

Luminescence property of Eu^{2+} in $\text{SiO}_2\text{-Al}_2\text{O}_3$ glass phosphor

Ki Woong Chae^a, Kyoung-Ho Lee^{a,b}, Chae Il Cheon^{a,b}, Nam In Cho^c and Jeong Seog Kim^{b,*}

^aDepartment of Materials Science and Engineering, Hoseo University, Chungnam 336-795, Korea

^bDepartment of Digital Display Engineering, Hoseo University, Chungnam 336-795, Korea

^cDept. of Electronic Engineering, Sunmoon University, Asan, Chungnam 336-708, Korea

Manufacturing process for silicate glass phosphors containing Eu^{2+} activator and their photoluminescence property have been studied. We adopted powder sintering process instead of traditional glass melting process for making glass phosphor. At first, phosphor powders were synthesized at 1200 °C for 2-3 hours under a reducing atmosphere with 10% H_2 -90% N_2 gas mixture. The reduced powders were compacted into discs and then the discs were sintered at 1400 ~ 1500 °C for 1 hr under a reducing atmosphere of 5% H_2 -95% N_2 . The enhancement of PL intensity by Al_2O_3 addition, XPS binding energy shift of Si 2p and O 1s, sintering shrinkage, and crystallization were characterized.

Key words: Glass, Phosphor, Sintering process, Photoluminescence, Eu^{2+} .

Introduction

Recently, glass phosphors have been studied for the applications in LED packages and solid state lasers. Traditionally powder phosphors have been coated on top of LED chip in a slurry form by mixing with organic epoxy resin. This phosphor molding process has been giving rise to several optical problems with LED packages, such as color coordinate change, deterioration of luminescence efficiency, life time, and binning problems. [1-2].

For resolving these problems, new molding processes such as conformal coating and glass phosphor plate have been developed. Replacing epoxy molding process with these new processes can not only simplify the LED packaging process but also improve the optical properties. [3, 4]

Phosphors containing Eu ions have been utilized in LEDs, fluorescent lamp, and emissive displays such as PDP, ELD, and FED. Divalent Eu ions in phosphors can emit wide range of visible light from blue to yellow color depending on host materials. Especially, the demand for phosphors in white light LED-lamp applications has increased than evermore. Host materials for Eu^{2+} activator can be BAM, oxynitride, and alkaline earth silicates ($x\text{MO-yAl}_2\text{O}_3\text{-zSiO}_2$, M = alkaline). Silicates are one of the most useful host materials with stable crystal structure and high chemical stability. [5-7]

Eu^{2+} ions show very intense luminescent intensity when compared to that of Eu^{3+} f-f transition and have many practical applications. Eu^{2+} ions can be incorporated

into a glass by using glass melting process. [1, 2] However, this melting process requires high temperature and strong reducing atmosphere. And, most of all, melted glass should be formed into a suitable shape for a practical application into devices such as LED packages.

This work reports a new manufacturing process for making silicate glass phosphor containing Eu^{2+} and their photoluminescence (PL) property. Instead of traditional glass melting process, the powder sintering process was adopted. Silicate glass phosphors without Al_2O_3 has very low luminescence efficiency that cannot be used in practical applications. Hence, Al_2O_3 was added for improving luminescence efficiency in this study.

This study is partly based on our previous report [8], in which substantial effect of Al_2O_3 addition on luminescence enhancement in silicate phosphors containing Eu^{2+} had been reported. Melting temperatures of SiO_2 and Al_2O_3 are very high, 1710 °C and 2053 °C respectively. The sintering temperature of silicate glass phosphors was reduced by adding mineralizers such as alkaline oxides (K_2O , Na_2O) and boride (B_2O_3).

PL characteristics along with glass compositions, sintering conditions, and crystal phase formation are analyzed. The origin of PL enhancement by adding Al_2O_3 was discussed in relation to the XPS binding energy of Si and O.

Experimental

Glass phosphor samples were synthesized by powder sintering process. Sample manufacturing process is shown schematically in Fig. 1. Nominal sample compositions were $6\text{SiO}_2\text{-xB}_2\text{O}_3\text{-yAl}_2\text{O}_3\text{:0.01Eu}_2\text{O}_3$ ($0.20 \leq x \leq 0.5$, $0.0 \leq y \leq 0.8$), $6\text{SiO}_2\text{-(0.34Na}_2\text{O, 0.16K}_2\text{O)-xAl}_2\text{O}_3\text{:0.01Eu}_2\text{O}_3$ ($0.02 \leq x \leq 1.8$), and $6\text{SiO}_2\text{-0.3B}_2\text{O}_3\text{-0.3K}_2\text{O-1.0Al}_2\text{O}_3\text{:0.01Eu}_2\text{O}_3$. Alkaline oxides (K_2O , Na_2O)

*Corresponding author:
Tel : +82-41-540-5921
Fax: +82-41-540-5929
E-mail: kimjungs@hoseo.edu

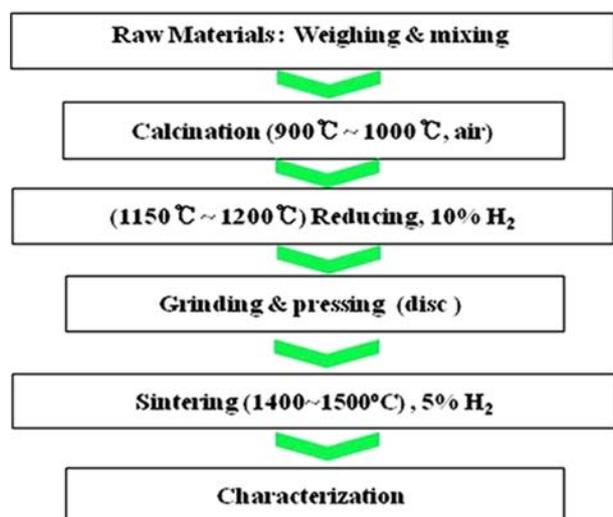


Fig. 1. Manufacturing process for glass phosphor samples.

and B_2O_3 were added to lower sintering temperature. x and y were varies independently.

Chemical reagents with high purity, Na_2CO_3 , K_2CO_3 , B_2O_3 , Al_2O_3 (nano sized), amorphous SiO_2 , and Eu_2O_3 were used as raw materials. At first, the raw materials were weighed and mixed thoroughly with an appropriate amount of ethanol in an agate mortar. The mixture of the raw materials was calcined at $900 \sim 1000^\circ C$ for 4 hours in air. Then the calcined powder samples were ground at room temperature and heat-treated under reducing atmosphere of 10% H_2 -90% N_2 gas mixture at $1200^\circ C$ for 2 ~ 3 hours. The reduced samples were cooled in furnace and then ground using an agate mortar. PL characteristic were analyzed on these powder phosphor samples.

These ground powders were compacted into disc with 9.0 mm diameter without adding organic binder. The discs were sintered at $1400 \sim 1500^\circ C$ for 1 hr under reducing atmosphere of 5 H_2 -95% N_2 .

The photoluminescence spectra of the samples were measured by a luminescence spectrometer (Perkin Elmer LS55). The X-ray diffraction data were obtained at room temperature. The XPS (Axis Nova, Kratos) measurements were carried out. The Al K α line (1486.6 eV) was used for the analysis. The spectra were recorded using a high resolution analyzer utilizing 20 eV pass energy.

Results and Discussion

The PL spectra of $6SiO_2-xB_2O_3-yAl_2O_3:0.01Eu_2O_3$ ($0.20 \leq x \leq 0.5$, $0.0 \leq y \leq 0.8$) samples which were reduced under reducing gas mixture 10% H_2 -90% N_2 at $1200^\circ C$ are represented in Fig. 2. The broad band positioned between 210 nm ~ 420 nm is 4f-5d absorption transition ($^8S_{7/2} \rightarrow 5d$ band) of Eu^{2+} with two components $5d t_{2g}$ (313 nm) and e_g (369 nm) splitted by crystal field near Eu^{2+} centers [9]. In the inset (Fig. 2) deconvoluted profiles are shown. In addition to the 4f-

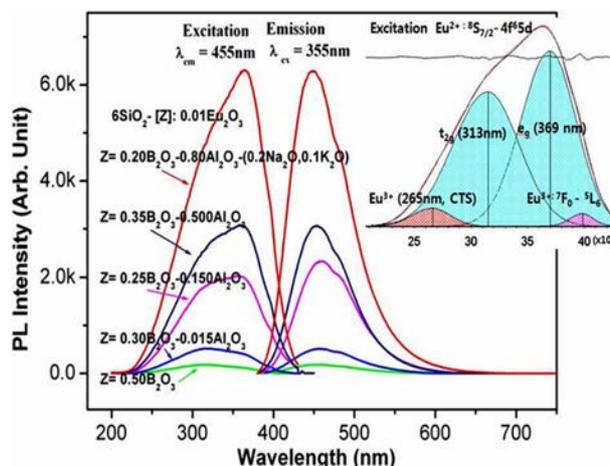


Fig. 2. PL spectra of $6SiO_2-xB_2O_3-yAl_2O_3:0.01Eu_2O_3$ ($0.20 \leq x \leq 0.5$, $0.0 \leq y \leq 0.8$) samples which were reduced at $1200^\circ C$ under reducing atmosphere of 10% H_2 -90% N_2 . The excitation spectrum measured while observing the emission line at 455 nm; the emission spectrum measured under the 355 nm excitation.

5d transition, the f-f-transition of Eu^{3+} ($^7F_0 - ^5L_6$, at 396 nm) and charge transfer state of $Eu^{3+}-O^{2-}$ can be additionally positioned. Deconvoluted spectrum was fitted well resulting in negligible residual profile [10]. PL deconvolution results indicate that most of the Eu ions were converted to Eu^{2+} during the reduction process of the 10% H_2 -90% N_2 atmosphere at $1200^\circ C$.

The emission band between 380 ~ 620 nm can be assigned to the 5d-4f transition of Eu^{2+} ions. [11] Interestingly, the f-d emission transition band can be also deconvoluted into two peaks, which correspond to the t_{2g} and e_g states of Eu^{2+} 5d. The effect of Al_2O_3 addition on PL intensity in $6SiO_2-xB_2O_3-yAl_2O_3:0.01Eu_2O_3$ samples ($x = 0.20 \sim 0.50$, $y = 0 \sim 0.8$) is quite drastic (Fig. 2). Without Al_2O_3 addition ($y = 0$) luminescence intensity is very low. With increasing Al_2O_3 amount luminescent intensity increases drastically and shows a maximum at $y = 0.8$. It appears that luminescence intensity depends only on y (Al_2O_3) amount; the intensity increases independently with xB_2O_3 amount. The effect of Al_2O_3 addition on the PL enhancement can be confirmed further by the PL spectra shown in Fig. 3.

Fig. 3 shows the PL spectra of $6SiO_2-(0.34Na_2O, 0.16K_2O) - xAl_2O_3:0.01Eu_2O_3$ ($0.02 \leq x \leq 1.8$) series. Similarly to the samples shown in Fig. 2, the PL intensity is proportional to Al_2O_3 amount. When x (Al_2O_3) is low the PL intensity remains very low. With increasing xAl_2O_3 the PL intensity increases and reaches a maximum at $x = 1.2$ and then decreases with further increase of x to 1.8). In this series (Fig. 3) Al_2O_3 addition is also indispensable for luminescence enhancement similarly to the case of $6SiO_2-xB_2O_3-yAl_2O_3:0.01Eu_2O_3$. The PL intensity in this series (Fig. 3) was enhanced at relatively higher amount of Al_2O_3 than that in the former series [$6SiO_2-xB_2O_3-yAl_2O_3:0.01Eu_2O_3$]. This different behavior appears to come from

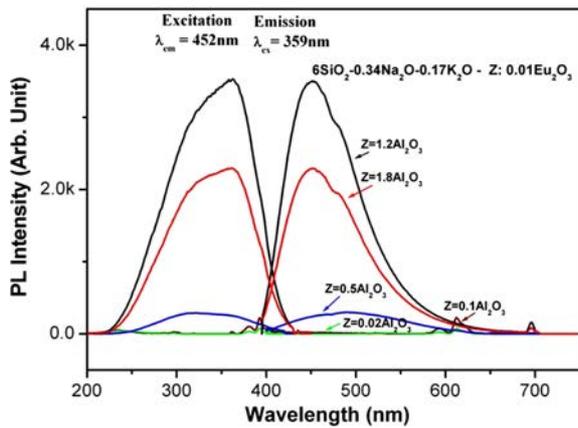


Fig. 3. PL spectra of $6\text{SiO}_2\text{-(}0.34\text{Na}_2\text{O, }0.16\text{K}_2\text{O)-}x\text{Al}_2\text{O}_3 : 0.01\text{Eu}_2\text{O}_3$ ($0.02 \leq x \leq 1.8$) samples synthesized at 1200°C under reducing atmosphere of $10\%\text{H}_2\text{-}90\%\text{N}_2$.

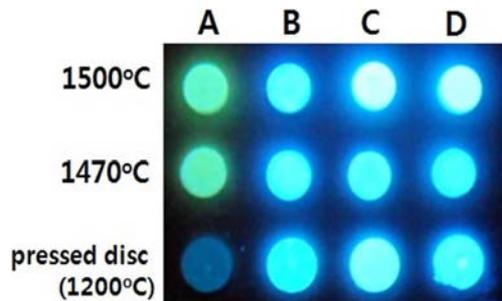


Fig. 4. Photographs of the sintered discs under 365 nm UV light. The samples were sintered at the range of $1400 \sim 1500^\circ\text{C}$ under $5\%\text{H}_2\text{-}95\%\text{N}_2$ gas mixture. [A : $6\text{SiO}_2\text{-}0.5\text{B}_2\text{O}_3 : 0.01\text{Eu}_2\text{O}_3$; B : $6\text{SiO}_2\text{-}0.5\text{B}_2\text{O}_3\text{-}1.0\text{Al}_2\text{O}_3 : 0.01\text{Eu}_2\text{O}_3$; C : $6\text{SiO}_2\text{-(}0.27\text{Na}_2\text{O, }0.14\text{K}_2\text{O)-}1\text{Al}_2\text{O}_3 : \text{Eu}_2\text{O}_3$; D : $6\text{SiO}_2\text{-}0.3\text{B}_2\text{O}_3\text{-}0.3\text{K}_2\text{O-}1.0\text{Al}_2\text{O}_3 : 0.01\text{Eu}_2\text{O}_3$]

the solubility difference of Al_2O_3 in the host material SiO_2 . The crystallization behaviors are represented in Fig. 5.

The enhancement of PL intensity by Al_2O_3 addition is visually observable when the samples are illuminated by 365 nm UV light (Fig. 4). The photograph clearly shows that without Al_2O_3 addition (A : $6\text{SiO}_2\text{-}0.5\text{B}_2\text{O}_3 : 0.01\text{Eu}_2\text{O}_3$) the emission intensity remains very low. With increasing sintering temperature to 1500°C ($5\%\text{H}_2\text{-}95\%\text{N}_2$ atmosphere) the PL intensity increases by somewhat extent in every samples. Among the samples sintered at 1500°C sample A shows the lowest emission intensity, and sample C [$6\text{SiO}_2\text{-(}0.27\text{Na}_2\text{O, }0.14\text{K}_2\text{O)-}1\text{Al}_2\text{O}_3 : \text{Eu}_2\text{O}_3$] and D [$6\text{SiO}_2\text{-}0.3\text{B}_2\text{O}_3\text{-}0.3\text{K}_2\text{O-}1.0\text{Al}_2\text{O}_3 : 0.01\text{Eu}_2\text{O}_3$] show the brightest emission image.

Table 1 shows linear shrinkage of the sintered discs. These pellets were prepared using the phosphor powders manufactured at 1200°C under reducing atmosphere of $10\%\text{H}_2\text{-}90\%\text{N}_2$ as described in the experiment section. Samples A and B have lower sintering shrinkage than those of the C and D. The addition of alkaline oxides ($\text{Na}_2\text{O, }0.14\text{K}_2\text{O}$) lowers the sintering temperature effectively than the B_2O_3 does. Highly fused discs were obtained from the alkaline oxide-added samples (C and D).

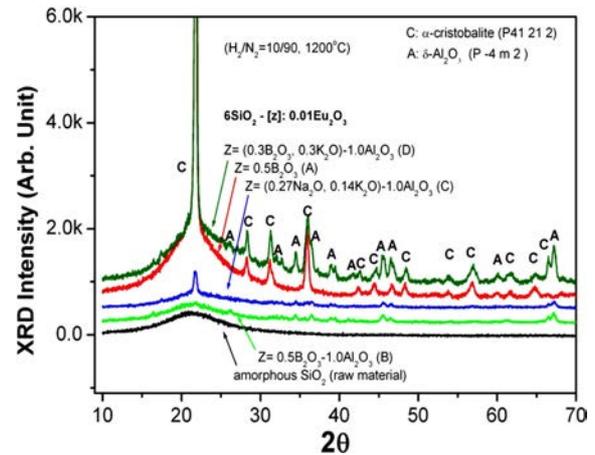


Fig. 5. XRD patterns of the powder phosphor samples (A-D) synthesized at 1200°C under reducing atmosphere of $10\%\text{H}_2\text{-}90\%\text{N}_2$. [A-D : sample compositions are the same as noted in Fig. 4]

Table 1. Linear shrinkages of the sintered samples $6\text{SiO}_2\text{-}[Z] : 0.01\text{Eu}_2\text{O}_3$ at the temperature range of $1400^\circ\text{C} \sim 1500^\circ\text{C}$ under reducing atmosphere of $5\%\text{H}_2\text{-}95\%\text{N}_2$. [Z = $0.5\text{B}_2\text{O}_3$ (A), $0.5\text{B}_2\text{O}_3\text{-}1.0\text{Al}_2\text{O}_3$ (B); $(0.27\text{Na}_2\text{O} - 0.14\text{K}_2\text{O})\text{-}1.0\text{Al}_2\text{O}_3$ (C); $0.3\text{B}_2\text{O}_3\text{-}0.3\text{K}_2\text{O-}1.0\text{Al}_2\text{O}_3$ (D)]

Sintering Temp.	A	B	C	D
1400°C	8.6%	8.5%	11.0%	10.4%
1470°C	10.6%	9.7%	11.7%	11.0%
1500°C	11.2%	11.2%	11.8%	11.7%

Fig. 5 shows XRD patterns for the powder samples (A-D) synthesized at 1200°C under reducing atmosphere of $10\%\text{H}_2\text{-}90\%\text{N}_2$. At the bottom side the XRD pattern of amorphous SiO_2 used as raw material is shown for comparison with the phosphor samples. The samples B and C mostly consist of amorphous SiO_2 phase. In sample A (without Al_2O_3 addition) α -cristobalite phase (SG P 41 21 2, $a = b = 5.551 \text{ \AA}$, $c = 23.106 \text{ \AA}$) was formed in the amorphous glass matrix. In sample D, δ - Al_2O_3 phase (P -4 m 2, $a = b = 5.551$, $c = 23.106 \text{ \AA}$) was produced in addition to α -cristobalite in amorphous matrix. When compared to the PL emission images (Fig. 4) the degree of crystallization appears to have no relation to the PL intensity. Only the amount of Al_2O_3 addition is a critical parameter influencing the PL intensity. Hence, the luminescence enhancement can be ascribed to the Al_2O_3 addition.

In rare earth (RE)-doped silicate glasses the incorporation of RE^{2+} ions requires very high melting temperature and strongly reducing atmosphere. The sintering temperature range of $1200^\circ\text{C} \sim 1500^\circ\text{C}$ used in this study is not sufficiently high enough to reduce the Eu^{3+} to Eu^{2+} ions by conventional solid state reaction method. Recently the incorporation of Sm^{2+} and Eu^{2+} ions was reported at relatively low temperature $< 1200^\circ\text{C}$ in silica matrix phase synthesized by sol-gel. [9, 11, 12] Nogami et al. [9] reported that Sm^{3+} could

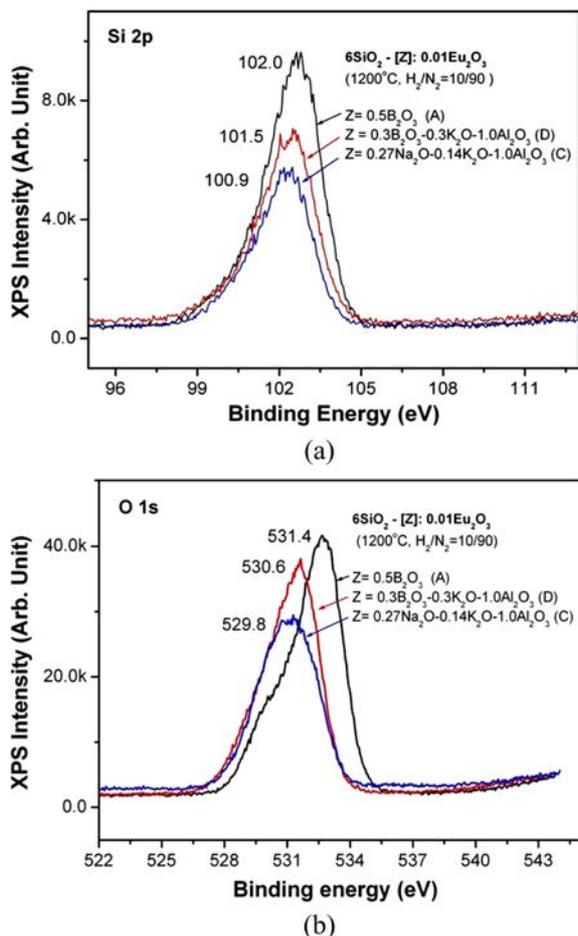


Fig. 6. XPS measurements for the Si 2p and O 1s levels of the powder phosphor samples synthesized at 1200 °C under reducing atmosphere of 10% H_2 -90% N_2 . [A, C, D : sample compositions are the same as noted in Fig. 4]

be reduced to Sm^{2+} under H_2-N_2 in Al_2O_3 - SiO_2 glass matrix only when Al^{3+} ions were co-doped into sol-gel glass. Biswas et al. suggested that Al^{3+} co-doping with Eu ions can reduce the trivalent state (Eu^{3+}) to Eu^{2+} in a significant proportion at low temperature and hence enhance the emission of Eu^{2+} ions. Moreover, Biswas et. al. [12] suggested that Al^{3+} co-doping with Eu^{3+} in porous sol-gel silica glass could spontaneously reduce Eu^{3+} to Eu^{2+} in air at temperature of 1125 ~ 1150 °C. These results were interpreted in terms of microscopic basicity; Al^{3+} in silica glass matrix increased the electron donation ability of oxygen to Eu^{3+} ions.

These previous reports conform to our results that only the amount of Al_2O_3 addition is a critical parameter which can enhance the PL intensity of the glass phosphors in this study. The Al^{3+} ions could decrease the basicity of silica glass and help oxygen ions to render their electrons to Eu^{3+} ions. [11] To know that if the postulation in the previous report is applicable to our silicate phosphor samples, XPS were measured for the Si 2p and O 1s levels of the samples (A, C, D) as shown Fig. 6. Both the Si 2p and O 1s

peaks shift to low energy side in the samples (C,D) which were added with 1.0 Al_2O_3 . This decrease of binding energy in the alumina added samples indicates that Eu^{3+} ions can be readily reduced to Eu^{2+} compared to the samples without Al_2O_3 . Hence luminescence intensity from Eu^{2+} centers can drastically increase by the alumina addition.

Conclusions

Highly fused glass phosphor could be produced by powder sintering method at the sintering temperature of 1470 ~ 1500 °C. This sintered glass phosphor showed very intense blue light emission, which had a center-wavelength of 452 nm in PL spectra. The degree of crystallization of the phosphor glass had no relation to the PL intensity. Only the amount of Al_2O_3 addition was a critical parameter for luminescence enhancement. Both the Si 2p and O 1s peaks shifted to low energy side by the addition 1.0 Al_2O_3 in the glass phosphor samples. Alumina could decrease the basicity of silica glass and help to reduce Eu^{3+} to Eu^{2+} . Luminescence intensity from Eu^{2+} centers drastically increases by the Al^{3+} incorporation in the glass.

Acknowledgements

This work was supported by grant No. RTI04-01-02 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy (MOCIE).

References

1. L.H.C. Andrade, S.M. Lima, A. Novatski, A. Steimacher, J.H. Rohling, A.N. Medina, A.C. Bento, M.L. Baesso, Y. Guyot, and G. Boulon, *Appl. Phys. Lett.* 95 (2009) 081104-3.
2. S. Nishiura and S. Tanabe, *IEEE J. of Selected Topics in Quantum Electronics* 15 [4] (2009) 1177-1180.
3. Y. Qiao, D. Chen, J. Ren, B. Wu, J. Qiu, and T. Akai, *J. Appl. Phys.* 103 [2] (2008) 023108-1-3.
4. M. Zhang, J. Wang, W. Ding, Q. Zhang, and Q. Su, *Opt. Mater.* 30 (2007) 571-578.
5. J.S. Kim, P.E. Jeon, Y.H. Park, J.C. Choi, and H.L. Park, *Appl. Phys. Lett.* 85 (2004) 3696-3698.
6. Y. Lin, Z. Tang, Z. Zhang, and C. W. Nan, *J. Alloy Comp.* 348 (2003) 76-79.
7. T.R.N Kutty and M. Nayak, *Mater. Chem. Phys.* 65 [2] (2000) 158-165.
8. J.S. Kim, J.-H. Choi, C.I. Cheon, in *Proceedings of Asia Display 2007 Mar. 2007*, edited by East China Normal University (2007) 1816-1821.
9. M. Nogami, T. Yamazaki, and Y. Abe, *J. Lumin.* 7 (1998) 63-68.
10. K.W. Chae, C.I. Cheon, N.I. Cho, and J.S. Kim, *J. Lumin.* 131 (2011) 2597-2605.
11. A. Biswas, C.S. Friend, G.S. Maciel, and P.N. Prasad, *J. Non-Crystal. Sol.* 261 (2000) 9-14.
12. A. Biswas, C.S. Friend, and P.N. Prasad, *Mater. Lett.* 39 (1999) 227- 231.