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An intense blue-emitting phosphor for near-ultraviolet pumped white-light-emitting diodes: Ce^{3+}-activated β-Ca_2SiO_4

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ABSTRACT

More recently, Ce^{3+} activated γ-Ca_2SiO_4 has been reported and it shows great potential application as a yellow-emitting phosphor for white LEDs. However, β-Ca_2SiO_4, another known phase of Ca_2SiO_4, doped with Ce^{3+} is not available. It is interesting to know if β-Ca_2SiO_4:Ce^{3+} can also be suitable for white LEDs. For this reason, we synthesized a series of β-Ca_2SiO_4:Ce^{3+} phosphors by solid state reaction. β-Ca_2SiO_4:Ce^{3+} exhibits an intense blue emission band peaked at 425 nm with a bandwidth of 68 nm which is attributed to the typical Ce^{3+} $4f^05d^1 \rightarrow 4f^1$ transitions. The integral intensity of the concentration-optimized β-Ca_2SiO_4:Ce^{3+} can be as high as 71% of the commercial BAM blue phosphor upon 360 nm excitation. The excitation spectra of β-Ca_2SiO_4:Ce^{3+} consist of three broad bands with maxima at 252, 289 and 348 nm , which are ascribed to the $4f^1 \rightarrow 4f^05d^1$ transitions of Ce^{3+}. Thermal quenching property of β-Ca_2SiO_4:Ce^{3+} was evaluated and the results show that the integral PL intensity at 150 °C maintains about 93% of that at room temperature. The excellent thermal stability and intense emission upon NUV light excitation suggest that β-Ca_2SiO_4:Ce^{3+} can be used as a potential blue-emitting phosphor for NUV white LEDs.

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1. Introduction

In recent years, white light emitting diodes (LEDs) based solid state lighting (SSL) has been significantly developed due to their advantages of high efficiency, long lifetime, eco-friendly and high stability characteristics [1–3]. The white LEDs employing blue LED and yellow YAG:Ce^{3+} phosphor suffer from the color shift against forward current due to that the die-blue involved in the synthesis of white light. Fortunately, the white LEDs combined near-ultraviolet (NUV) LED chips with red/green/blue tri-color phosphors can solve this problem because of the insensibility of human eyes to UV light, i.e. the white light is completely phosphor converted [4]. Therefore, the NUV-converted phosphor could have great potential applications in white LEDs.

The Eu^{2+} activated alkaline earth orthosilicates (M_2SiO_4, M=Ca, Sr, Ba) phosphors have found their important applications as a kind of high efficient NUV-converted phosphor for white LEDs in the recent few years [5–8], although they were reported early in 1960s by Blasse et al. and Barry [9,10]. The significant feature is that their emission color can be easily controlled from green to yellow by tuning the composition of M cations [5,10]. Besides Eu^{2+}, Ce^{3+} is another well-known high efficient activator due to its allowed 5d-4f transitions [11,12]. Despite the photoluminescence properties of Ce^{3+} activated Sr_2SiO_4 and Ba_2SiO_4 were reported respectively early in 1970s [13], to the best of our knowledge, few of literatures are available for that of Ce^{3+} activated Ca_2SiO_4 till now. Recently, Jang et al. reported a new yellow-emitting γ-Ca_2SiO_4:Ce^{3+}, Li^+ phosphor that has a strong yellow emission band peaked at around 559 nm under blue light excitation and shows great potential for application in white LEDs [14]. As we known, the stable Ca_2SiO_4 polymorph at room temperature is the γ type, which has an orthorhombic olivine structure (space group Pbnm, number 62) [2,15]. At room temperature, Ca_2SiO_4 also possesses a metastable β phase, which is isotypic with the β-Sr_2SiO_4 phase [15]. Therefore, the investigation on the photoluminescence of β-Ca_2SiO_4:Ce^{3+}, Li^+ will be interesting for justifying if the beta phase Ca_2SiO_4 could also be an applicable phosphor material for white LEDs. For this reason, we successfully synthesized a series of β-Ca_2SiO_4:Ce^{3+}, Li^+ phosphors. The photoluminescence properties have been investigated by means of emission and excitation spectra, and fluorescence decay curves. In this paper, the results of the photoluminescence properties of β-Ca_2SiO_4:Ce^{3+}, Li^+ will be analyzed detailedly, and the thermal quenching characteristic which is significant for white LEDs applications was also evaluated.

2. Experimental

2.1. Synthesis

Synthesis of the β-$Ca_{2-2x}SiO_4$:xCe^{3+}, xLi^+ (x=0.005, 0.01, 0.03, 0.05, 0.07, and 0.09) powder samples was conducted using solid state reaction. The starting materials used were high pure $CaCO_3$

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(99.9%), SiO_2 (99.9%), CeO_2 (99.99%), Li_2CO_3 (99.9%). The charge compensation for the substitution of Ca^{2+} by Ce^{3+} is achieved by adding equimolar concentrations of Li^+. Added as flux was 5 mol% of CaF_2. Stoichiometric amounts of the starting materials were pestled for 1 h in an agate mortar for homogenization. Then, the mixtures were kept in an alumina crucible boat inside a horizontal tubular furnace and slowly heated to 1250 °C under a reducing atmosphere (5% H_2+95% N_2). The samples were kept at this temperature for 4 h and then cooled to room temperature by furnace cooling, maintaining the flow of reducing gas till the furnace reaches room temperature.

2.2. Characterization

A Bruker D8-Focus X-ray diffractometer (XRD) was employed to check the phase of the phosphors. The photoluminescence (PL) emission and excitation (PLE) spectra were measured using an Edinburgh Instruments FL920 steady-state spectrophotometer with a 450 W xenon lamp as the excitation source. The fluorescence decay curves of Ce^{3+} were measured also by FL920 with a hydrogen flash lamp. All of the measurements above were performed at room temperature. A thermostat (Omega CN76000) was used to obtain the temperature-dependent photoluminescence (25–205 °C) spectra which were performed via Hitachi F-4500 spectrometer.

3. Results and discussion

3.1. Phase formation

The powder XRD patterns of β-$Ca_{2-2x}SiO_4$:$x$$Ce^{3+}$, $x$$Li^+$ (x=0.005, 0.01, 0.03, 0.05, 0.07, and 0.09) were shown in Fig. 1, as well as the standard JCPDS data of β-Ca_2SiO_4. All the reflections could be indexed according to the patterns of standard β-Ca_2SiO_4 (No. 33-0302), suggesting that the dopant Ce^{3+} and Li^+ do not significantly influence the XRD patterns of the host. Considering that the ionic radius of Ce^{3+} is close to that of Ca^{2+} and the ionic radius of Si^{4+} is too small compared with Ce^{3+} and Ca^{2+}, it is high probability that the Ce^{3+} ions substitute for Ca^{2+} sites in β-Ca_2SiO_4. The β-Ca_2SiO_4 crystallizes into a monoclinic structure based on space group of $P2_1/n$ (14) and two different types of Ca sites, Ca (1) and Ca (2). The coordination numbers around Ca (1) and Ca (2) were 7 and 8 with the average bond length of 2.5105 and 2.4975 Å, respectively [16]. The substitution of Ce^{3+} for Ca^{2+} sites will be described below.

3.2. Photoluminescence studies

According to the monoclinic structure of β-Ca_2SiO_4 mentioned above, two Ce^{3+} luminescence centers may possibly exist in β-Ca_2SiO_4 lattice due to two Ca^{2+} sites for Ce^{3+} substitution. In order to distinguish these two potential emission bands, different excitation wavelength were chosen to obtain the PL spectra and different emission positions were monitored for PLE spectra. However, as shown in Fig. 2, the PL spectra coincide well with each other except a little red shift from λ_{ex}=320 nm to λ_{ex}=360 nm which is likely caused by the effect of inhomogeneous broadening, which is evidenced by the PLE spectra that also showed red shift from λ_{em}=400 nm to λ_{em}=460 nm. The expected distinguish PL/PLE spectra from two activator sites do not appear. Therefore, it could be deduced that the primary contributors to the luminescence of β-$Ca_{1.94}SiO_4$:0.03Ce^{3+}, 0.03Li^+ might come from a single Ce^{3+} luminescence center. This phenomenon is consistent with the case of γ-Ca_2SiO_4:Ce^{3+}, Li^+ in which it is determined that the Ce^{3+} ions at the Ca (1) sites in the host lattice are the primary contributors to the luminescence by the method of density

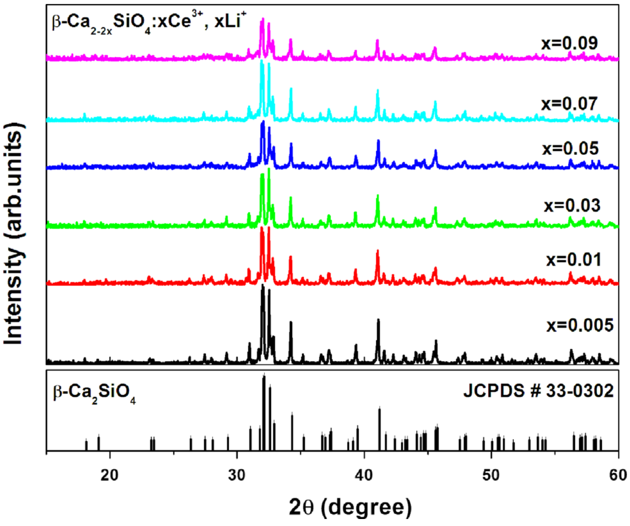

Fig. 1. XRD patterns of the series of β-$Ca_{2-2x}SiO_4$:$x$$Ce^{3+}$, $x$$Li^+$ (x=0.005, 0.01, 0.03, 0.05, 0.07, and 0.09) phosphors and the standard patterns of β-Ca_2SiO_4.

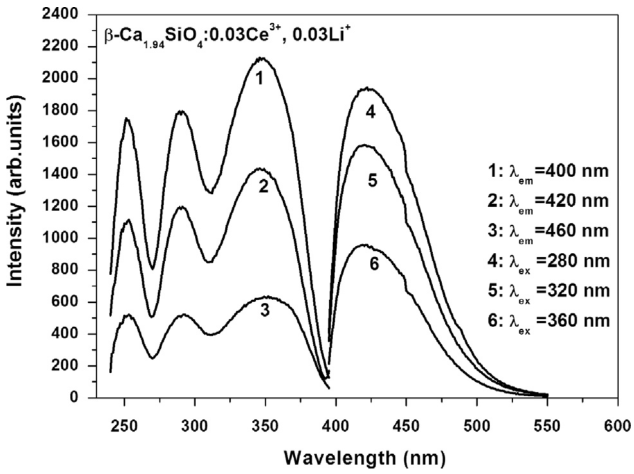

Fig. 2. Excitation and emission spectra of β-$Ca_{1.94}SiO_4$:0.03Ce^{3+}, 0.03Li^+.

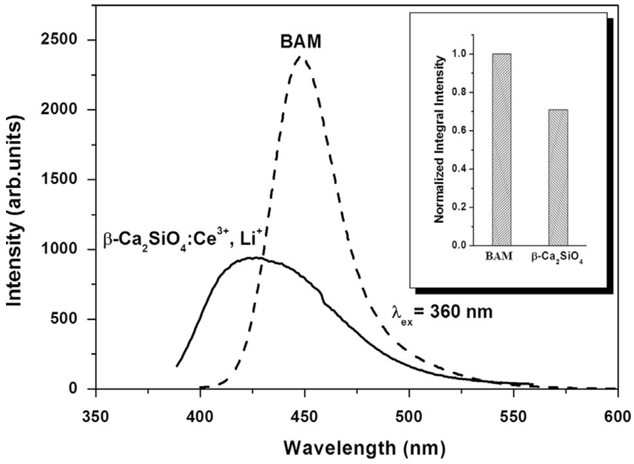

Fig. 3. Comparison of PL spectra of β-Ca1.94SiO_4:0.03Ce^{3+}, 0.03Li^+ with commercial BAM blue phosphor under 360 nm NUV excitation. Inset: Integrated intensity histogram.

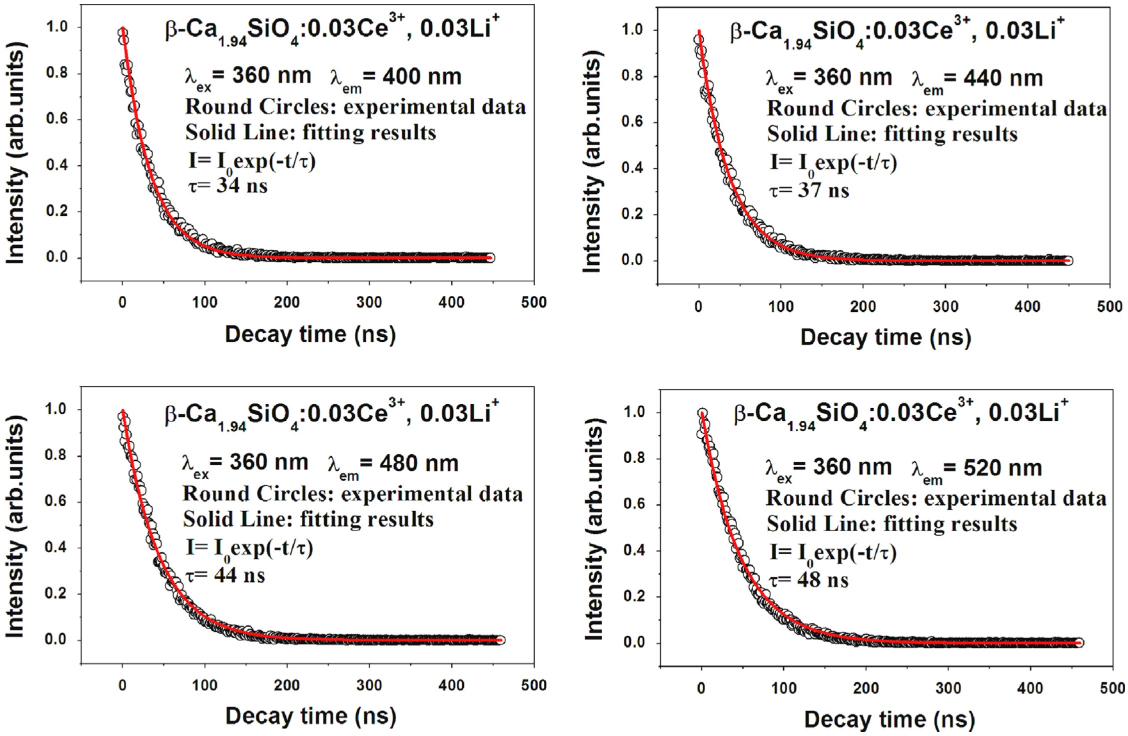

Fig. 4. Fluorescence decay curves of β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^+$ monitored at 400 nm, 440 nm, 480 nm, and 520 nm.

functional theory (DFT) calculations [14]. The similar work for β-Ca_2SiO_4:Ce^{3+}, Li^+ will be undertaken in the future.

The influence of the Ce^{3+} concentration on the emission intensity of Ce^{3+}-activated β-Ca_2SiO_4 is investigated and the optimum doping concentration of Ce^{3+} is determined to be $x=0.03$, beyond which the PL intensity decreases because of the concentration quenching process. Therefore, only the PL and PLE spectra of β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^+$ are shown in Fig. 2 as a representative. It can be seen that the excitation spectra of Ce^{3+} in β-Ca_2SiO_4 obviously consist of three broad bands with maxima at 252, 289 and 348 nm respectively, which are attributed to the $4f^1 \rightarrow 4f^05d^1$ transitions of Ce^{3+}. The excitation spectra are similar with that of other orthosilicates [13,17]. The broad excitation band covering the NUV region meets the criterion of high absorption of NUV by phosphors, a necessary condition for phosphors for white LEDs based on NUV LED chips. The emission spectra exhibit a typical asymmetric band of Ce^{3+} peaked at about 425 nm with a broad bandwidth of 68 nm which is assigned to $Ce^{3+}4f^05d^1 \rightarrow 4f^1$ transitions. The emission peak position is longer than that in Ba_2SiO_4 (384 nm) and Sr_2SiO_4 (399.5 nm) [13] which is likely caused by the stronger crystal field strength in β-Ca_2SiO_4.

3.3. PL comparison with commercial BAM blue phosphor

The PL spectra of commercial blue emitting $BaMgAl_{10}O_{17}$:Eu^{2+} (BAM, Shanghai Yuelong New Materials Co. Ltd.) phosphor was measured accurately under the same condition for comparison with β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^+$, as shown in Fig. 3. Under the excitation wavelength at 360 nm, the integrated emission intensity of β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^+$ is 71% as intense as that of BAM, intuitively shown in the inset of Fig. 3. It is believed that this inferior intensity will be improved by further optimization including starting material, reaction temperature, time, flux, technical process and so on. Anyway, these results indicate that β-Ca_2SiO_4:Ce^{3+}, Li^+ is a high efficient phosphor which can be used as a novel blue-emitting phosphor for LED applications.

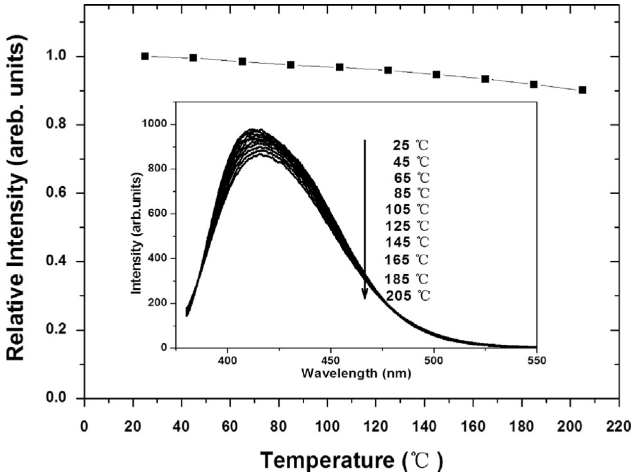

Fig. 5. The relative PL intensities of β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^+$ at various temperatures in the range of 25–205 °C.

3.4. Fluorescence decay characteristics

Fig. 4 shows the fluorescence decay curves of Ce^{3+} in monoclinic β-Ca_2SiO_4. In order to understand excited state processes detailedly, we chose four emission positions which are uniformly distributed in the emission band to monitor to cover the different excited state levels, i.e. 400 nm, 440 nm, 480 nm, and 520 nm. As shown in Fig. 4, all the decay curves can be well-fitted into single-exponential function as $I=I_0\exp(-t/\tau)$ in which τ is the decay lifetime, and the lifetimes are determined to be about 34 ns, 37 ns, 44 ns, and 48 ns. They are on the same order of magnitude as that of Ce^{3+} in other hosts [18,19]. Furthermore, the decay time at shorter emission wavelengths is shorter than that at longer emission wavelengths. This behavior may be due to the energy transfer from high energy Ce^{3+} ions to low energy Ce^{3+} ions in inhomogeneous environment of the activator ions. Similar phenomenon has been observed previously in LuAG:Ce^{3+} garnet phosphors [19]. These well-fitted single-exponential decay curves further prove that there is only one type of Ce^{3+} luminescence centers in the host lattice.

3.5. Evaluation of the thermal stability

Fig. 5 shows the thermal quenching of luminescence spectra of β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^{+}$ at various temperatures in the range of 25–205 °C. The luminescence intensity at 150 °C, the usual temperature that phosphor suffers when LED operating, remains 93% of that at room temperature implying the excellent thermal quenching properties of β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^{+}$ and this is great better than that in γ-Ca_2SiO_4:Ce^{3+}, Li^{+} in which the PL intensity only remains 56% when the temperature of the phosphor was elevated from room temperature to 150 °C [14].

4. Conclusions

An intense blue-emitting phosphor of Ce^{3+}-activated β-Ca_2SiO_4 was synthesized by solid-state reaction. The photoluminescence spectra show that this phosphor is excitable efficiently by NUV light and shows intense blue emission bands peaking at about 425 nm with a bandwidth of 68 nm. The integral intensity of the β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^{+}$ can be as high as 71% of the commercial blue phosphor BAM upon 360 nm excitation. Furthermore, β-$Ca_{1.94}SiO_4$:$0.03Ce^{3+}$, $0.03Li^{+}$ shows good performance on thermal stability against temperature, i.e. the luminescence intensity at 150 °C maintains 93% of that at 25 °C. The excellent thermal stability and intense emission upon NUV light excitation suggest that β-Ca_2SiO_4:Ce^{3+} can be used as a potential blue-emitting phosphor for NUV white LEDs.

Acknowledgements

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