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Tricolor emitting and energy transfer in the phosphor $Ba_2ZnSi_2O_7$:Ce^{3+},Eu^{3+},Eu^{2+} for white-LED based near-UV chips

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Abstract: The red, green and blue (R/G/B) tricolor emitting phosphors $Ba_2ZnSi_2O_7$ co-doped with Ce^{3+} and Eu^{3+} were synthesized in air atmosphere by a conventional high temperature solid-state reaction technique. All of the excitation spectrum of the phosphor $Ba_2ZnSi_2O_7$:Ce,Eu showed a strong broad band absorption in the n-UV region whenever monitored by red (630 nm)-emitting or by green (500 nm)- and blue (402 nm)-emitting. Under the excitation of 330 nm, the emission spectrum containing a blue-violet emission band, a green emission and four sharp lines originated from the characteristic transitions of Ce^{3+}, Eu^{2+} and Eu^{3+} ions, of which the relative intensities of the three emission bands could be controlled by the doping concentration of Ce^{3+}. The *ca.* CIE chromaticity coordinates (x=0.317, y=0.309) of the phosphor $Ba_{1.94}ZnSi_2O_7$:0.03Eu,0.01Ce was very close to the standard white (x=0.33, y=0.33), which suggested that it was a novel single-phased white-light emitting phosphor for LED-based near-UV chip. The mechanisms of energy transfer from Eu^{2+} to Eu^{3+} via Ce^{3+} was also discussed.

Keywords: rare earths; $Ba_2ZnSi_2O_7$:Eu,Ce; R/G/B tricolor emitting phosphor; white-LEDs

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White light-emitting diodes (LEDs)[1,2] have been widely applied in consumer electronics as well as in solid lighting. As is well known, there are two common methods to generate white-LEDs, one is to combine a near-ultraviolet (near-UV) LED chip with tricolor phosphors[3] (red[4–6], green[7] and blue[8]), the other is to combine a blue chip with a yellow phosphor YAG:Ce^{3+}. However, the former shows the poor luminous efficiency owing to the strong reabsorption of blue light by the red and green phosphors[9–11], the latter has a low color rendering index *Ra* (around 80) because the yellow light emission from the phosphor YAG:Ce lacks sufficient red emission. To overcome problems like these for white-LEDs, singly phased white-light phosphors have been an active research area in the study of luminescent materials.

Recently, singly phased white-light phosphors for near-UV excitation have been reported, such as $NaBa_4(BO_3)_3$:Ce^{3+},Eu^{3+} [12], $Ca_3Y(GaO)_3(BO_3)_4$:Ce^{3+},Mn^{2+},Tb^{3+} [13], $Ca_9Y(PO_4)$:Eu^{2+},Mn^{2+} [14], $Sr_3Lu(PO_4)_3$:Eu^{2+},Mn^{2+} [15], $CaScAlSiO_6$:Ce^{3+},Tb^{3+},Mn^{2+} [16], $Sr_2MgSi_2O_7$:Ce^{3+},Tb^{3+},Eu^{3+} [17] and $Sr_{1.5}Ca_{0.5}SiO_4$:Eu^{3+},Tb^{3+},Eu^{2+} [18]. Silicates, an important family of luminescent materials, have attracted much attention owing to their excellent thermal stability and environmental benignity potential.

In addition, Eu^{3+}, Eu^{2+} and Ce^{3+} are three important trivalent rare earth ions which have been used to produce red, green and blue green emission, respectively. And multi-color-emitting phosphors are usually designed according to the energy transfer between different activators (such as Ce^{3+}-Eu^{2+}, Ce^{3+}-Eu^{3+}) in a number of hosts[19–25]. At present, the luminescence characteristics of Eu^{3+} or Eu^{2+} singly doped $Ba_2ZnSi_2O_7$ have also been investigated[26,27], in which Eu^{3+} ion shows typical red emission and Eu^{2+} shows two broad band emissions centered at 373 nm and 500 nm, respectively. Ce^{3+} is an effective sensitizer for Eu^{3+} and Eu^{2+}, which could enhance the luminescence intensity of Eu^{3+} and produce red and green emission. Hence, the tricolor emission bands of the phosphor $Ba_2ZnSi_2O_7$ triply doped with Eu^{3+}, Eu^{2+} and Ce^{3+} may combine to give out white light. Nevertheless, no report of such work has been found in the previous literatures.

In present work, we reported our recent investigation results on the luminescence properties of the phosphor $Ba_2ZnSi_2O_7$ doped with Ce^{3+} and Eu^{3+}, in which energy transfer from Eu^{2+} to Eu^{3+} via Ce^{3+} was also discussed.

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1 Experimental

1.1 Preparation of $Ba_{2-(x+y)}ZnSi_2O_7$:*x*Eu,*y*Ce samples

All of the samples were synthesized directly by the general high temperature solid-state reaction. Eu_2O_3 (99.99%), $CeCl_3$ (99.95%), $BaCO_3$ (A.R.), ZnO(A.R.), H_2SiO_3 (A.R.) and Li_2CO_3 (A.R.) were used as raw materials. A LED phosphor consists of alkaline earth pyrosilicates co-activated by Eu^{3+} and Ce^{3+}, whose design formula is $Ba_{2-(x+y)}ZnSi_2O_7$:*x*Eu,*y*Ce. Ce^{3+} and Eu^{3+} are expected to occupy Ba^{2+} according to the effect of the ionic sizes of the cations. In addition, stoichiometric Li_2CO_3 that is equal to the amount of Eu^{3+} and Ce^{3+} ions was used as a charge compensator in order to maintain the charge neutrality of the crystal.

The stoichiometric amounts of starting materials were thoroughly mixed by grinding in an agate mortar and heated at 1200 ºC for 4 h in air atmosphere. Therefore, the samples $Ba_{2-(x+y)}ZnSi_2O_7$:*x*Eu,*y*Ce, (*x*, *y*=0–0.05) were prepared by a conventional solid-state reaction technique.

1.2 Apparatuses and measurements

The crystalline phase of the prepared samples was examined by the X-ray diffractometry (XRD) with Cu Kα radiation at 40 kV and 300 mA (Rigaku D/MAX-2500 X-ray diffractometry, Tokyo, Japan). Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were measured using a Hitachi F-4500 luminescence spectrofluorometer, equipped with a 175 W xenon lamp as an excitation source, 400V photomultiplier tube voltage, and UV390 nm filter.

2 Results and discussion

2.1 Phase composition of the obtained phosphor

Fig. 1 is the XRD pattern of Ce^{3+}-Eu^{3+} co-doped $Ba_{1.94}ZnSi_2O_7$:0.03Eu,0.01Ce sample. And the XRD patterns of all samples are similar. As shown in Fig. 1, all of the diffraction peaks were found to agree well with the XRD data of $Ba_2ZnSi_2O_7$ reported in Ref. [27], indicating that the singly or doubly doped Ce^{3+} and Eu^{3+} did not generate any impurity or led to significant changes in the host structure as we introduced activators Ce^{3+} and Eu^{3+} in our experimentally used concentration range. All samples crystallized in the monoclinic structure with *C*2/*c* space group.

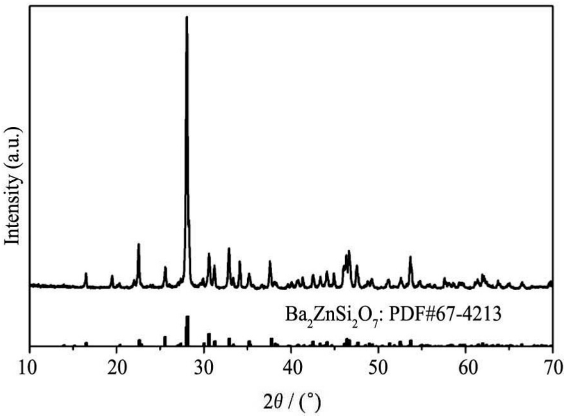

Fig. 1 XRD patterns of sample $Ba_{1.94}ZnSi_2O_7$:0.03Eu,0.01Ce

2.2 Luminescent properties

PL and PLE spectra of solely doped Ce^{3+} or Eu^{3+} and Ce^{3+}-Eu^{3+} co-doped $Ba_2ZnSi_2O_7$ phosphors are shown in Fig. 2. For Ce^{3+} singly doped sample $Ba_{2-y}ZnSi_2O_7$:$y$$Ce^{3+}$, its excitation and emission spectra are illustrated in Fig. 2(a). The excitation spectrum exhibits a set of characteristic optical transitions of Ce^{3+} centered at about 330 nm. Under excitated by 330 nm, the emission spectrum shows a broad asymmetric band with a maximum at 402 nm, which is due to the typical band emission of Ce^{3+} 5d–4f ($^2F_{5/2}$ and $^2F_{7/2}$). Above results reveal that the $Ba_2ZnSi_2O_7$:Ce^{3+} is a good blue-emitting phosphor suited to near-UV chip.

For Eu singly doped $Ba_2ZnSi_2O_7$, the luminescent properties of $Ba_2ZnSi_2O_7$:Eu^{3+} prepared by sol-gel process[26] and $Ba_2ZnSi_2O_7$:Eu^{2+} prepared by the combustion synthesis method[27] have been reported, respectively. But our results show some remarkable differences from theirs. The excitation spectra of $Ba_2ZnSi_2O_7$:0.03Eu prepared in the present work are shown in Fig. 2(b). It consists of two excitation bands at 394 and 465 nm. When monitoring the emission of Eu^{3+} 4f–4f transition, some strong sharp lines peaking at 394 nm and 465 nm correspond to the characteristic f–f transitions of Eu^{3+} within its $4f^6$ configuration, and their relative intensity gradually increases with the increasing Eu^{3+} concentration in our experimental range ($0 \leq x \leq 0.05$); the weak band from 200 to 350 nm corresponds to the charge transfer transition between host and Eu^{3+}. However, the excitation spectrum is composed of two obvious broad excitation bands of Eu^{2+} centered at 350 and 402 nm when monitoring the emission of Eu^{2+} 5d–4f transition at 500 nm, and the latter is dominant band. Clearly, a broad excitation band from 300 to 450 nm is assigned to the electronic transitions from ground state to different crystal field splitting bands of excited 5d of Eu^{2+}. Under the excitation of 330 nm, it can be seen clearly that the emission spectra consist of three bands: a weak broad band with a maximum at 373 nm, an intense broad band ranging maximum at 500 nm and four sharp lines in the 575–750 nm longer wavelength range. The former, two broad band emissions, could be readily assigned to spin-allowed $4f^75d$–$4f^7$ transitions of Eu^{2+}, with their exact position being dependent on the crystal field of the lattice; the latter, sharp peaks, can be explained in terms of internal Eu^{3+} 4f→4f transitions, with the peaks at 591, 615, 650 and 700 nm assigned to $^5D_0 \rightarrow {}^7F_J$ (*J*=1, 2, 3, 4) of Eu^{3+} ions, respectively. The luminescent phenomenon is due to the fact