Characterization and Properties of Green Emitting $Ca_3SiO_4Cl_2$:Eu^{2+} Powder Phosphor for White Light-emitting Diodes

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An efficient green emitting phosphor, Eu^{2+}-doped $Ca_3SiO_4Cl_2$, is reported. Its excitation band is extending from 260 to 470 nm, which is coupled well with the emission of UV LED (350–410 nm) and blue LED (450–470 nm). It exhibits a strong green emission centered at 505 nm with chromatic coordination (0.25, 0.57), which indicates that it could be a good green phosphor candidate for creating white light in phosphor-converted white LEDs.

Recently, tremendous progress has been achieved in the development of solid-state lighting based on GaN semiconductors. GaN-based diodes emit bright violet-blue light, which can be used to pump longer wavelength phosphors. The first commercially available white LED based on phosphors was produced in 1996, which combines a blue light emitting (In,Ga)N with a yellow $(Y_{1-x}Gd_x)_3(Al_{1-y}Ga_y)_5O_{12}$:$Ce^{3+}$ (YAG:Ce) phosphor.[1] However, this type of white light has poor color rendering because of the color deficiency in the red- and blue-green region. To solve this problem, some green and red phosphors are introduced.[2] In addition to the blue LED/yellow phosphor approach, white light can be produced by the pumping of red, green, and blue phosphors with a deep blue or UV LED.[3] For excellent color render index, both methods need efficient green phosphors that should have the excitation wavelength matching with the emission wavelength of the blue LEDs ($\lambda_{em} = 440$–470 nm) or the UV LEDs ($\lambda_{em} = 350$–410 nm). Currently, some sulfide phosphors, such as ZnS:Cu, Al[3] and $SrGa_2S_4$:Eu^{2+},[4] are commonly used as green phosphors for white LEDs. As well known, sulfides have low chemical stabilities against humidity and strong irradiation from GaN chip. Recently, a new green-emitting phosphor with stable sturcture, β-SiAlON:Eu^{2+}, is reported. However, its synthesis technique is very stiff, and β-SiAlON:Eu^{2+} powder phosphor is synthesized at 1900 °C for 8 h at 10 atm nitrogen atmosphere.[5] Therefore, it is necessary to develop alternative green phosphors with comparable or superior performance to sulfides and comparatively modest synthesis technique.

In this paper, we have synthesized an interesting green emitting phosphor candidate Eu^{2+}-doped $Ca_3SiO_4Cl_2$. Structural investigations have shown that $Ca_3SiO_4Cl_2$ is composed of the layers of calcium chloride and dicalcium silicate and has stable crystal structure and high decomposition temperature,[6] which makes it suitable for use as a host material.

Eu^{2+}-doped $Ca_3SiO_4Cl_2$ phosphors were synthesized by a high-temperature solid-state reaction. The starting materials, $CaCO_3$, $CaCl_2$, and SiO_2 of reagent grade, were mixed together with a mole ratio of $CaCO_3$, $CaCl_2$, and SiO_2 = 2:1.2:1. A small amount of high-purity Eu_2O_3 was added into the mixture. The well-mixed reactants were placed in a crucible closed with a lid. The crucible was buried by carbon grains. The reactants were calcined at 850 °C in CO reducing atmosphere for 3 h. The excess of calcium chloride was removed by washing with anhydrous alcohol. The synthesized powders were identified by X-ray powder diffraction (XRD, Rigaku D/M AX-2500 V), operating with 50 kV and 250 mA and using Cu Kα radiation ($\lambda = 1.54056$ Å). The powder phosphor determined from card JCPDS 23-873 is $Ca_3SiO_4Cl_2$. Emission and excitation spectra were measured using a Hitachi F4500 spectrometer. A xenon lamp was used as the excitation lamp. All the measurements were performed at room temperature.

The Eu^{2+}-activated $Ca_3SiO_4Cl_2$ is an efficient green-emission phosphor under either ultraviolet or blue excitation. The PL and PLE spectra of $Ca_3SiO_4Cl_2$:$0.02Eu^{2+}$ are shown in Figure 1. Upon 370-nm excitation, $Ca_3SiO_4Cl_2$:$0.02Eu^{2+}$ shows a very strong green emission band with a peak at 505 nm and a half width of 59 nm and a weak blue band peaking around 427 nm. It has been reported that the broad emission bands of $CaCl_2$:Eu^{2+} and Ca_2SiO_4:Eu^{2+} peak around 430 and 505 nm, respectively.[7,8] Additionally, $Ca_3SiO_4Cl_2$ is composed of the alternating layers of $CaCl_2$ and Ca_2SiO_4. Therefore, it is believed that the blue emission band at around 427 nm is attributed to Eu^{2+} at Ca sites in the $CaCl_2$ layers and the green emission band at around 505 nm is assigned to Eu^{2+} ions at Ca sites in the Ca_2SiO_4 layers of $Ca_3SiO_4Cl_2$. With different excitation wavelengths of 270, 370, 400, and 450 nm, there are little changes in the green emission except the emission intensity. The decay time of 505 nm emission is 1.94 µs. The quantum efficiency of $Ca_3SiO_4Cl_2$:$0.02Eu^{2+}$ amounts to about 60% under 370-nm

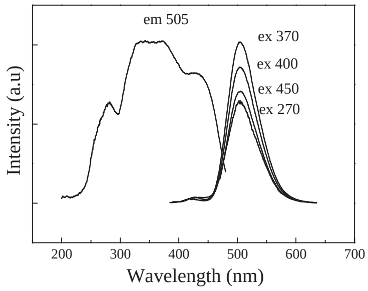

Figure 1. PL and PLE spectra of $Ca_3SiO_4Cl_2$:$0.02Eu^{2+}$ (λ_{em} = 505 nm for excitation and λ_{ex} = 270, 370, 400, and 450 nm for emission).

excitation. As shown in Figure 1, the very broad excitation spectrum for 505 nm emission has several excitation bands peaking around 270, 330, 370, and 440 nm. The structure in the excitation spectrum is assigned to the crystal field splitting of the 5d level of the Eu^{2+} ions. The excited 5d levels are not shielded from the ligand field, giving rise to a marked splitting of the excited level. The symmetry of coordinating ligands determines the number of the split level. The Ca sites in the Ca_2SiO_4 layers are asymmetric polyhedral sites with seven coordination, which makes the excited 5d levels split into more levels.[9]

The effect of the Eu^{2+} concentration x on the emission intensity of Eu^{2+}-doped $Ca_3SiO_4Cl_2$ is shown in Figure 2. The emission intensity under 370 nm excitation increases with increasing Eu^{2+} concentration, maximizing at about $x = 0.02$. Concentration quenching occurs, when the Eu^{2+} concentration is beyond 0.02. Concentration quenching is mainly caused by the nonradiative energy transfer among Eu^{2+}, which usually occurs as a result of an exchange interaction, radiation reabsorption or a multipole–multipole interaction.[10] Since the fluorescent mechanism of Eu^{2+} in $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor is the 4f–5d allowed electric-dipole transition, the process of energy transfer should be controlled by electric multipole–multipole interaction.[11] If the energy transfer occurs among the same sorts of activators, the intensity of multipolar interaction can be determined from the change of the emission intensity from the emitting level which has the multipolar interaction. The emission intensity (I) per activator ion follows eq 1:[12,13]

$$I/x = K[1 + \beta(x)Q/3]^{-1}. \qquad (1)$$

Where x is the activator concentration; $Q = 6$, 8, or 10 for dipole–dipole, dipole–quadrupole, or quadrupole–quadrupole interaction, respectively; and K and β are constant for the same excitation condition for a given host crystal. It can be seen from the inset figure in Figure 2 that the dependence of $\log(I/x)$ on $\log(x)$ is linear and the line slope is -1.98. The value of Q can be calculated as 5.94, which is approximately equal to 6. It indicates that dipole–dipole interaction is the concentration quenching mechanism of Eu^{2+} emission in the $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor.

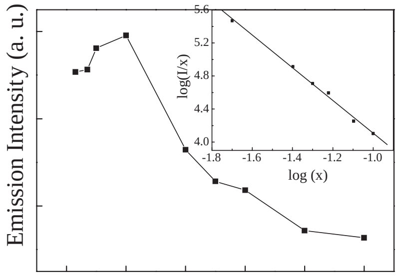

Figure 2. Concentration dependence of the emission intensity of $Ca_3SiO_4Cl_2:xEu^{2+}$ ($\lambda_{ex} = 370$ nm), the curve of $\log I/x$ vs $\log x$ is shown in the inset.

The Commission International del'Eclairage (CIE) chromaticity coordination of the $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor is shown in Figure 3. The chromaticity coordinates of $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor are $x = 0.25$ and $y = 0.57$. For comparison, the chromaticity coordinates of $SrGa_2S_4:Eu^{2+}$, ZnS:Cu,Al, and β-SiAlON:Eu^{2+} are also introduced. The color property of $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor is comparable with that of ZnS:Cu,Al,[3] $SrGa_2S_4:Eu^{2+}$,[4] and β-SiAlON:Eu^{2+}.[5] However, the sulfide phosphor has low chemical stabilities against humidity. β-SiAlON:Eu^{2+} has stable crystal structure, but its synthesis temperature is as high as 1900 °C. The excitation band of $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor is ranging from 260 to 470 nm, which is coupled well with the emission of UV LED (350–410 nm) and blue LED (450–470 nm). It is hence suggested that $Ca_3SiO_4Cl_2:Eu^{2+}$ phosphor could be a good green phosphor candidate for white LED.

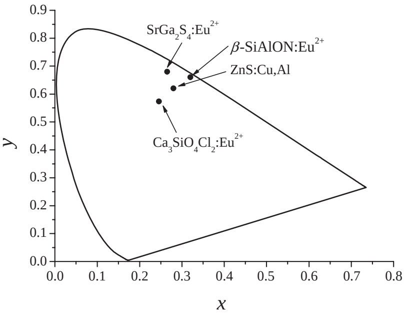

Figure 3. CIE chromatic coordinations of $Ca_3SiO_4Cl_2$: $0.02Eu^{2+}$.

In conclusion, we have synthesized a green phosphor, Eu^{2+}-doped $Ca_3SiO_4Cl_2$. Under UV and blue excitation, it exhibits a strong emission band centered at 505 nm. Its color property is comparable with commercially available green phosphor. It is believed to be a good green phosphor candidate for creating white light in phosphor-converted white LEDs.

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