Crystal Structure and Luminescent Properties of Green Phosphor $Ba_3Y_2(SiO_4)_3$:Eu^{2+} for LED Applications

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(Received July 27, 2009; CL-090696; E-mail: yexinyu@mail.jxust.cn)

We have developed a new silicate-based phosphor $Ba_3Y_2(SiO_4)_3$:Eu^{2+} without using expensive raw materials. The host crystal structure was firstly indexed as an orthorhombic-type instead of garnet-type. The phosphor absorbs near-ultraviolet light around 365 nm and emits green light with a peak at about 505 nm, which results from the 5d–4f transition of the Eu^{2+}. The optimum concentration of Eu^{2+} activator is 4 mol % relative to the Ba^{2+} content in the $Ba_3Y_2(SiO_4)_3$ host. It is a promising candidate for application in LEDs as a green-emitting color converter.

Compared with conventional lamps, light-emitting diodes (LEDs) are expected to be useful as environmentally friendly lighting systems due to many advantages such as low energy consumption, brightness, long lifetime, and lack of pollutants such as Hg. Currently, the combination of a blue LED and yellow phosphor YAG:Ce^{3+} is commonly used for white-light generation.[1–4] However, these devices have a lower color rendering index and higher color temperature because of the red and blue-green light deficiency of YAG:Ce^{3+} phosphor. In recent years, the combination of UV–LED and tricolor phosphor has attracted intensive interest[5] as it can produce LEDs with full color. A mixture of green and red phosphors instead of a yellow phosphor has also been proposed as a color converter.[6,7] To successfully apply phosphor-combined UV–LED or blue LED to lighting, green phosphors with high efficiency, high stability, and low-temperature quenching are required. Recently, a new oxide-based phosphor $Ca_3Sc_2Si_3O_{12}$:Ce^{3+}, which is applicable as a green-emitting color converter for white LEDs has been developed by Shimomura et al.[8,9] This is the first report of a phosphor whose host material is a silicate garnet. The phosphor was less quenched than the YAG:Ce^{3+} phosphor. However, the Sc_2O_3 raw material is the most expensive rare earths oxide, which limits its potential application of this phosphor to a great extent.

Here, we report a novel green-emitting phosphor excited by UV–LED. The phosphor comprises a silicate host and Eu^{2+} activator. The host crystal was characterized as a stable orthorhombic structure instead of garnet-type with the composition $Ba_3Y_2(SiO_4)_3$. The route using inexpensive raw materials benefits the preparation both for laboratory research and wide industrial applications.

The starting materials $BaCO_3$ (A.R.), SiO_2 (A.R.), and Y_2O_3 (A.R.) were weighted in a stoichiometric ratio, pressed into pellets at 10 MPa, and fired at 1350 °C for 6 h to study the crystal structure of $Ba_3Y_2(SiO_4)_3$. High purity Eu_2O_3 (99.99%) was added to produce $Ba_3Y_2(SiO_4)_3$:Eu^{2+}. The atomic ratio of Ba, Y, Si, and Eu was typically set to 2.94:2:3:0.06. After mixing and grinding thoroughly in an agate mortar, the homogeneous mixture was fired at 1300 °C for 2 h to generate $Ba_3Y_2(SiO_4)_3$:Eu^{2+} under a hydrogen atmosphere. The calcined products were ground and washed with 0.5 mol L^{-1} HCl several times. The crystal structure of the sample was checked using a D8 Advance (BRUKER AXS) X-ray diffractometer. The excitation and emission spectra of the sample were detected using a SPEX FluroMax-2 fluorescence spectrometer. Relative luminescent intensity of the sample was recorded with a PMS-50 spectrophotometer.

The formula $Ba_3Y_2(SiO_4)_3$ is similar to that of a garnet, a very common group of nesosilicates. In the $A_3B_2(SiO_4)_3$ garnet structure, atoms A and B are in eightfold triangular dodecahedral sites and sixfold octahedral sites. The combination of Ba^{2+} and Y^{3+} radii for the A and B sites is slightly out of the stability field for silicate garnets predicted by Novak et al.[10] using the effective radii of Shannon et al.[11] However, the X-ray diffraction data of $Ba_3Y_2(SiO_4)_3$ has not been reported in the literature until now.

As shown in Figure 1, the refined lattice parameters obtained by using Cu Kα radiation ($\lambda = 1.540598$ nm) is: orthorhombic, space group *Pnma*, $a = 15.1341$, $b = 12.3896$, $c = 3.9412$ Å, $\alpha = \beta = \gamma = 90°$, $V = 738.9965$ Å^3, $Z = 4$, which is isostructural with $Ca_3Y_2(SiO_4)_3$.[12] The Miller (*hkl*) planes were indexed on the pattern. Three strong peaks located at 30.375, 31.220, and 29.278° are in accordance with (510), (240), and (221) planes, respectively. As shown in Figure 1, raw materials SiO_2 and Y_2O_3 were not found in the products and the crystal structure of $Ba_3Y_2(SiO_4)_3$:Eu^{2+} is almost identical to that of matrix. Small amounts of impurity phases of $Y_2Si_2O_7$ (JCPDS 076-

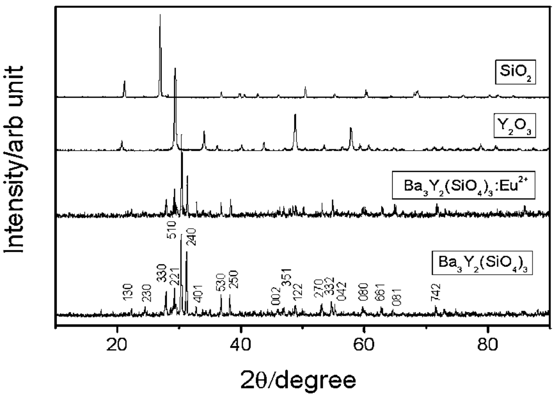

Figure 1. X-ray powder diffraction patterns of $Ba_3Y_2(SiO_4)_3$, $Ba_3Y_2(SiO_4)_3$:Eu^{2+}, Y_2O_3, and SiO_2. The indexed Miller planes were added in the pattern of $Ba_3Y_2(SiO_4)_3$.

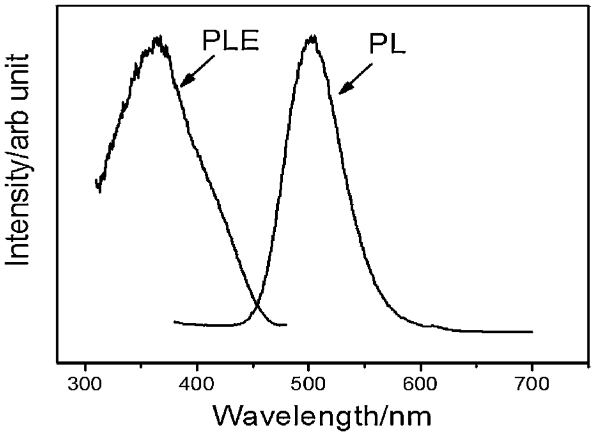

Figure 2. Photoluminescence under 365-nm excitation and excitation spectra monitored at 505 nm of $Ba_3Y_2(SiO_4)_3$:Eu^{2+}.

0204) may be generated, which can be removed during acid washing. When the annealing temperature was raised to 1450 °C, a slightly green but transparent melted product was generated (naturally cooled to room temperature). The same X-ray diffraction pattern was found. Further work is required for quantitative analysis.

Tb^{3+}, Ce^{3+}, and Mn^{2+} are good general activators for green phosphors. But in this case, $Ba_3Y_2(SiO_4)_3$ doped with Tb^{3+}, Ce^{3+}, and Mn^{2+} does not emit visible light under 365- or 254-nm excitation. It was only found that $Ba_3Y_2(SiO_4)_3$ doped with Eu^{2+} is a potential good phosphor. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra are shown in Figure 2.

As we can see, PL peak wavelength was about 505 nm. The CIE color coordinates calculated between 380 and 780 nm were $x = 0.1325$ and $y = 0.4221$. The peak wavelength in the PLE spectrum was about 365 nm, which is very suitable for a color converter of white LED that uses UV–LED as the primary light source. The absorption arises from 4f–5d transition of Eu^{2+} and not from host crystal absorption because $Ba_3Y_2(SiO_4)_3$ showed no emission around 505 nm.

By varying the content of the Eu^{2+} activator in the host, we determined the composition with the highest PL emission intensity. Figure 3 demonstrates the dependence of the PL emission intensity on the doping concentration (x) of Eu^{2+} in $Ba_{3-x}Y_2(SiO_4)_3$:$Eu^{2+}{}_x$. The PL emission intensity increases with the increase of Eu^{2+} content (x) first, reaches a maximum value at $x = 12$ mol %, and then decreases due to concentration quenching. Thus, the optimum concentration of Eu^{2+} is 4 mol % relative to the Ba^{2+} content in $Ba_3Y_2(SiO_4)_3$ host. The external quantum efficiency found to be 17% with a SPR-960 phosphor Test System for white LED.

The valence state of Eu and Y in this phosphor was examined by X-ray photoelectron spectroscopy.[13] It was concluded that Eu is divalent and Y is trivalent because the binding energies of Eu 4d electrons and Y 3d electrons were located at 132 and 157 eV, which are in good agreement with those data for Eu^{2+} and Y^{3+} in the literature.[14,15] However, the valence of Eu ion often remains trivalent in the host including Y, but the valence of Eu ion in this phosphor is divalent. It is supposed that the reaction atmosphere played a crucial role in the stability of Eu^{2+}. Under an oxidative atmosphere, Eu maintains its trivalent state (94.7 pm, radius of six-coordinate) and trends to replace Y^{3+} (90 pm), while under a reducing atmosphere, Eu with divalent state (117 pm) trends to replace a divalent ion, Ba^{2+} (136 pm) in this case instead of Y^{3+} to maintain charge balance and also closer radius.

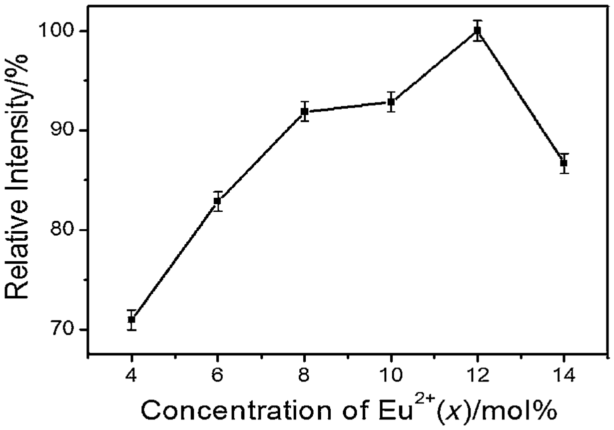

Figure 3. Dependence of relative luminescence intensity of $Ba_3Y_2(SiO_4)_3$:Eu^{2+} on the concentration of Eu^{2+}.

In conclusion, a new green-emitting phosphor has been developed. The host crystal structure of the phosphor was indexed as orthorhombic. The photoluminescence results from 5d–4f transition of Eu^{2+} ions. This type of phosphor reaches the maximum photoluminescence intensity when 4% of the Ba position was replaced by Eu. The phosphor originated from inexpensive raw materials is a promising candidate for color conversion phosphor for white LEDs.

The authors are thankful for the financially support of Jiangxi Province Science Foundation for Youths and Technology R&D Program.

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