Preparation and Photoluminescent Properties of Ca$_2$PO$_4$Cl Activated by Divalent Europium

In Yong Park†

Department of Materials Science and Engineering, Hanbat National University, 125 Dongseodaro, Yuseong-gu, Daejeon 34158, Korea

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Abstract: Divalent europium-activated Ca$_2$PO$_4$Cl phosphor powders were prepared by a chemical synthetic method followed by heat treatment in reduced atmosphere, and the crystal structures, morphologies and photoluminescence properties of the powders were investigated by x-ray powder diffraction, scanning electron microscope and spectrometer. The effect of Ca/P mole ratio at the starting materials on the final products was evaluated. The optimized synthesis condition obtained in this study was Ca/P mole ratio of 2.0. The present phosphor materials had higher photoluminescence intensity and better color purity than the commercial blue phosphor powders, (Ca,Ba,Sr)$_6$(PO$_4$)$_6$Cl$_2$:Eu$^{2+}$. The result of excitation spectrum measurement indicated that the excitation efficiency of the synthesized powders was higher for the long-wavelength UV region than that of the commercial phosphor. It was thus concluded that the samples prepared in this study can be successfully applied for the light-emitting devices such as LED excited with long-wavelength UV light sources.

Keywords: Ca$_2$PO$_4$Cl:Eu$^{2+}$, phosphor, photoluminescence, apatite, excitation

1. Introduction

Alkaline earth halophosphates for phosphors belong to a family ofapatite compounds like the general formula of M$_2$(PO$_4$)$_2$:X: A, where M is Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ or combinations of these, X is F$, Cl^-$ of anion, and A is Eu$^{2+}$, Sb$^{3+}$, Mn$^{2+}$ of activator ions.$^{11}$ These phosphors emit the light of range from vacuum ultraviolet to infrared.$^{12}$ Also, the emission efficiency of these compounds is superior to other systems, and applied to three-band lamps and lightings for long time.$^{2-9}$ Divalent europium-activated apatitic compounds show the possibility for the purpose of LED (light emitting diode) phosphors due to the effective blue emission from excitation by long wavelength ultraviolet light source.$^{10}$

Among the alkaline earth halophosphates, chlorospodiosite (Ca$_2$PO$_4$Cl) has the same crystal structure of spodiosite (Ca$_2$PO$_4$F).$^{10}$ Ca$_2$PO$_4$Cl has orthorhombic crystal structure, which has a=6.185±0.002 Å, b=6.983±0.002 Å and c=10.816±0.004 Å.$^{10}$ The PO$_4^{3-}$ tetrahedra are significantly distorted from the ideal configuration.$^{10}$ Ca$_2$PO$_4$Cl:Eu$^{2+}$ is known as an efficient luminescent material, but the research on this phosphor is very few.$^{11-14}$ Ca$_2$PO$_4$Cl decomposes into apatite Ca$_3$(PO$_4$)$_2$Cl and liquid at above 1040°C, which has incongruent melting point.$^{15}$ Therefore, heat treatment should be conducted below this point.

Ca$_2$PO$_4$Cl compounds are mainly synthesized via solid-state reaction, and CaCl$_2$ salts are used as starting materials for this method. However, CaCl$_2$ salts are deliquescent and it is not easy to handle the salts in ambient atmosphere. Also research on wet chemical synthesis of Ca$_2$PO$_4$Cl:Eu$^{2+}$ is not reported to the best of our knowledge. In this study, homogeneity in composition mixing was achieved using a wet chemical method, and the effect of mole ratio change on the properties of Ca$_2$PO$_4$Cl:Eu$^{2+}$ phosphors was evaluated. For comparison of optical properties, the commercial phosphor of (Ca,Ba,Sr)$_6$(PO$_4$)$_6$Cl$_2$:Eu$^{2+}$ was chosen as a reference, which is used as blue phosphor for lamps.

2. Experimental Procedure

The starting materials were as follows: CaCl$_2$:2H$_2$O (Aldrich Co.; 99.99%), EuCl$_3$:6H$_2$O (Aldrich Co.; 99.9%), H$_3$PO$_4$ (Aldrich Co.; 98%, crystals), HCl (reagent grade), and aqueous ammonia (reagent grade). All reagents were used without further purification.

The Ca$_2$PO$_4$Cl:Eu$^{2+}$ blue phosphor powders were pre-
pared using a coprecipitation method through the following procedure. Mole ratio of Ca/P in the starting solution was changed from 1.6 to 2.4, and mole ratio of Eu/P was fixed to be 0.06. The chemicals of CaCl$_2$·2H$_2$O, EuCl$_3$·6H$_2$O and H$_3$PO$_4$ were dissolved with distilled water, and 0.1N HCl solution was added to the mixed salt solution. The concentrations of EuCl$_3$, H$_3$PO$_4$ and HCl were adjusted to 0.06 mole/L, 1 mole/L and 8.3×10$^{-4}$ mole/L, respectively, whereas CaCl$_2$ concentration was varied with mole ratio of Ca/P. In other beaker, concentrated aqueous ammonia corresponded to the chemical equivalent of H$_3$PO$_4$, CaCl$_2$, EuCl$_3$ and HCl was diluted with distilled water to 4 mole/L. The mixed solution of CaCl$_2$/EuCl$_3$/H$_3$PO$_4$ was added to the aqueous ammonia solution with vigorous stirring, and the white precipitates were formed. The pH of the colloidal solution after the reaction was about 9. And then the resulting suspension was stirred continuously and heated with hot plate to evaporate water. The dried precursor cakes were produced. The cakes were put into alumina crucible and calcined at 500°C for 1 h. After cooling down to ambient temperature, the white powders were prepared by milling. These powders were placed into the alumina boat and were heat-treated under the reduction atmosphere of 4%H$_2$/96%Ar at 900°C for 2 h. After washing with distilled water for several times and drying at 100°C, the Ca$_3$PO$_4$Cl:Eu$^{2+}$ blue phosphor powders were produced.

Crystalline structure of the phosphor powders was measured by X-ray diffractometer (XRD; Rigaku D/MAX 2500H) using CuK$_\alpha$ radiation. The microstructure of the powders was examined by scanning electron microscope (SEM; JEOL JSM-6300). The photoluminescence (PL) properties were investigated for 300~800 nm range using spectrometer with He-Cd laser. Excitation and CIE color coordinates were characterized by spectrometer with excitation source of xenon lamp.

3. Results and Discussion

Fig. 1 shows XRD results of the blue phosphor powders obtained with various Ca/P mole ratios. The heat treatment was performed under the reduced atmosphere of 4%H$_2$/Ar mixed gas at 900°C for 2 h. For Ca/P mole ratio of 1.6 in the starting solution, a crystalline apatite phase of Ca$_3$(PO$_4$)$_2$Cl, which is assigned to JCPDS Card No. 33-0271, was formed. The two crystalline phases of Ca$_3$PO$_4$Cl (JCPDS Card No. 19-0247) and the apatite were coexisted for Ca/P mole ratio of 1.8. Theoretical Ca/P mole ratio for apatite is about 1.67, and that of Ca$_3$PO$_4$Cl is 2.0. Since calcium was deficient in the case of Ca/P=1.6, therefore, only the apatite phase was formed. In the case of the mole ratio of Ca/P=1.8 located between theoretical ones of apatite and Ca$_3$PO$_4$Cl, and the apatite and Ca$_3$PO$_4$Cl phases were obtained.

For the Ca/P mole ratio of 2.0 and over, only Ca$_3$PO$_4$Cl crystalline phase existed and any other crystalline compound containing europium was not found, which means that all ions of Eu$^{2+}$ ions were participated in Ca$_3$PO$_4$Cl crystal formation from the following aspect. The apatite phase was formed after precipitation reaction. The Ca$_3$PO$_4$Cl phase was then formed during heat treatment procedure under reduction atmosphere at high temperature. Divalent europium ion can be easily substituted for divalent calcium ion in the Ca$_3$PO$_4$Cl structure due to similar ionic radius (Eu$^{2+}$=0.112 nm, Ca$^{2+}$=0.099 nm). Consequently, the Ca/P mole ratio is needed to be over 2.0 in order to synthesize single phase of Ca$_3$PO$_4$Cl.

SEM micrographs of the blue phosphor powders obtained by changing Ca/P mole ratio in the starting solutions are shown in Fig. 2. The particle sizes of these phosphor powders were changed with the mole ratio of Ca/P. In Fig. 2(a) having apatite phase, the fine particles of 0.1~0.2 μm were formed. For the Ca/P mole ratios of 2.0 and over, their average particle sizes slightly differed from one another, but the powders were made up of several micrometer-sized particles having well-developed crystal facets. In Ca/ P=1.8, on the contrary, the powders consisted of submi-
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Fig. 2. SEM micrographs of the heat-treated powders with various Ca/P atomic ratios (900°C 2h under 4%H$_2$/Ar atmosphere): (a) 1.6, (b) 1.8, (c) 2.0, (d) 2.2, (e) 2.4, and (f) commercial (Ca,Ba,Sr)$_{10}$(PO$_4$)$_6$Cl$_2$:Eu$^{2+}$ blue phosphor.

crometer-sized fine particles and around 1 μm-sized ones having well-developed facets as shown in Fig. 2(b). Over 10 μm-sized, porous and irregular shaped particles were also observed, which were not shown in SEM micrograph of Fig. 2(b). The submicrometer-sized particles in Fig. 2(b) are the same crystalline apatite phase as that of Fig. 2(a), and the bigger particles with highly developed facets correspond to the Ca$_2$PO$_4$Cl phase. The SEM photographs of the Ca$_2$PO$_4$Cl crystals showed the irregular but well-developed faceted particles. For the comparison, SEM micrograph of commercially available phosphor powders, (Ca,Ba,Sr)$_{10}$(PO$_4$)$_6$Cl$_2$:Eu$^{2+}$, is shown in Fig. 2(f). The surfaces of the apatite particles were rougher, and their crystalline facets were not well-developed than those of the Ca$_2$PO$_4$Cl in this study. In the XRD result, the XRD pattern of the apatite phase corresponds to that of Sr$_{10}$(PO$_4$)$_6$Cl$_2$ (JCPDS Card No. 16-0666), but the d-spacings were slightly different to each other due to the mixture of Ca, Ba and Sr.

Fig. 3 represents the photoluminescence spectra of the Ca$_2$PO$_4$Cl:Eu$^{2+}$ phosphor powders with change in mole ratio of Ca/P. The PL spectra were measured using He-Cd laser ($\lambda_{ex}$=325 nm) at room temperature. The position of maximum intensity was blue-shifted with increase in Ca/P mole ratio from 453.5 nm in Ca/P=1.6 to 449 nm in Ca/P=2.4. The full width at half maximum intensity of the PL spectrum showed a minimum value of 52 nm at Ca/P=2.0. The higher the Ca/P ratio, the lower the symmetry of the bands was. The composition showing maximum PL intensity was found at Ca/P=2.0, and then the intensity gradually decreased at the above. For Ca/P=1.6, lower emission intensity derived from apatite phase and smaller particle size. The PL spectra showed the radiative transition of Eu$^{2+}$ from excited state (4f$^6$5d) to ground state (4f$^7$).$^{11,12}$

Fig. 3. Room-temperature PL emission spectra ($\lambda_{ex}$=325 nm) of Ca$_2$PO$_4$Cl:Eu$^{2+}$ blue phosphor powders: (a) 1.6, (b) 1.8, (c) 2.0, (d) 2.2, and (e) 2.4.

The excitation spectra of a Ca$_2$PO$_4$Cl:Eu$^{2+}$, which was prepared with Ca/P=2.0, and the commercial (Ca,Ba,Sr)$_{10}$(PO$_4$)$_6$Cl$_2$:Eu$^{2+}$ powders are shown in Fig. 4. After the photodetector of spectrophotometer was set to 456 nm, which position showed strongest light emission for the blue phosphor powders, the excitation spectra were measured using xenon lamp at room temperature. Comparison between the Ca$_2$PO$_4$Cl:Eu$^{2+}$, which showed the maximum emission intensity in Fig. 3 (Ca/P=2.0), and the commercial blue powders was conducted. The excitation spectra showed the similar shapes of Eu$^{2+}$-activated alkaline earth halophosphates one another.$^{13}$ The maximum excitation intensity of the prepared Ca$_2$PO$_4$Cl:Eu$^{2+}$ powders at 370 nm showed about 1.6 times higher than that of the commercial one, and the present excitation curve had significantly high emission efficiency for the long wavelength ultraviolet region. Therefore, application to the light-emitting devices as LED...
excited with long-wavelength UV light sources may be possible.  

Fig. 5 demonstrates the PL spectra of the prepared Ca$_2$PO$_4$:Eu$^{2+}$ and the commercial blue phosphors for application to the light-emitting devices. The spectra were measured using xenon lamp with 380 nm excitation source. The maximum intensities of the Ca$_2$PO$_4$:Eu$^{2+}$ and the commercial phosphors were revealed at 456 nm and 453 nm, respectively. However, the intensity of the Ca$_2$PO$_4$:Eu$^{2+}$ phosphor at the peak wavelength was also about 1.6 times higher than that of the commercial one. The spectrum of the Ca$_2$PO$_4$:Eu$^{2+}$ phosphor was more symmetrical and had the narrower full-width at the half maximum intensity than the commercial one. This narrow and symmetric energy spectral distribution can be explained by constitution of only one kind of alkaline earth metal. On the contrary, the emission spectrum of the commercial (Ca,Ba,Sr)$_6$(PO$_4$)$_3$(Cl:Eu$^{2+}$) phosphor was skewed toward longer wavelength region and showed asymmetrical shape, which is originated from combination of three kinds of alkaline earth metals.

CIE color coordinates for PL spectra obtained by 380nm excitation source were $x=0.147$, $y=0.046$ for the Ca$_2$PO$_4$Cl:Eu$^{2+}$ phosphor, and $x=0.153$, $y=0.127$ for the commercial one, respectively. Color coordinate of the Ca$_2$PO$_4$Cl:Eu$^{2+}$ phosphor was similar to that of Palilla and O’Reilly ($x=0.147$, $y=0.046$). In terms of color purity, the color coordinate of the commercial (Ca,Ba,Sr)$_6$(PO$_4$)$_3$(Cl:Eu$^{2+}$) phosphor was inferior to that of Ca$_2$PO$_4$Cl:Eu$^{2+}$, which can be explained by the following facts. When cation is identical and when Ba is not a major component in alkaline earth halophosphates, the most saturated emissions are obtained. When cation is Ba or a cationic combination including Ba, desaturation of blue emission color occurs. According to the above results, the present Ca$_2$PO$_4$Cl:Eu$^{2+}$ phosphor was much superior to the commercial one for PL emission and excitation properties and CIE color purity, which is considered to be due to the fact that the crystal surface of Ca$_2$PO$_4$Cl:Eu$^{2+}$ phosphor (Fig. 2(c)) is more developed than that of commercial phosphor (Fig. 2(f)).

4. Conclusions

Using a chemical synthesis method, Ca$_2$PO$_4$Cl:Eu$^{2+}$ blue phosphor powder was successfully synthesized. For the strong PL intensity, mole ratio of Ca/P in the starting materials should be 2.0 and over. PL emission intensity and color purity of Ca$_2$PO$_4$Cl:Eu$^{2+}$ were superior to those of the commercial (Ca$_2$PO$_4$Cl:Eu$^{2+}$). The Ca$_2$PO$_4$Cl:Eu$^{2+}$ blue phosphor showed the maximum excitation efficiency at 370 nm of excitation source, and also revealed good efficiency in the broad UV region. Therefore, Ca$_2$PO$_4$Cl:Eu$^{2+}$ can be applied to blue phosphor for long-wavelength UV LED.

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