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Short communication

Tunable white-light emission of SiAlON-base crystal/glass composite phosphor by variation of excitation wavelength

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Abstract

Tunable white light of Eu^{2+} doped SiAlON crystal/glass composite phosphor with blue-yellow dual-emissions was demonstrated by variation of excitation wavelength in this work. The excitation properties of blue emission originated from the transition of Eu^{2+} ions in the Si–Al–B–O–N glass matrix and that of yellow emission originated from the transition of Eu^{2+} ions in the SiAlON lattice were investigated, respectively. By varying the excitation wavelength in the range of 330–380 nm, white emission was tuned from cool white to warm white for this SiAlON crystal/glass composite phosphor owing to the various excitation properties of these two emission bands. Presented results indicate that this tunable SiAlON crystal/glass composite white-light phosphor might be applied in white LED, combining with UV chips with different emitting wavelengths in the range of 330–380 nm.

Keywords: Phosphor; Luminescence; Tunable white light; Excitation wavelength

1. Introduction

White-light-emitting diodes (WLEDs) have widely applied in lighting and display fields because of their outstanding merits in high efficiency, long lifetime and lower energy consumption [1,2]. The generally strategies for encapsulation of WLEDs are the combination of a blue LED chip with a yellow phosphor, the mixture of multi-phosphors with a UV LED chip, as well as the blending of multi-LED chips [3,4]. One of the current academic interests is the development of direct white-light phosphor to overcome the intrinsic shortages in poor color stability and high cost for the strategy of multi-LED chips and that in device complication and self-absorption for the strategy of multi-phosphors. Examples can be found in the research fields of semiconducting nanocrystals [5], organic compounds [6], complexes [7] inorganic–organic hybrid materials [8], and rare earth doped inorganic phosphors [9].

In the past decades, rare earth doped inorganic phosphors with direct white light have received intense interest due to their high luminescent efficiency, excellent chemical stability, as well as the outstanding color adjustment to meet the technology requirements in WLEDs. According to the white light emitting mechanisms, rare earth doped direct white light phosphors can be classified into following groups: (1) Eu^{2+}–Mn^{2+} or Ce^{3+}–Mn^{2+} or Ce^{3+}–Eu^{2+} or Ce^{3+}–Tb^{3+} co-doped direct white light phosphors basing on the energy transfer between the dopant couple, e.g. $KCaY(PO_4)_2$:Eu^{2+}, Mn^{2+} [10], $Ba_{1.2}Ca_{0.8}SiO_4$:Ce^{3+}, Mn^{2+} [11], $Sr_3Al_2O_5Cl_2$:Ce^{3+}, Eu^{2+} [12], $Ca_8Mg(SiO_4)_4Cl_2$:Ce^{3+}, Tb^{3+} [13]; (2) blue-, green- and red-luminescent centers tri-doped direct white light phosphors with the mixture of the tri-colors, exampling as $Ca_3Y(GaO)_3(BO_3)_4$:Ce^{3+}, Tb^{3+}, Mn^{2+} [14] and Y_2GeO_5:Tm^{3+}, Tb^{3+}, Eu^{3+} [15]; (3) Dy^{3+} or Pr^{3+} or Eu^{3+} single-doped direct white light phosphors originated from the multi-transition

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emissions of dopants, for examples, $CaMgSi_2O_5:Dy^{3+}$ [16], $Sr_2SiO_4:Pr^{3+}$ [17], $BaY_2ZnO_5:Eu^{3+}$ [18]; (4) Eu^{2+} single-doped direct white light phosphors with multi-substitution sites for dopants, for instance $BaSrMg(PO_4)_2:Eu^{2+}$ [19]. Additionally, a mixed valence Eu co-doped $LaAlO_3$ direct white light phosphor with the blending of the intrinsic emission of Eu^{2+} and Eu^{3+} was explored by our group [20,21]. Very recently, we demonstrated a novel strategy for the generation of direct white light by fabricating blue-emitting glass phase on Eu^{2+} doped SiAlON yellow-emitting phosphor particle via melting corrosion [22–24]. Excellent color adjustment for these direct white light phosphors is highly expected to meet the different application demands. Generally, the emission properties for white light phosphors are tuned from the perspective of phosphor itself substantially, such as the white light of Eu^{2+}–Mn^{2+} co-doped phosphor can be tuned by their energy transfer. Alternatively, tunable emission color for some white light luminescence materials was also demonstrated by variation of excitation light, expanding the applications for these materials through combining with difference excitation sources [6]. As to our previous reported Eu^{2+} doped SiAlON-based crystal/glass composite phosphor, varied excitation properties for Eu^{2+} ions doped in the crystal lattice and the glass matrix were observed because of their distinguished coordination environment, indicating the potential color adjustment by variation of excitation light.

Therefore, the emission adjustment of Eu^{2+} doped SiAlON-based crystal/glass direct white light composite phosphor will be demonstrated by variation of excitation wavelength in this work. The excitation properties of Eu^{2+} ions doped in the SiAlON lattice and glass matrix are investigated respectively. Tunable white emission from cool white to warm light is shown by changing the excitation wavelength in the range of 330–380 nm, indicating the potential application in WLEDs combining with UV chips with different emitting wavelengths.

2. Experimental

Eu^{2+} doped SiAlON crystal/glass composite phosphor with direct white light emission was synthesized by two steps. Firstly, α-SiAlON:Eu^{2+} yellow-emitting phosphor in the nominal composition $Ca_{0.98}Si_9Al_3ON_{15}:0.02Eu^{2+}$ was prepared from α-Si_3N_4 (SN-E10, UbeIndustries, Japan), AlN (Type F, Tokuyama Corp., Japan), $CaCO_3$ (99.99%, Aladdin, China) and Eu_2O_3 (99.99%, Aladdin, China) powders by the conventional high temperature solid-state reaction as reported in Ref. [25]. Secondly, B_2O_3 (AR, Aladdin, China) and the pre-obtained α-SiAlON yellow-emitting phosphor in a proportion of 1:3 in weight were mixed thoroughly (B_2O_3:α-SiAlON = 1:3), and then heated rapidly at 1200 °C for 30 min under N_2 atmosphere in a high-frequency induction furnace with a graphite heater. Upon cooling down naturally to room temperature and grinding, Eu^{2+} doped SiAlON-based crystal/glass composite white light emission phosphor was obtained.

The SEM images of the obtained samples were taken on a JSM-6700 F field-emission scanning electron microscope equipped with an X-ray energy dispersive spectrometer (EDS). The photoluminescence (PL) and photoluminescence of excitation (PLE) were measured on a FluoroMax®-4 fluorescence spectrometer equipped with a xenon light source. The slits for both excitation and emission were set as 1 nm. Commission International deI'Eclairage (CIE) chromaticity coordinates and correlated color temperatures (CCT) were examined on a PMS-80 Plus UV–vis-near IR Spectro-photocolorimeter (EVERINE, China) system.

3. Results and discussion

The SEM images of the pre-obtained α-SiAlON:Eu^{2+} phosphor sample and the obtained Eu^{2+} doped SiAlON-based crystal/glass composite phosphor sample are shown in Fig. 1(a) and (b), respectively. It is found that the obtained α-SiAlON:Eu^{2+} phosphor is about 1–2 μm in particle size whereas the obtained Eu^{2+} doped SiAlON-based crystal/glass composite phosphor sample has larger particles with size of 3–4 μm, indicating the coating on α-SiAlON particles or the aggregation of α-SiAlON particles induced by the B_2O_3 additive during the heat treatment procedure. Our previous work has clarified that the formation mechanism of SiAlON-based crystal/glass composite phosphor materials is the melting corrosion effect of lower melting oxides (B_2O_3 or nano-SiO_2) on α-SiAlON particles [22–24]. Herein, the increasing of particle size can be ascribed to the glass coating resulted from the melting corrosion of B_2O_3 on α-SiAlON particles. In addition, we will find the surface of the pre-obtained α-SiAlON:Eu^{2+} phosphor particles is smoother than that of the obtained Eu^{2+} doped SiAlON-based crystal/glass composite phosphor particles, further revealing the melting corrosion of B_2O_3 on α-SiAlON particles. Fig. 1(c) and (d) displays the EDS element analysis of the pre-obtained α-SiAlON:Eu^{2+} phosphor sample and that of the obtained Eu^{2+} doped SiAlON-based crystal/glass composite phosphor sample, respectively. It is found that the content of Ca, Si, Al, N element is higher while that of O element is lower for the pre-obtained α-SiAlON:Eu^{2+} phosphor sample, compared with Eu^{2+} doped SiAlON-based crystal/glass composite phosphor sample. These changes can be also ascribed to the incorporation of B_2O_3 via melting corrosion procedure. It worth to note that boron element is not detected in the EDS element analysis for crystal/glass composite sample because of boron element is too light.

The PL and PLE spectra of Eu^{2+} doped SiAlON-based crystal/glass composite phosphor are expressed in Fig. 2. It is found that a broad blue emission band positioned at 430 nm and a broad yellow emission band peaked at 555 nm are observed under the excitation of 340 nm UV light. As a result, the mixture of these two emission bands can generate direct white. Our previous work has clarified the luminescent mechanism for this blue-yellow dual-emissions crystal/glass composite phosphor [22–24]. The blue emission band and the yellow emission band was assigned to be the $4f^65d$–$4f^7$ transition emission of Eu^{2+} ions doped in the Si–Al–B–O–N glass matrix and SiAlON crystal lattice, respectively. The shorter wavelength emission of Eu^{2+} ions doped in the glass

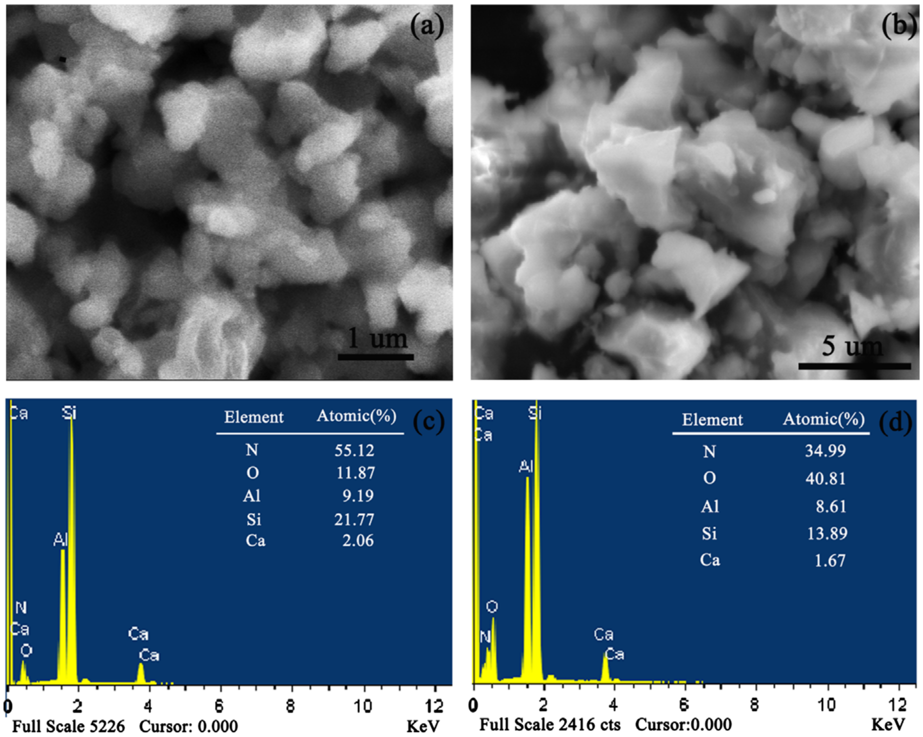

Fig. 1. (a), (b) SEM images and (c), (d) EDS element analysis of pre-obtained α-SiAlON:Eu^{2+} phosphor sample and obtained Eu^{2+} doped SiAlON-based crystal/glass composite phosphor sample, respectively.

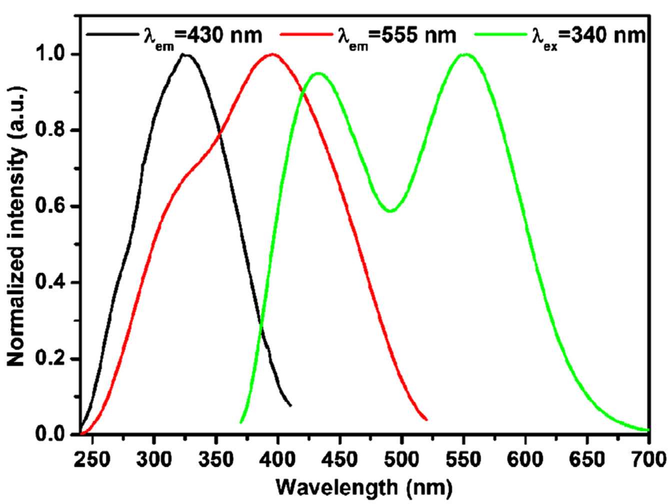

Fig. 2. The PL and PLE spectra of Eu^{2+} doped SiAlON-based crystal/glass composite phosphor with direct white light emission.

phase is ascribed to the weaker covalence of glass phase owing to the introduction of B_2O_3, compared with the longer wavelength emission of Eu^{2+} ions doped in the SiAlON crystal lattice. From the PLE spectra, we can find that the blue-emitting glass phase and the yellow-emitting crystal phase can be pumped effectively by the 250–400 nm UV light and 250–500 UV-blue light, respectively. The optimal excitation wavelength for blue emission and that for yellow emission is detected at 325 nm and 395 nm, respectively. Being reminded by the various excitation properties of blue and yellow emission, we will find that both the blue-emitting glass phase and yellow-emitting crystal phase can be pumped simultaneously by the light of 325–395 nm. It is worth to note that the excitation intensity decreases for blue emission while that increases for yellow emission in the range of 325–395 nm, indicating that each of emission bands can be tuned continuously. Consequently, the white light emission of this Eu^{2+} doped SiAlON-based crystal/glass composite phosphor is tuned by variation of excitation light.

Furthermore, it is observed that the PLE spectrum monitored at yellow emission peak comprises two excitation bands positioned at 320 nm and 395 nm, which can be ascribe to the excitation transition $4f^7$–$4f^65d(e_g)$ and $4f^7$–$4f^65d(t_{2g})$ of Eu^{2+} ions doped in SiAlON crystal lattice, respectively. Where e_g and t_{2g} represent the two crystal-field splitting components of $4f^65d$ excited state in SiAlON host. Only one excitation band positioned at 325 nm is recorded on PLE spectrum monitored at the blue emission peak and is assigned to the $4f^7$–$4f^65d$ excitation transition of Eu^{2+} ions doped in glass matrix. The single $4f^65d$ excited state component of Eu^{2+} ion indicates the weaker splitting effect in Si–Al–B–O–N glass phase. The energy level schematic diagram of Eu^{2+} ions doped in crystal lattice and glass matrix is presented in Fig. 3.

Tunable PL spectra and the CIE chromaticity coordinates of this Eu^{2+} doped SiAlON-based crystal/glass composite white light phosphor by varying the excitation light are shown in Fig. 4(a) and (b), respectively. It is found that the intensity of blue emission band decreases while that of yellow emission band increases with variation of excitation from 330 nm to 380 nm. Equivalent emission intensity for blue and yellow emission bands is observed when the excitation wavelength is

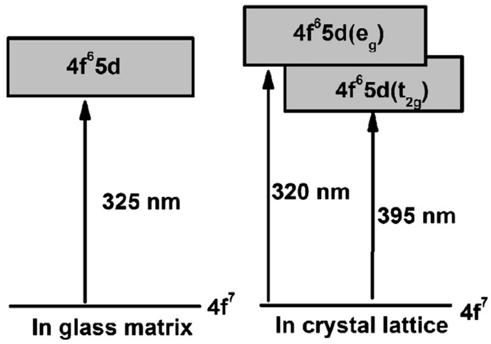

Fig. 3. The energy level schematic diagram of Eu^{2+} ions doped in crystal lattice and glass matrix.

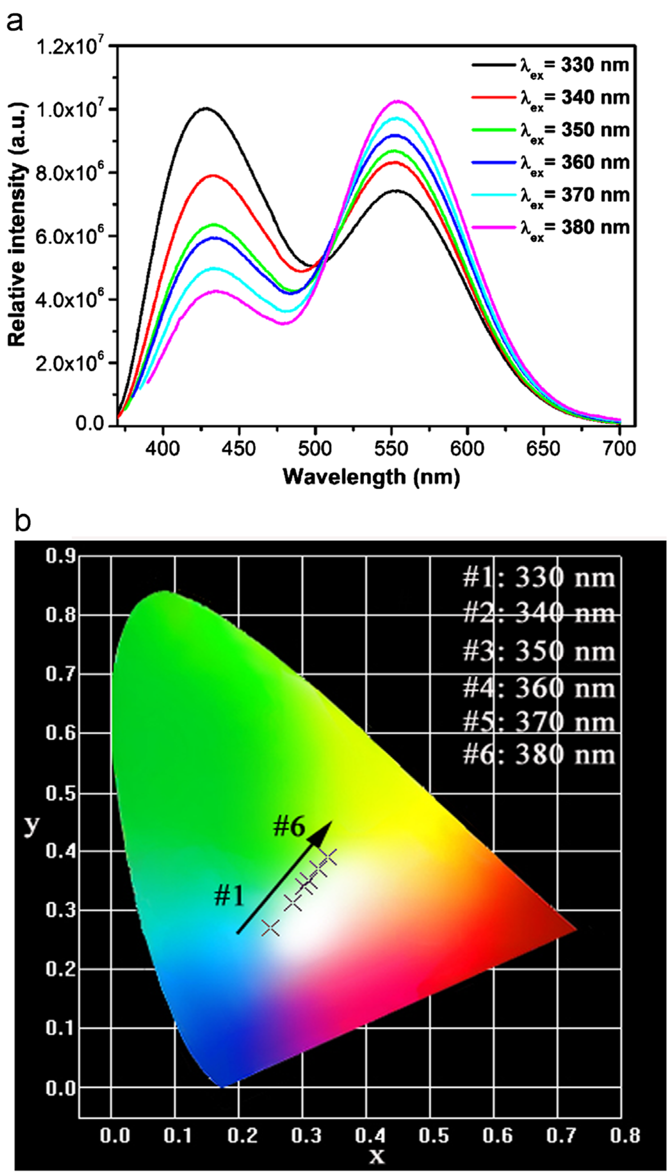

Fig. 4. Tunable (a) PL spectra and (b) CIE chromaticity coordinates of Eu^{2+} doped SiAlON-based crystal/glass composite phosphor by variation of excitation light (λ_{ex}=330, 340, 350, 360, 370, 380 nm).

340 nm. From these tunable PL spectra, it is obvious that the luminescent properties can be adjusted by variation of excitation light. In addition, the emission peaks of these two bands show on shift when change the excitation wavelength, indicating that only the emission intensity is adjusted by variation of excitation light. From the CIE chromaticity coordinates, we can find that all the test chromaticity coordinates corresponding to various excitation wavelengths locate in the white light region. With the increase of excitation wavelength, the emission color shifts from bluish white light to yellowish white light. Additionally, the CCT can be also adjusted from 13000 K to 5300 K for this SiAlON-based crystal/glass composite phosphor by varying excitation wavelength from 330 nm to 380 nm. Presented results indicate that this tunable SiAlON-based crystal/glass composite white-light phosphor might be applied potentially in white LED, combining with UV chips with different emitting wavelengths in the range of 330–380 nm.

4. Conclusion

In conclusion, tunable white light emission of Eu^{2+} doped SiAlON crystal/glass composite phosphor was realized by variation of excitation wavelength, owing to the varied excitation property of Eu^{2+} ions doped in crystal lattice and glass matrix. White light emission from cool white (CCT=13000 K) to warm white (CCT=5300 K) was demonstrated by varying excitation wavelength from 330 nm to 380 nm, indicating the potential application in white LED combining with different emitting wavelength UV chips.

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