Effect of mixed alkaline earth doping on phosphorence properties

of BaAl₂O₄:Eu²⁺, Dy³⁺

B. K. Singh and H. J. Ryu*

Advanced Materials Division, Korea Research Institute of Chemical Technology,

P.O.Box 107, Yuseong, Daejeon 305-600, Republic of Korea

Abstract

Long lasting phosphor materials are in great demand for their applications in the area of light emitting diodes (LEDs), commercial displays and warning signals. After glow longevity, brightness, photoresistance and chemical and environment stability are most important qualities that are desired for these materials. Alumina as host lattice with various rare earth elements has been found to be good at the same time inexpensive material for the synthesis of the phosphor materials. This communication explored the effect of mixed rare earth metal on the luminescence properties of these materials for the first time. Various permutations and combinations of Sr²⁺ and Ba²⁺have been investigated in order to achieve robust and high luminescence characteristics in the tailored phosphor materials

1. INTRODUCTION

Long persistence materials are needed in applications like signing and display [1-2]. For these purpose rare earth ion doping in alkali earth aluminates have been tried in literature as persistence time in these materials are 10 times longer than that of doped sulfides [3-4]. The aluminates material generally generates more defect related traps when they are doped with rare earth ions. Many aluminates have been investigated and used as photoluminescence, catholuminescence and plasma display panel phosphors for their high quantum efficiency in the visible region. Notably barium and strontium aluminates have been reported to be good host material. However, the admixture of more than one rare earth metal in the host matrix and their implication on phosphor characteristics has not been reported till date. Due to the size variation between the barium and strontium it is expected to create defects in the host matrix that would have influence on the phosphor properties. Considering this, in this paper we have prepared BaAl₂O₄ based materials with partial replacement of Ba by Sr by 25%, 50% and 75% moles

with Eu²⁺ and Dy³⁺ ions as dopent to get long afterglow. The properties of these materials were compared with SrAl₂O₄ as host matrix also. All these results related to synthesis and characterization of these materials is reported in this paper.

2. EXPERIMENTAL AND RESULTS

In all six compositions having general formula $Sr_xBa_yAl_2O_4$: Eu^{2^+} , Dy^{3^+} (x=y= 0/ 0.25/ 0.50/ 0.75) were prepared by solid state reaction method using appropriate quantities of BaCO₃, $SrCO_3$, Al_2O_3 , Eu_2O_3 , Dy_2O_3 and B_2O_3 . Composition of starting materials, X= BaO/ (BaO+Al₂O₃) is taken to 0.45 that were doped with 0.25 mol% Eu_2O_3 and 0.25mol% Dy_2O_3 . Well grounded powders were mixed thoroughly and sintered at 1200°C for 6h in an air atmosphere. Finally the powders were heated at 1300°C for 4h in a reducing atmosphere (5% H₂-Ar gas) to assure complete conversion of Eu^{3^+} to Eu^{2^+} .

The crystal structures of phosphor were investigated by Rigaku D/MAX-2200V X-ray diffractometer with CuK_{α} radiation. The photoluminescence (PL) emission of powder samples were obtained on a Perkin-Elmer LS50B luminescence spectrometer. Each sample was loaded on a circular holder that was excited with 254 nm radiation using a pulsed xenon lamp. The emission spectra were scanned in the wavelength range of 350-700 nm. Scanning electron microscopy (SEM, Jeol JSM 6700F) was employed to observe the morphology of products.

3. Results and Discussion

Crystal Structures of BaAl₂O₄:Eu²⁺, Dy³⁺, SrAl₂O₄:Eu²⁺, Dy³⁺ and Sr/BaAl₂O₄:Eu²⁺, Dy³⁺ were characterizes by XRD prior to their photoluminescence studies. The X-ray pattern of BaAl₂O₄:Eu²⁺, Dy³⁺showed hexagonal phase. A monoclinic strontium aluminate with space group P2₁ (4) was identified as the main crystalline phase in the case of SrAl₂O₄:Eu²⁺, Dy³⁺. Interestingly Sr₄Al₁₄O₂₅ and monoclinic strontium aluminate was found for Sr/BaAl₂O₄:Eu²⁺, Dy³⁺ phosphor material.

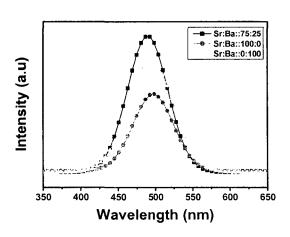


Fig. 1. PL spectra of $Sr_x/Ba_vAl_2O_4$: Eu^{2+} , Dy^{3+} where x=0 or 75; y=25 or 100

PL intensity of $Sr/BaAl_2O_4$: Eu^{2+} , Dy^{3+} at different concentration of Sr and Ba were studied. PL intensity increases with the increase in Sr concentrations with little red shift near 506nm. The emission intensity originates from $5d \rightarrow 4f$ transition of Eu^{2+} ions. High intensity emission with narrow band width was found for 75 mol% of Sr doping. It was also observed that the peak position (nm) vary with different Sr concentrations (506>502>495 for 75>50>25 mol %) implies that crystal field that affect the 5d electron is influenced by the compositional variation. Also, PL intensity of $Sr/BaAl_2O_4$: Eu^{2+} , Dy^{3+} was found to be greater as compared with $SrAl_2O_4$: Eu^{2+} , Dy^{3+} and $BaAl_2O_4$: Eu^{2+} , Dy^{3+} (Fig. 1). This may be due to influence of 5d electron states of Eu^{2+} in the crystal field because of atomic size variation causing crystal defects. The possibility of synergetic effect between the two alkaline earths present in the crystal field causing increased PL emission can not be ruled out.

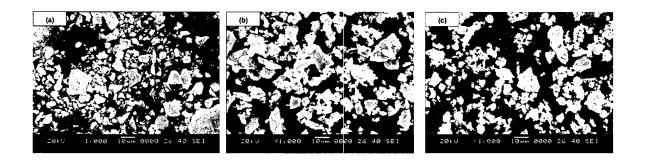


Fig. 2. SEM microstructure of (a) Sr:Ba::75:25, (b) Sr:Ba::100:0 and (c) Sr:Ba::0:100

SEM microstructures of as prepared (a) Sr:Ba::75:25, (b) Sr:Ba::100:0 and (c) Sr:Ba::0:100 is shown in figure 2. All the three samples showed agglomeration of crystals with sharp edges having size ranging from submicron to 30 μm. distinctly material with Sr: Ba:: 75:25 showed better crystallinity, which also Showed stronger photoluminescence

3. Conclusion

In conclusion, we have studied the enhancement of the green emission property by the addition of an additional alkaline earth element-Sr to BaAl₂O₄:Eu²⁺, Dy³⁺ phosphor. The Sr addition leads to an increase in the PL intensity with red shift possibly due to its influence on 5d electron states of Eu²⁺ in the crystal field because of the variation in atomic size, thereby causing crystal defects. These defects are advantageous for PL properties of the as-synthesized materials. Therefore, it can be concluded that the two alkaline earths present in the crystal field may have some synergetic effect on PL emission.

References

- 1. S. H. Ju, U. S. Oh, J. C. Choi, H. L. Park, T. W. Kim, C. D. Kim," Tunable color emission and solid solubility limit in $Ba_{1-x}Ca_xAl_2O_4$: $Eu_{0.001}^{2+}$ phosphors through the mixed states of $CaAl_2O_4$ and $BaAl_2O_4$, Mater. Res. Bull. 35, p.1831-1835, 2000.
- 2. D. Jia, Xiao-Jun Wang, E. vander Kolk, W. M. Yen, "Site dependent thermoluminescence of long persistent phosphorescence of BaAl₂O₄:Ce³⁺", Optics communications **204**, pp.247-251, 2002.
- 3. D. Jia, J. Zhu, B. Wu, "Trapping Centers in CaS:Bi³⁺ and CaS:Eu²⁺,Tm³⁺",
- J. Electrochem. Soc., 147, p.386-389, 2000.
- 4. W. Jia, H. Yuan, L. Lu, H. Liu, W. M. Yen, "Phosphorescent dynamics in SrAl₂O₄: Eu²⁺, Dy³⁺ single crystal fibers",
- J. Lumin. 76&77, pp.424-428, 1998.