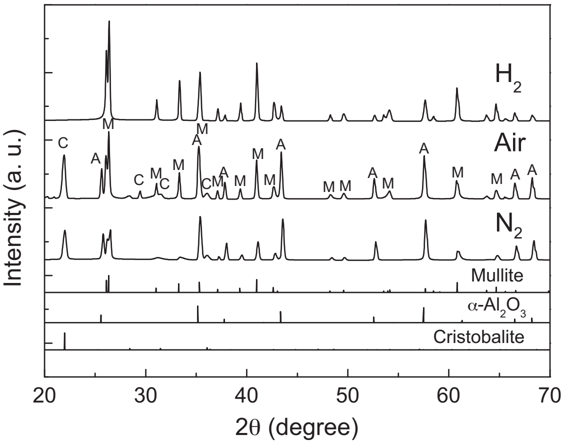

Fig. 5. XRD patterns of $3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders prepared at N_2, H_2, and air, respectively.

in α-Al_2O_3 + amorphous SiO_2 were efficiently activated, leading to a strong blue emission at 445 nm. Wechtel [9] revealed that the strong excitation spectra could be attained from Eu^{2+} doped mullite + the second phase (amorphous SiO_2 or α-Al_2O_3), leading to the blue emissions due to Eu^{2+} ions located between these two phases, whereas the emission from well-defined single phase such as α-Al_2O_3, amorphous SiO_2, and $3Al_2O_3$–$2SiO_2$ was very low or rarely detectable. Dierre et al. suggested that Si played a key role in the blue emission properties around 470 nm of AlN:Eu^{2+},Si^{4+} systems by increasing the solubility of Eu^{2+} ions in the AlN lattices [15]. In Eu^{2+} doped Al_2O_3–SiO_2 glass, blue emissions generated from the $4f^7$ to $4f^65d^1$ transition of Eu^{2+} ions, which were positioned at the void or open structure due to the oxygen defects [10,11]. Al^{3+} in Al_2O_3–SiO_2 glass contributed to the dispersion and reduction of Eu^{2+}.

According to our results and the previous works, it was almost impossible to determine how the luminescence was produced from mixed phases (α-Al_2O_3, quartz, and amorphous SiO_2), because each phase or mixed phase could act as host materials for the activation of Eu^{2+} ions. However it was evident that the increase in the temperature caused two discrete peaks and their red-shifts in PLE spectra. The change from a merged and weak PLE band at 1100 °C to two distinctive strong bands at 1400 °C implied that the splitting of the excited d-state of Eu^{2+} ions ($4f^65d^1$) by the crystal field became stronger with increasing the temperature.

Mullite single phase prepared at 1500–1600 °C exhibited similar PL and PLE spectra to those synthesized at 1100–1400 °C, but actual luminescent mechanism was completely different from one another because of the discrete crystal structures. Theoretically the excited d-states of Eu^{2+} under the octahedral or tetrahedral crystal field are split into two degenerated states of t_{2g} and e_g, leading to only two excitation bands, respectively [16]. In mullite, if Eu^{2+} ions were incorporated into the octahedral and tetrahedral sites, the lattice distortion, which would occur due to the large-sized Eu^{2+} ions, lowered the symmetry and allowed more than two PLE peaks. Consequently, only two excitation bands meant that Eu^{2+} occupied the cavity rather than 4- and or 6-coordinated (tetrahedral and octahedral, respectively) sites. The cavities generate from the substitution of Al^{3+} for Si^{4+} in the tetrahedral configuration, and these are located at the tetrahedral linking positions [2,3]. Mullite prepared at 1600 °C was slightly superior to that at 1500 °C in PL intensity.

$3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders were prepared under N_2, H_2, and air atmospheres, respectively, and each powder was referred to as AS–N_2, AS–H_2, and AS–air. In AS–N_2 and –air, cristobalite and α-Al_2O_3 as well as mullite strongly appeared as shown in Fig. 5, whereas mullite single phase with a negligible α-Al_2O_3 was attained in AS-H_2. This implied that the N_2 and air atmosphere supplied a suitable thermodynamic circumstance for the mixed phases rather than for mullite single phase. Corresponding PLE and PL spectra are shown in Fig. 6. The shape of PLE spectrum of AS-H_2 was nearly in accordance with that of AS–N_2, indicating that they generated from Eu^{2+} ions presented at the same crystal field, namely, the same host material (mullite). Consequently, PL emission intensity was also almost same with each other, whereas the emission peak of AS–H_2 slightly moved to the longer wavelength (the red-shift) compared to that of AS–N_2. Because AS–N_2 had considerable cristobalite phase, mullite in AS–H_2 had more SiO_2 content than that in AS–N_2, resulting in the red-shift. This result

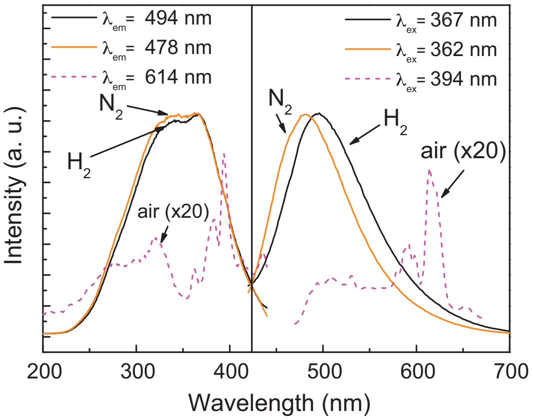

Fig. 6. PL and PLE of $3Al_2O_3$–$2SiO_2$–$0.005Eu_2O_3$ powders prepared at N_2, H_2, and air, respectively.

coincided with previous works [3,8], which demonstrated that the increased SiO_2 content in mullite led to the red-shift in PL due to the enhancement of covalency. The PL spectra of AS–air exhibited the red emissions due to $^5D_0–^7F_j$ ($j = 0, 1, 2,\ldots$) energy transition of Eu^{3+} ions, and f–f transition bands were also showed in PLE.

4. Conclusions

$3Al_2O_3–2SiO_2–0.005Eu_2O_3$ powders were fired at various temperatures of 1100–1600 °C under H_2 atmosphere. The samples composed of three phases of α-Al_2O_3, quartz, and amorphous SiO_2 were obtained at 1100–1400 °C, resulting in strong greenish-blue emission bands around 475–485 nm. Their two discrete peaks and the red-shifts in PLE spectra demonstrated that the splitting of the excited d-state of Eu^{2+} ions ($4f^65d^1$) by the crystal field became stronger with increasing the temperature. 3/2-mullite single phase was synthesized at 1500–1600 °C, which exhibited similar luminescent spectra to the mixed phase at 1100–1400 °C. The firing atmosphere affected the emission and excitation properties of Eu^{2+} doped 3/2-mullite. The greenish-blue emission was obtained under H_2 and N_2, whereas the red one was produced under air atmosphere.

Acknowledgement

This work was supported by Kyonggi University Research Grant 2009.

References

[1] S. Aryal, P. Rulis, W.Y. Ching, Density functional calculations of the electronic structure and optical properties of aluminosilicate polymorphs (Al_2SiO_5), American Mineralogist 93 (2008) 114–123.

[2] H. Schneider, S. Komarneni, Mullite, Wiley-VCH, Weinheim, 2005.

[3] T.R.N. Kutty, M. Nayak, Photoluminescence of Eu^{2+}-doped mullite ($xAl_2O_3 \cdot ySiO_2$; $x/y = 3/2$ and 2/1) prepared by a hydrothermal method, Materials Chemistry and Physics 65 (2000) 158–165.

[4] S. Durovic, Refinement of the crystal structure of mullite, Chemické Zvesti 23 (1969) 113–128.

[5] S. Kanzaki, H. Tabata, T. Kamazawa, S. Oita, Sintering and mechanical properties of stoichiometric mullite, Journal of the American Ceramic Society 68 (1985) C-6–C-7.

[6] S.O. Agrell, J.V. Smith, Cell dimensions, solid solution, polymorphism, and identification of mullite and sillimanite, Journal of the American Ceramic Society 43 (1960) 69–78.

[7] T. Ban, K. Okada, Structure refinement of mullite by the rietveld method and a new method for estimation of chemical composition, Journal of the American Ceramic Society 75 (1992) 227–230.

[8] J.K. Park, M.A. Lim, C.H. Kim, H.D. Park, S.Y. Choi, Effect of composition on luminescence properties of Eu^{2+}-activated mullite, Journal of the Electrochemical Society 150 (10) (2003) H246–H249.

[9] A. Wechtel, Eu^{2+} activated aluminosilicate phosphors, Journal of the Electrochemical Society 116 (1) (1969) 61–64.

[10] Y. Kishimoto, X. Zhang, T. Hayakawa, M. Nogami, Blue light emission from Eu^{2+} ions in sol–gel-derived $Al_2O_3–SiO_2$ glasses, Journal of Luminescence 129 (2009) 1055–1059.

[11] M. Nogami, T. Hagiwara, G. Kawamura, G. El-Sayed, T. Hayakawa, Redox equilibrium of samarium ions doped in $Al_2O_3–SiO_2$ glasses, Journal of Luminescence 124 (2007) 291–296.

[12] P.A. Tanner, Z. Pan, N. Rakov, G.S. Maciel, Luminescence of Eu^{3+} in α-Al_2O_3 powders, Journal of Alloys and Compounds 424 (2006) 347–349.

[13] O. Ozuna, G.A. Hirata, J. McKittrick, Luminescence enhancement in Eu^{3+}-doped α- and γ-Al_2O_3 produced by pressure-assisted low-temperature combustion synthesis, Applied Physics Letters 84 (8) (2004) 1296–1298.

[14] N. Rakov, G.S. Maciel, Photoluminescence analysis of α-Al_2O_3 powders doped with Eu^{3+} and Eu^{2+} ions, Journal of Luminescence 127 (2007) 703–706.

[15] B. Dierre, X.L. Yuan, K. Inoue, N. Hirosaki, R. Xie, T. Sekiguchi, Role of Si in the luminescence of AlN:Eu,Si phosphors, Journal of the American Ceramic Society 92 (6) (2009) 1272–1275.

[16] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer-Verlag, Berlin, 1994.