

Flux-adjusted phase transformation from Ca_2SiO_4 to $\text{Ca}_3\text{Si}_2\text{O}_7$ with Eu^{2+} activator for white light emitting diodes*

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Eu^{2+} -activated reddish-orange-emitting $\text{Ca}_3\text{Si}_2\text{O}_7$ phosphors were synthesized with the addition of NH_4Cl flux. When the phosphors were synthesized in a nominal composition of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_3\text{Si}_2\text{O}_7$ without flux addition, a $\text{Ca}_3\text{Si}_2\text{O}_7$ phase responsible for reddish-orange emission was identified to coexist with an intermediate phase of $\hat{\alpha}\text{-Ca}_2\text{SiO}_4$ for green emission. With the addition of NH_4Cl flux, $\hat{\alpha}\text{-Ca}_2\text{SiO}_4$ was suppressed while the pure phase $\text{Ca}_3\text{Si}_2\text{O}_7$ was obtained as the flux content was 3 wt%. Through varying the amount of flux, the emission color of samples can be tuned from green to reddish-orange, corresponding to the phase transformation from $\hat{\alpha}\text{-Ca}_2\text{SiO}_4$ to $\text{Ca}_3\text{Si}_2\text{O}_7$. Through optimizing the doping concentration of Eu^{2+} , the optimized photoluminescence (PL) properties for reddish-orange emission can be achieved, which makes this kind of phosphor prospective in the applications of the phosphor-converted white light emitting diodes (PC-WLEDs).

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Phosphor-converted white light emitting diode (PC-WLED) with a combination of blue AlInGaN chip and YAG: Ce^{3+} phosphors is the mainstream technology to generate white light^[1,2]. However, this white light suffers from the higher correlated color temperature (CCT) and lower color render index (CRI) due to the lack of efficient red and green color component. Great efforts have been made in the development of red phosphors excited by blue light effectively to compensate the deficiency of red light component. The sulphide-based red phosphors have been limited in applications owing to their thermal and chemical instability^[3-5]. Meanwhile, a series of nitride/oxy-nitride-based phosphors with excellent thermal and chemical stability emerged recently, such as Eu^{2+} -activated $\text{M}_2\text{Si}_5\text{N}_8$ ^[6,7], CaAlSiN_3 ^[8] and $\text{MSi}_2\text{O}_2\text{N}_2$ (M= Ba, Sr, Ca)^[9]. However, severe synthesizing conditions at high temperature and high pressure of nitrogen greatly limit their practical applications. Alternatively, silicate-based phosphors have long been recognized due to their adequate stability and relative mild preparation conditions. Toda et al^[10] reported that Eu^{2+} -activated $\text{Ca}_3\text{Si}_2\text{O}_7$ emits red light with a peak

at 600 nm under blue excitation. Nakanishi et al^[11] also demonstrated 600 nm-peaked band emission for $\text{Ca}_3\text{Si}_2\text{O}_7:\text{Eu}^{2+}$ micron-sized crystals separated from glass matrix under near ultraviolet radiation. However, Yoon et al^[12] reported a discrepancy that the green emission positioned at 521 nm exists, which is responsible for the electronic transition emission of Eu^{2+} in $\text{Ca}_3\text{Si}_2\text{O}_7$ instead of Ca_2SiO_4 , as we speculate.

In this paper, Eu^{2+} -activated reddish-orange-emitting phase-pure $\text{Ca}_3\text{Si}_2\text{O}_7$ phosphors were synthesized with proper flux addition. The luminescence properties of mixed reddish-orange and green color for Eu^{2+} -activated $\text{Ca}_3\text{Si}_2\text{O}_7$ and Ca_2SiO_4 are identified by tracing the evolution of phase transformation. The optimization of flux amount and doping content of Eu^{2+} is carried out to achieve the desired photoluminescence (PL).

Phosphor samples were synthesized by high-temperature solid-state synthesis procedure. A group of samples were prepared in the nominal composition of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_3\text{Si}_2\text{O}_7$ with reagents of CaCO_3 (99%), nano-sized SiO_2 (99.99%) and Eu_2O_3 (99.99%) as starting materials. The starting mate-

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rials were mixed thoroughly in an agate mortar, followed by pre-firing at 1000 °C in an alumina crucible under air for 3 h, and then cooled down to room temperature in furnace. One part of the pre-fired powder was re-fired at 1300 °C, 1350 °C and 1400 °C, respectively, in a horizontal tube furnace for 6 h under a weak reductive atmosphere of 8 vol.% H₂/92 vol.% N₂ mixture to reduce Eu³⁺ to Eu²⁺. The other part of pre-fired powder was well ground again with the addition of flux NH₄Cl with varying amount of *x* wt.% (*x*=1, 2, 3), and re-fired at 1300 °C in the same process as above. A series of (Ca_{1-*x*}Eu_{*x*})₃Si₂O₇ (*x*=0.010, 0.015, 0.020, 0.025, 0.030) phosphors with an addition of 3 wt.% NH₄Cl were prepared at 1300 °C. The prepared phosphor powder was cooled down to room temperature naturally in the furnace for characterization.

PL and PL excitation (PLE) were acquired on a fluorescence spectrophotometer (FL3-2-IHR320-NIR-TCSPC, USA) with a xenon lamp (Xe-lamp) with power of 450 W as excitation source. The split of both PL and PLE measurement is set to be 1 nm. The crystal graphical data of samples were collected using an X-ray powder diffractometer (Rigaku D/max-2500/PC, Japan) with a graphite monochromator using Cu-K_{α1} radiation ($\lambda = 0.154062$ nm), which is operated at 40 kV and 150 mA by using continuous scan mode with a step of 0.02° and a scanning speed of 4 °/min in the range of $2\theta = 10^\circ\text{--}80^\circ$. The Commission International de l'Éclairage (CIE) colorimetric parameters were recorded on a PMS-50 Plus UV-VIS-near-IR spectrophotometer (Everine, China). All of these measurements were carried out at room temperature.

Fig. 1 shows the X-ray diffraction (XRD) patterns of phosphor samples in a nominal composition of (Ca_{0.99}Eu_{0.01})₃Si₂O₇ fired at different temperatures without the addition of NH₄Cl. In the case of firing at 1300 °C, the dominant diffraction pattern was identified to correspond well to that of the β -Ca₂SiO₄ phase which has the monoclinic structure with a space group of P2₁/n (14) (JCPDS 83-0461). With increasing firing temperature up to 1350 °C, the monoclinic phase β -Ca₂SiO₄ co-exists with Ca₃Si₂O₇ phase. The phase of Ca₃Si₂O₇ has the same monoclinic structure but a different space group of P21/a (14) (JCPDS 76-0623). As the temperature is increased up to 1400 °C, the Ca₃Si₂O₇ phase tends to be dominant, and β -Ca₂SiO₄ phase is unobvious. This change indicates that the mixed crystalline structures in the samples transform from the monoclinic phase β -Ca₂SiO₄ to the monoclinic phase Ca₃Si₂O₇ as the temperature increasing.

Fig. 2 depicts the normalized PLE and PL spectra of phosphor samples with the composition of (Ca_{0.99}Eu_{0.01})₃Si₂O₇ fired at different temperatures of 1300 °C, 1350 °C and 1400 °C, respectively. The phosphor sample fired at 1300 °C exhibits a single green emission band peaked at 505 nm under the

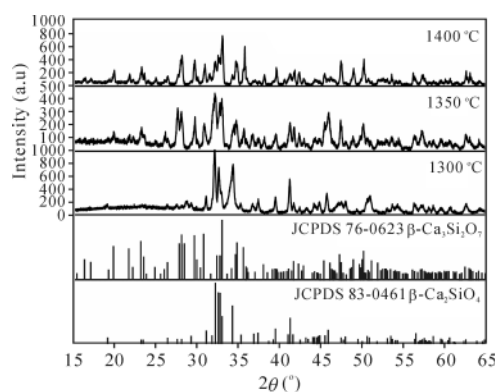


Fig. 1 XRD patterns of phosphor samples with nominal composition of (Ca_{0.99}Eu_{0.01})₃Si₂O₇ fired at different temperatures

excitation at 365 nm. With increasing temperature up to 1350 °C, the emission spectrum is observed to be with double bands peaked at 513 nm and 600 nm, but the intensity of green emission is dominant simultaneously. With increasing temperature further up to 1400 °C, the relative PL intensity of the reddish-orange emission peaked at 600 nm exhibits a sharp increase, whereas that of the green emission decreases. Associated with the XRD results, we deduce that the green and red emissions are ascribed to the allowed electronic transitions from the 4f⁶5d excitation states to 4f⁷ ground states for Eu²⁺ ions in β -Ca₂SiO₄ and Ca₃Si₂O₇ hosts, respectively. As monitored at green and red emission peaks, the excitation spectra of samples were measured to have the same broad band profile. Specifically for reddish-orange emission of Ca₃Si₂O₇, the broad excitation spectrum is observed to cover the wavelength range from 250 nm to 525 nm, indicating that Eu²⁺-activated Ca₃Si₂O₇ can be employed as the potential red-emitting phosphors to lower CCT and to increase CRI in blue-based WLED device.

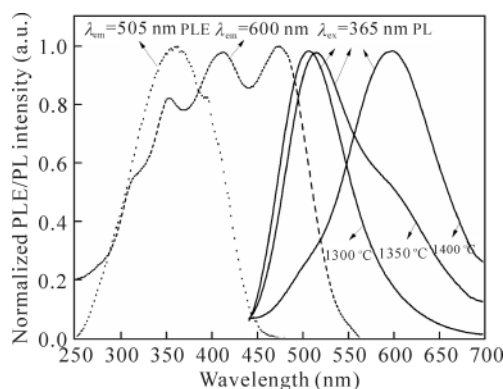
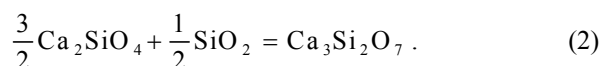
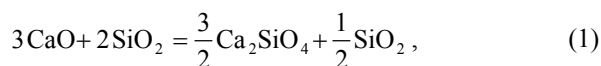


Fig. 2 Normalized PLE and PL spectra of phosphors with the composition of (Ca_{0.99}Eu_{0.01})₃Si₂O₇ fired at different temperatures

An underlying reaction mechanism determines the phase

transformation and its change of PL. The reagent of CaCO_3 was decomposed into CaO and CO_2 during the pre-firing process. The newly formed CaO reacted with SiO_2 to form Ca_2SiO_4 firstly, and then to form $\text{Ca}_3\text{Si}_2\text{O}_7$ at firing temperature, most likely expressed as



In terms of the reactions above, the phase of Ca_2SiO_4 can be considered as an intermediate of $\text{Ca}_3\text{Si}_2\text{O}_7$ phase when the reaction of 3CaO and 2SiO_2 does not reach a thermodynamic equilibrium. Meanwhile, the minor amount of preliminary SiO_2 can coexist with the intermediate phase $\beta\text{-Ca}_2\text{SiO}_4$ in the three received samples, but the featured diffraction pattern of SiO_2 is not identified from the above XPD patterns in Fig. 1.

In order to obtain phase-pure $\text{Ca}_3\text{Si}_2\text{O}_7$ so as to increase the intensity of reddish-orange emission, the reaction temperature should be increased continuously according to the XRD analysis and reaction mechanism analysis. However, extremely high firing temperature beyond 1400°C is observed to lead to melting the samples. Therefore, phase-pure $\text{Ca}_3\text{Si}_2\text{O}_7$ phosphors are hardly synthesized only through increasing the reaction temperature.

The addition of flux is commonly used for synthesizing luminescent materials. It has been well recognized that the flux addition in the firing process generally promotes the mixing uniformity of raw particles and rare earth ions, the grain growth and the surface smoothing, and more importantly, the formation of liquid phase with flux addition may adjust phase equilibrium and promote the reaction kinetics through enhancing ions diffusion to achieve single phase^[13-16].

As mentioned above, the $\beta\text{-Ca}_2\text{SiO}_4$ is formed as an intermediate phase in the synthesis of $\text{Ca}_3\text{Si}_2\text{O}_7$, and the addition of flux may help to obtain Eu^{2+} -activated single phase of $\text{Ca}_3\text{Si}_2\text{O}_7$ and to intensify the reddish-orange emission. Fig. 3 gives the XRD results of phosphor samples with a nominal composition of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_3\text{Si}_2\text{O}_7$ with the addition of NH_4Cl flux in amount of x wt.% ($x=1, 2, 3$) fired at 1300°C . For $x=1$ and 2 , a little amount of impurity phase of $\beta\text{-Ca}_2\text{SiO}_4$ (JCPDS 83-0461) is identified besides the main crystal phase of $\text{Ca}_3\text{Si}_2\text{O}_7$. But for $x=3$, all the diffraction peaks are consistent with those in the standard card of $\text{Ca}_3\text{Si}_2\text{O}_7$ (JCPDS 76-0623). It can be seen that the addition of NH_4Cl can effectively inhibit the formation of intermediate phase $\beta\text{-Ca}_2\text{SiO}_4$, and promote the formation of $\text{Ca}_3\text{Si}_2\text{O}_7$ phase. The phase-pure $\text{Ca}_3\text{Si}_2\text{O}_7$ phosphors can be obtained when the addition amount of NH_4Cl is set to be 3 wt.%. Fig. 4 shows the PL spectra of the

samples with x wt.% ($x=1, 2, 3$) NH_4Cl flux together with the PL spectrum of the sample fired at 1300°C without addition of NH_4Cl ($x=0$) for comparison. With the change of NH_4Cl addition amount, all the three PL spectra are found to be centered at 600 nm under 365 nm excitation. When $x=3$, the maximum of PL intensity occurs at a single 600 nm-peaked band emission, and the PL spectrum profile exhibits an asymmetry with full width at half maximum of around 107 nm. In this way, the emission color of samples can be tuned from green to reddish-orange with the phase transformation from $\beta\text{-Ca}_2\text{SiO}_4$ to $\text{Ca}_3\text{Si}_2\text{O}_7$ through changing the amount of flux addition. The intensities of reddish-orange band emission of samples with $x=1$ and 2 are weaker than that with $x=3$ due to the re-distribution of Eu^{2+} activators in the intermediate phase $\beta\text{-Ca}_2\text{SiO}_4$. In order to obtain more satisfied intensity of reddish-orange emission, the doping concentration of Eu^{2+} in $\text{Ca}_3\text{Si}_2\text{O}_7$ should be optimized further.

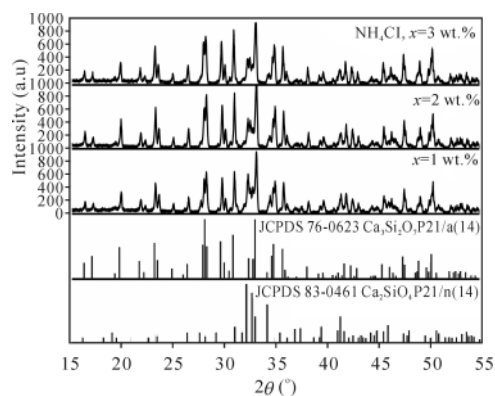


Fig.3 XRD patterns of phosphor samples with a nominal composition of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_3\text{Si}_2\text{O}_7$ added with x wt.% NH_4Cl ($x=1, 2, 3$) fired at 1300°C

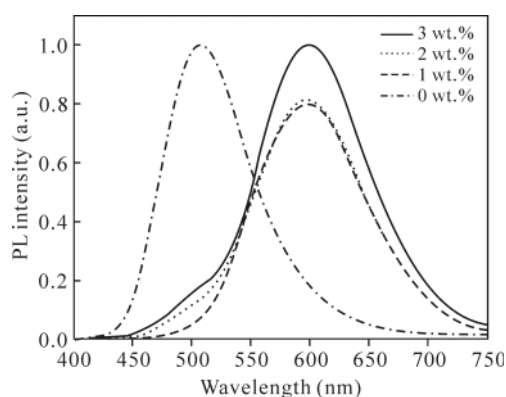


Fig.4 PL spectra of phosphor samples with a nominal composition of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_3\text{Si}_2\text{O}_7$ added with x wt.% NH_4Cl ($x=0, 1, 2, 3$) ($\lambda_{\text{ex}} = 365$ nm) fired at 1300°C

Fig.5 shows the emission spectra of the received $\text{Ca}_3\text{Si}_2\text{O}_7$: Eu^{2+} phosphors by changing the Eu^{2+} content under 460 nm

excitation. The 600 nm-peaked emission band shows no shift when the content of Eu^{2+} changes, and only the relative emission intensity becomes different. The strong emission intensity is achieved at $x=0.025$ (2.5 mol. % of Ca ions) in $(\text{Ca}_{1-x}\text{Eu}_x)_3\text{Si}_2\text{O}_7$. When the Eu^{2+} content is greater than 0.025, the emission intensity decreases sharply, indicating the concentration quenching. The Commission International del'Eclairage (CIE) 1931 chromaticity of $(\text{Ca}_{0.975}\text{Eu}_{0.025})_3\text{Si}_2\text{O}_7$ phosphors was measured to be at (0.547, 0.450), indicating the potential as a red color compensation of YAG:Ce³⁺-based white LEDs or to generate white light by combining green and blue phosphors with near ultraviolet (NUV) chip.

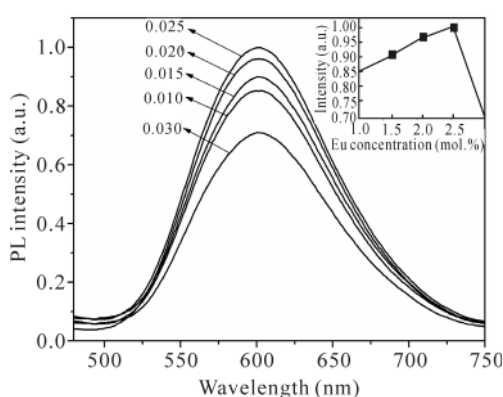


Fig.5 PL spectra of $(\text{Ca}_{1-x}\text{Eu}_x)_3\text{Si}_2\text{O}_7$ phosphors ($\lambda_{\text{ex}} = 460$ nm) added with 3 wt.% NH_4Cl and synthesized at 1300 °C

The phosphor samples in a nominal composition of $(\text{Ca}_{0.99}\text{Eu}_{0.01})_3\text{Si}_2\text{O}_7$ were prepared by solid-state synthesis procedure at 1300–1400 °C under 8 vol.% $\text{H}_2/92$ vol.% N_2 atmospheres. A coexistence of an intermediate phase $\beta\text{-Ca}_2\text{SiO}_4$ and a $\text{Ca}_3\text{Si}_2\text{O}_7$ phase is verified. The green band emission is originated from $4f^65d^1 \rightarrow 4f^7$ electronic transition of Eu^{2+} in $\beta\text{-Ca}_2\text{SiO}_4$ host, and the reddish-orange band emission from $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} in the $\text{Ca}_3\text{Si}_2\text{O}_7$ host. The addition of NH_4Cl flux can effectively inhibit the formation of intermediate phase $\beta\text{-Ca}_2\text{SiO}_4$ and promote the formation of $\text{Ca}_3\text{Si}_2\text{O}_7$ phase. Phase-pure $\text{Ca}_3\text{Si}_2\text{O}_7:\text{Eu}^{2+}$ phosphors can be obtained with addition of NH_4Cl flux at the amount of 3 wt.% synthesized at 1300 °C. Under the excitation of light from NUV to blue region, phase-pure $\text{Ca}_3\text{Si}_2\text{O}_7:\text{Eu}^{2+}$ shows a 600

nm-peaked broad band emission ranging from 500 nm to 750 nm. The doping concentration of Eu^{2+} in $\text{Ca}_3\text{Si}_2\text{O}_7$ is optimized to be 2.5 mol.%. This kind of reddish-orange-emitting phosphors are potential to lower the CCT of PC-WLEDs in the applications of lighting and display fields.

References

- [1] Schubert E. F. and Kim J. K., *Sci.* **308**, 1274 (2005).
- [2] SONG Guo-hua, MIAO Jian-wen, XU Shu-wu and JI Xiang-ming, *Journal of Optoelectronics • Laser* **21**, 1785 (2010). (in Chinese)
- [3] Kuo T. W., Liu W. R. and Chen T. M., *Opt. Express* **18**, 8187 (2010).
- [4] Xia Y. J., Huang F. Q., Wang W. D., Wang Y. M., Yuan K. D., Liu M. L. and Shi J. L., *Opt. Mater.* **31**, 311 (2008).
- [5] QIU Kun, XU Suo-cheng, TIAN Hua, ZHENG Xi, LV Tian-shuai, LU Qi-fei and WANG Da-jian, *Optoelectronics Letters* **7**, 350 (2011).
- [6] Zeuner M., Schmidt P. J. and Schnick W., *Chem. Mater.* **21**, 2467 (2009).
- [7] Wei X. D., Cai L. Y., Lu F. C., Chen X. L., Chen X. Y. and Liu Q. L., *Chin. Phys. B* **18**, 3555 (2009).
- [8] Li Y. Q., Hirosaki N., Xie R. J., Takeda T. and Mitomo M., *Chem. Mater.* **20**, 6704 (2008).
- [9] Meijerink A., Bachmann V., Ronda C., Oeckler O. and Schnick W., *Chem. Mater.* **21**, 316 (2009).
- [10] Toda K., Kawakami Y., Kousaka S., Ito Y., Komeno A., Uematsu K. and Sato M., *IEICE Electron. Express* **E89c**, 1406 (2006).
- [11] Nakanishi T. and Tanabe S., *Phys. Status Solidi. A* **206**, 919 (2009).
- [12] Yoon D. H., Park W. J., Jung M. K., Kang S. M. and Masaki T., *J. Phys. Chem. Solids* **69**, 1505 (2008).
- [13] Zhuang W. D., Deng C. Y., He D. W., Wang Y. S., Kang K. and Huang X. W., *J. Rare Earths* **22**, 108 (2004).
- [14] Lee G. H., Yoon C. and Kang S., *J. Mater. Sci.* **43**, 6109 (2008).
- [15] Zhang X. Y., Cheng G., Liu Q. S., Cheng L. Q., Lu L. P., Sun H. Y., Wu Y. Q., Bai Z. H. and Qiu G. M., *J. Rare Earths* **28**, 526 (2010).
- [16] Ma L., Wang D. J., Zhang H. M., Gu T. C. and Yuan Z. H., *Electrochem. Solid State Lett.* **11**, E1 (2008).