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# $CaAl_2O_4:Eu^{2+}$ 靑色 螢光體의 $Nd^{3+}$ 도핑 最適化에 관한 硏究†

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# Optimization of $Nd^{3+}$ ion co-doping in $CaAl_2O_4$: $Eu^{2+}$ blue phosphor†

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## 요 약

$Eu^{2+}$, $Nd^{3+}$로 도핑된$CaAl_2O_4$ 청색 형광체를 고상반응법으로 제조하였다. 1 mol% $Eu^{2+}$로 doping된 형광체에 다양한 조성의 $Nd^{3+}$를 co-doping함에 따라 고휘도, 장잔광 특성을 보였다. 제조한 형광체에 대하여 XRD, SEM, TEM, 빛발광 특성을 조사하였다. $CaAl_2O_4:Eu^{2+}:Nd^{3+}$의 넓은 밴드의 UV로 여기된 빛발광 특성이 $Eu^{2+}$의 $4f^65d^1$에서 $4f^7$의 상태로 천이에 의해 기인된 청색영역($\lambda_{max}=440$ nm)에서 관찰되었다. $Nd^{3+}$로 co-doping한 형광체는 여기광을 차단하였을 때 장잔광 발광 특성을 나타내었다.

**주제어** : 청색 형광체, 고상반응, 장잔광 발광, $Nd^{3+}$ 도핑

## Abstract

Blue phosphor calcium aluminate, $CaAl_2O_4$: $Eu^{2+}$ co-doped with $Nd^{3+}$ was prepared by solid state synthesis method. Phosphor materials with 1 mol% $Eu^{2+}$ and varying compositions of $Nd^{3+}$ show high brightness and long persistent luminescence. The synthesized phosphor materials were investigated by powder X-ray diffraction (XRD), SEM, TEM, photoluminescence excitation and emission studies. Broad band UV excited luminescence of the $CaAl_2O_4:Eu^{2+}:Nd^{3+}$ was observed in the blue region ($\lambda_{max}$= 440 nm) due to transitions from the $4f^65d^1$ to the $4f^7$ configuration of the $Eu^{2+}$ ion. $Nd^{3+}$ ion doping in the phosphor results in long afterglow phosphorescence when the excitation light is cut off.

**Key words :** Blue phosphor, solid state reaction, long persistent luminescence, $Nd^{3+}$ ion co-doping

## 1. Introduction

Phosphor materials having bright luminescence at low accelerating voltage are much in demand for various applications. The growing demand for phosphor materials in high-definition television screens and field-emission displays has triggered targeted studies to find new phosphors[1,2]. Phosphors with long persistence can light up for a long time in the darkness after irradiation with sunlight or artificial light. The phosphor materials based on alkaline earth aluminate $MAl_2O_4:Eu^{2+}$ (M: Ca, Sr, Ba) phosphors with strong photoluminescence at the blue-green visible region have been studied extensively[3-5]. Rare earth ion doped calcium aluminate, $CaAl_2O_4$, phosphors, because of their high efficiency, anomalous long phosphorescence and good stability, have been studied extensively and used widely. The afterglow lifetime and intensity can be enhanced by co-doping with some other rare earth ions[6,7]. Those phosphors exhibit a rapid initial decay from the $Eu^{2+}$ ion followed by a long persistence.

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Compared with sulfide phosphorescent phosphors, Sr and Ca based aluminate phosphors possesses safer, chemically stable, very bright and long-lasting photoluminescence with no radiation. This results in an unexpectedly large field of applications, such as luminous paints in highway, airport, buildings and ceramics products, as well as in textile, the dial plate of glow watch, warning signs and escape routine, etc[8]. $Eu^{2+}$ doped phosphors usually show intense broad band photoluminescence (PL) with a short decay time of the order of tens of nanoseconds. The emission of $Eu^{2+}$ is very strongly dependent on the host lattice and can occur from the ultraviolet to the red region of the electro-magnetic spectrum. This is because the 5d↔4f transition is associated with the change in electric dipole and the 5d excited state is affected by crystal field effects. It is well known that the valence state of the activator dictates the emission wavelength[9]. Similarly the trivalent $Eu^{3+}$ ions show red luminescence properties in highly stable lead based heavy metal oxide glasses[10].

We present the results on the effect of Nd co-doping on crystal structure and PL characteristics of $CaAl_2O_4:Eu^{2+}$ phosphor prepared by solid-state reaction method. Photoluminescence (PL) and decay time measurements were carried out. Powder X-ray diffraction (XRD), SEM and TEM measurements were performed to investigate the phase and crystallinity of the material.

## 2. Experiments

Phosphor material $CaAl_2O_4:Eu^{2+}$, $Nd^{3+}$ with Eu concentration keeping 1 mol% and varying concentrations of Nd (2, 3 and 5 mol %) were prepared by solid state reaction method. High purity (Aldrich make, 99.99%) raw materials; $CaCO_3$, $Al_2O_3$, $Eu_2O_3$, $Nd_2O_3$ and $B_2O_3$ were used for preparation of the charge. The quantity of the flux $B_2O_3$ is very crucial and dictates the calcination and reduction temperatures. Composition for each material is weighted in stoichiometric ratios and mixed thoroughly with ethanol in an agate mortar. The resulting slurry was dried at 80°C in a vacuum oven for 4h. Well mixed and grounded powders were sintered at 900°C for 6h in an air atmosphere. Finally the powders were annealed at 1300 °C for 2 h in a reducing atmosphere (5% $H_2$ and 95% Ar) to ensure the complete reduction of $Eu^{3+}$ to $Eu^{2+}$. Phase and crystallinity of the synthesized compositions were investigated by powder XRD using Rigaku D/MAX-2200V diffractometer with Cu $K_a$ radiation. SEM and TEM studies were done to investigate the crystallinity and surface morphology. Samples for TEM were prepared by suspending the particles in ethanol by ultrasonification and drying a drop of the suspension on a carbon coated copper grid. TEM was carried out employing Philips Tecnai $G^2$-20 (FEI) machine operating at 200 kV. The photoluminescence (PL) excitation and emission spectra were taken on Perkin-Elmer LS50B luminescence spectrometer. Each sample was loaded into a circular holder and excited with 254 nm radiation from a pulsed xenon lamp. The emission spectra were scanned in the range of wavelengths from 360 to 700 nm. To measure the excitation spectra, the analyzer monochromator was set to the maximum wavelength of the emission spectra and then an excitation monochromator was scanned in the range of 200 to 400 nm. The decay time was recorded using a pulsed Xenon lamp and oscilloscope.

## 3. Results and Discussion

It is well known that the blue phosphor $CaAl_2O_4:Eu^{2+}$ show very high photoluminescence with low persistence decay time, of the order of few nano seconds. When the second rare earth ion is doped in this phosphor it shows very long persistence decay. Therefore we have prepared and investigated calcium aluminate, $CaAl_2O_4$ co-doped with $Eu^{2+}$ and $Nd^{3+}$

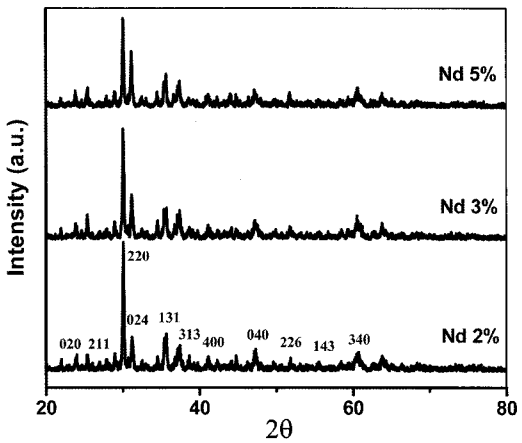


**Fig. 1.** Representative XRD pattern of $CaAl_2O_4:Eu^{2+}$, $Nd^{3+}$ (for 2, 3 and 5 mol% Nd).

(with 2, 3 and 5 mol% of $Nd_2O_3$). Fig. 1 shows the representative powder XRD pattern for the $CaAl_2O_4$:$Eu^{2+}$ for 2, 3 and 5 mol% $Nd_2O_3$. As can be seen, pure monoclinic phase diffraction peaks of parent $CaAl_2O_4$ are dominant in the XRD patterns, and are matching with the JCPDS data file (No. 23-1036). No other phase or unreacted starting material was observed. This confirms the synthesized phase is low-temperature monoclinic phase (α-phase). The calculated lattice parameters for monoclinic crystal system were a= 8.702 Å, b=8.095 Å and c=15.213Å. There is no visible difference in these XRD patterns except small variation in the intensity. Small amount of doped rare earth active ions $Eu^{2+}$ and $Nd^{3+}$ has almost no effect on $CaAl_2O_4$ basic crystal structure.

Scanning electron microscopy (SEM) study was carried out to investigate the surface morphology and crystallite sizes of the synthesized phosphor powder. The powder samples reduced at temperature 1300°C were taken for these experiments. Fig. 2 (a, b, c) shows the representative SEM micrographs taken for

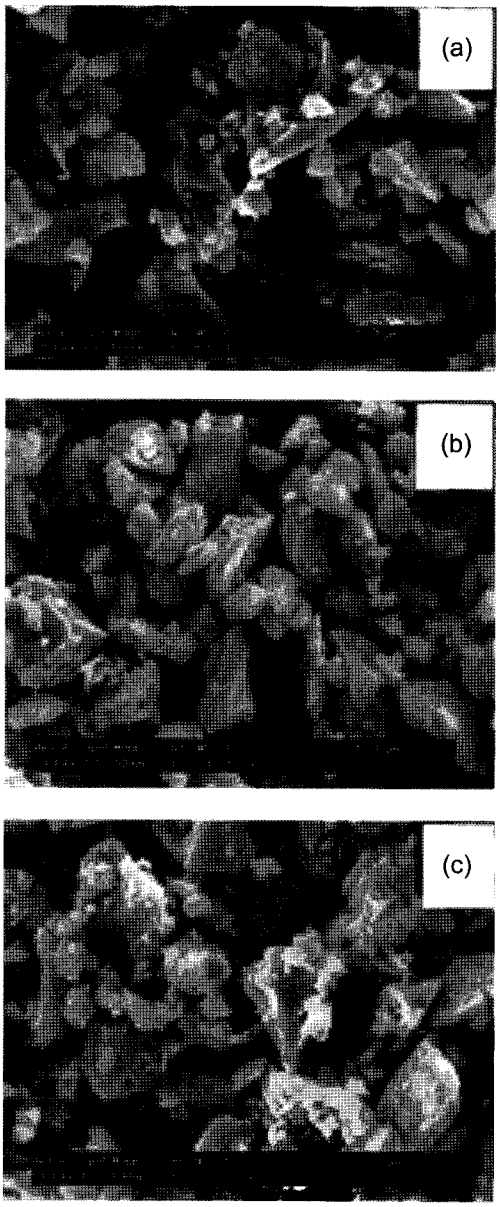


**Fig. 2.** SEM micrographs of the sample $CaAl_2O_4$:$Eu^{2+}$, $Nd^{3+}$ (for 2, 3 and 5 mol% Nd).

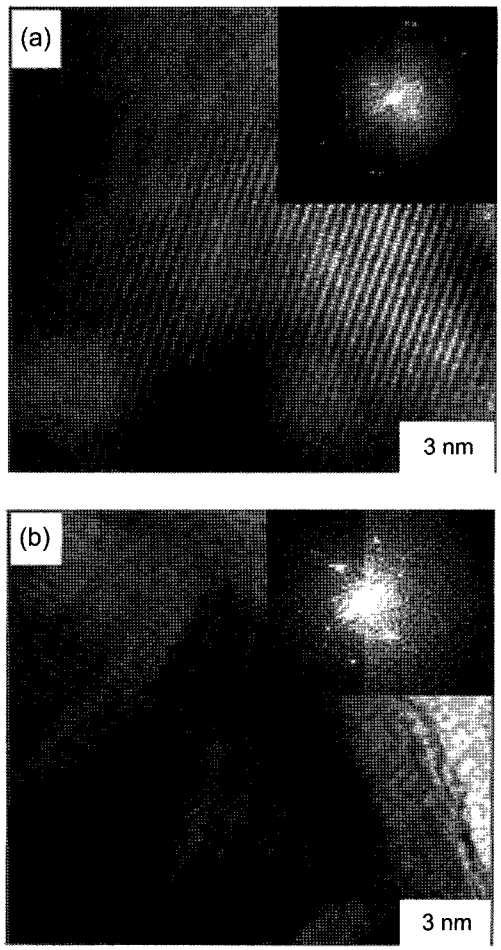


**Fig. 3.** Representative TEM micrograph and corresponding SAD patterns of $CaAl_2O_4$:$Eu^{2+}$, $Nd^{3+}$, 2 mol% Nd and (b) 5 mol% Nd.

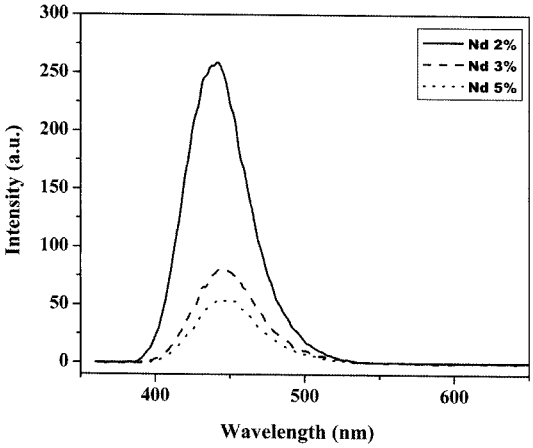


**Fig. 4.** Emission spectra for $CaAl_2O_4:Eu^{2+}$, $Nd^{3+}$(for 2, 3 and 5% Nd).

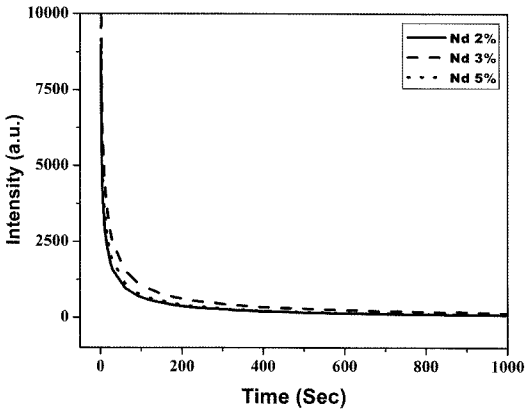


**Fig. 5.** Decay time for $CaAl_2O_4:Eu^{2+}$, $Nd^{3+}$ (for 2, 3 and 5% Nd).

$CaAl_2O_4:Eu^{2+}$ for three different Nd composition (2, 3, and 5 mol%) samples. It is clearly seen from these micrographs that the crystallites sizes are varying from few microns to several tens of microns. However, the crystallites are having sharp surface morphology of single crystalline grains.

TEM studies were conducted to investigate the effect of doping on the microstructure and crystallinity of the synthesized material. Fig. 3 (a, b) shows the representative bright field high resolution (HREM) image for the 2 and 5 mol% Nd samples. The corresponding selected area diffraction (SAD) patterns are inserted in the micrograph. The clarity of the HREM micrograph shows that the synthesized material crystallizes in single phase and no trace of secondary phases are observed. The difference in intensity is due to the thickness variation. The SAD pattern inserted in Fig. 3 (a, b) are indicative of the crystalline particles have sufficient size to give the clear and strong diffraction spots. However, the streaks along the diffraction spots and diffuse scattering present in the SAD pattern is due to the point defects produced by doping of Eu and Nd active ions. Higher diffuse scattering and streaks can be seen for higher Nd concentration in Fig. 3(b).

The prepared phosphor compositions exhibit blue emission. This indicates that the matrix has the monoclinic calcium aluminate phase and the Eu ion is in divalent ($Eu^{2+}$, blue emission) rather than trivalent ($Eu^{3+}$, red emission) state. The emission spectra for $CaAl_2O_4:Eu^{2+}$ with various $Nd^{3+}$ concentrations are shown in Fig. 4. The emission is a symmetrical band at 440 nm which is attributed to the typical $4f^6\,5d^1 - 4f^7$ transition of $Eu^{2+}$ ion. When the phosphor materials were doped with 1 mol% $Eu^{2+}$ and 2 mol% $Nd^{3+}$, the emission spectra have highest intensity. The mechanism of the long persistence is due to the holes trapped– transported–detrapped process[11]. The $Nd^{3+}$ ion works as traps of holes, and the trap levels lie in-between the excited state and the ground state of $Eu^{2+}$ ion. The cross section between the trap and rare earth levels is appropriate for obtaining of the effective depopulation of the excited states. After excited by the irritation lights, electron and hole pairs are produced in $Eu^{2+}$ ions, and the $Nd^{3+}$ traps capture some of the free holes moving in the valence band. When the excitation source is cut off, some holes captured by the $Nd^{3+}$ traps are thermally released slowly and relaxed to the excited state of $Eu^{2+}$, finally, returning to the ground state of $Eu^{2+}$ accompanied with emitting light. This is why this family of phosphor maintains a long persistent period after the excitation is cut off. When we further increase the $Nd^{3+}$ concentration (above 2 mol%) the emission intensity goes down. The reason seems to be that the concentration of $Nd^{3+}$ ions more than the optimum number produces more crystalline defects apart from the traps. These defects neutralize the electron - hole recombination processes, therefore, reduces the emission intensity as well as traps

responsible for the long persistence.

Persistent luminescence curves for the 2, 3 and 5 mol% Nd co-doped $CaAl_2O_4:Eu^{2+}$ phosphors are shown in Fig. 5. It can be seen from these curves that the samples show quite long decay time when the powder was efficiently activated by using a pulsed Xenon lamp for 15 min. When the source lamp was switched off, the intensity of the persistence decreased rapidly and finally formed a stable long persistent emission for several tens of minutes.

## 4. Conclusions

Phosphor compositions $CaAl_2O_4:Eu^{2+}$ co-doped with varying $Nd^{3+}$ were synthesized using solid state synthesis method. XRD analysis shows that the synthesized compositions retain the low-temperature monoclinic phase (α-phase). SEM and TEM investigations confirm the single phase material with large size crystallites. The effect on PL intensity and decay time was investigated for varying $Nd^{3+}$ doping concentrations. It was optimized that the highest PL intensity is for the co-doping combination of 1 mol% Eu and 2 mol % Nd. The decay time of the persistence indicated that the persistent luminescence phosphor has bright phosphorescence and maintains duration of several minutes.

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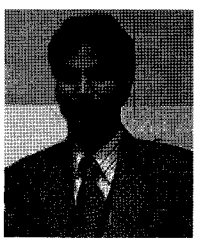

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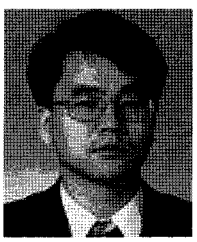

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