Journal of Solid State Lighting
a SpringerOpen Journal

RESEARCH ARTICLE Open Access

A high color purity red emitting phosphor $CaYAlO_4:Mn^{4+}$ for LEDs

Yan Chen, Meng Wang, Jing Wang*, Mingmei Wu* and Chengxin Wang

* Correspondence:
ceswj@mail.sysu.edu.cn;
ceswmm@mail.sysu.edu.cn
State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, School of Chemistry and Chemical Engineering, Sun Yat-sen University Guangzhou, Guangdong 510275, P.R. China

Abstract

An intense red phosphor, $CaYAlO_4:Mn^{4+}$, was developed by solid state reaction. The photoluminescence excitation and emission spectra, concentration effect, thermal-dependent luminescence quenching properties and decay curves are investigated. The results show Mn^{4+} ion exhibits a broadband excitation extending from 250 to 550 nm and emits an intense red light at 710 nm with high color purity and stable chromaticity coordinates. These results demonstrate that Mn^{4+} ion can play a role of activator in narrow red emitting phosphor potentially useful in UV (~370 nm) GaN-base or Blue (~460 nm) InGaN-base LED.

Keywords: Phosphor; Photoluminescence; Light-Emitting Diode (LED)

Background

Nowadays, phosphor-converted (pc-) white LEDs are attracting significant attention [1-3]. They can be classified into two approaches: blue (440 ~ 470 nm) InGaN and near (n)-UV (350 ~ 420 nm) GaN chip combined with phosphors. Recently, the commonly commercial white LED is based on the combination of blue InGaN chip and yellow YAG: Ce^{3+} phosphor. However, such white LEDs encounter low color-rendering index (Ra < 80) due to the scarcity of red emission [4-6].

Red emitting phosphor is one of key tricolor luminescent materials for white LEDs. Up to now, many researchers have been done on Eu^{3+} [7-9] or Sm^{3+} [10-12] ion doped phosphors. Unfortunately, the red phosphor doped by Eu^{3+}or Sm^{3+}show weak absorption peaks at about 400 nm or 460 nm because the 4f-4f absorption transitions are forbidden by the parity selection rule and its optical oscillator strength is small. Furthermore, the price of rare earth is quite high. Furthermore, some nitride based phosphors have been developed to increase the color index, or create warm-white lighting [13-15]. However, the synthesize conditions of nitride phosphors are usually very harsh, such as high temperature (1500–2000°C), oxygen-free environment.

Generally, Mn^{4+} ion with $3d^3$ configurations in octahedral site gives a deep red emission and has broad absorption in visible region, such as K_2SiF_6: Mn^{4+}, K_2GeF_6: Mn^{4+}, K_2TiF_6: Mn^{4+} and $CaAl_{12}O_{19}$: Mn^{4+} [16-18]. $CaYAlO_4$ (CYA) crystallizes in the perovskite phase with tetragonal K_2NiF_4 structure [19]. Al^{3+} ion is octahedrally coordinated with six oxygens. Therefore, Mn^{4+} ion may emit red ligtht when occupied Al^{3+} ion site in $CaYAlO_4$. In this paper, an intense red phosphor, $CaYAlO_4:Mn^{4+}$, was developed by solid state reaction. The photoluminescence excitation and emission spectra, concentration effect, thermal-dependent luminescence quenching properties and decay curves are investigated.

Methods

Syntheses: All samples $CaYAlO_4:Mn^{4+}{}_x$ (x = 0.001, 0.005, 0.01, 0.03, 0.05) were prepared by a conventional solid-state reaction technique. The starting materials, $CaCO_3$ (A.R.), Al_2O_3 (A.R.), Y_2O_3 (99.99%) and $MnCO_3$ (A.R.) were weighed in stoichiometric amounts. Subsequently the powder mixture was thoroughly mixed in an agate mortar by grinding and was transferred into crucibles. Finally, they were sintered at 1250°C for 4 h in air.

Measurements: The phase purity of the prepared phosphors was investigated by a Rigaku D/max-IIIA X-ray Diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 30 mA. The XRD patterns were collected in range of $10° \leq 2\theta \leq 80°$.

The photoluminescence (PL), photoluminescence excitation (PLE) spectra, temperature-dependent PL spectra and the decay curves at room temperature were measured by FSP920 Time Resolved and Steady State Fluorescence Spectrometers (Edinburgh Instruments) equipped with a 450 W Xe lamp, a 100w μF920H lamp with a pulse width of 1 ~ 2 μs, a repetition rate of 50 Hz and the lifetime range of 100 μs ~ 200 s, TM300 excitation monochromator and double TM300 emission monochromators, Red sensitive PMT and R5509-72 NIR-PMT in a liquid nitrogen cooled housing (Hamamatsu Photonics K.K). The spectral resolution is about 0.05 nm in UV–VIS.

For the high temperature PL spectra in 300–500 K, the powder sample was mounted in an Optistat DNV actively cooled optical cryostat with an ITC601 temperature controller.

The powder diffuse reflection spectra (DRS) of these samples were measured on a Cary 5000 UV–vis-NIR spectrophotometer (Varian) equipped with double out-of-plane Littrow monochromator, using polyfluortetraethylene as a standard reference in the measurements.

The room temperature quantum efficiency (QE) of the sample was measured using a barium sulfate coated integrating sphere (150 mm in diameter) attached to the FSP920.

Results and discussion

The XRD patterns of CYA: $Mn^{4+}{}_x$ (x =0, 0.001, 0.005, 0.05) are shown in Figure 1. The results indicate that all the peaks of Mn^{4+} ion doped CYA can be indexed to a pure $CaYAlO_4$ (JCPDS 81–0742). The dopants have no obvious influence on the crystalline structure of the host. The $CaYAlO_4$ has tetragonal system with a space group of I4/mmm (139) and a = 3.6750(5) Å c = 12.011(2) Å c/a = 3.2683 V = 162.22(4) $Å^3$, Z = 2 [20]. There are two types of cation sites in $CaYAlO_4$. The Ca^{2+} and Y^{3+} ions are distributed in the nine-coordinated sites and the Al^{3+} ions occupy the six-coordinate site. It is reported that the effective ionic radius of Ca^{2+} ion (CN = 9), Y^{3+} ion (CN = 9), Al^{3+} ion (CN = 6) and Mn^{4+} ion (CN = 6) are 1.18 Å, 1.075 Å, 0.535 Å and 0.53 Å, respectively [21]. It is obvious that the ionic radius of Mn^{4+} is close to Al^{3+} and smaller than Ca^{2+} or Y^{3+}, suggesting that Mn^{4+} ions prefer to occupy Al^{3+} site in the present host.

Figure 2 shows the powder DRS of CYA: $Mn^{4+}{}_x$ (x = 0.001, 0.005, 0.01, 0.03, 0.05). It is clearly observed that the phosphors of CYA: $Mn^{4+}{}_{0.001}$ shows a platform of high reflection in the wavelength range of 580–1200 nm and then starts to decrease

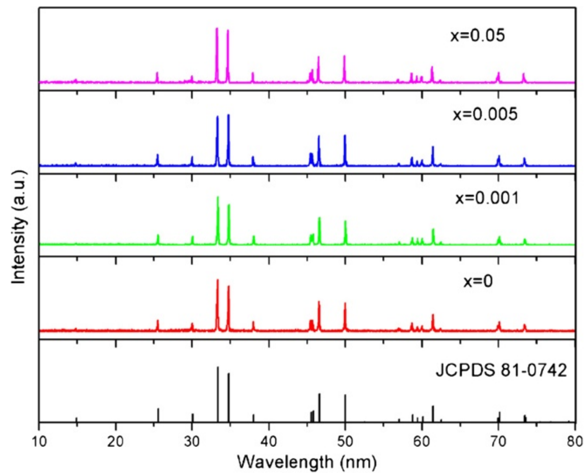

Figure 1 Powder XRD patterns of CYA: $Mn^{4+}{}_x$ (x =0, 0.001, 0.005,0.05).

dramatically from 580 to 200 nm. As the increasing of Mn^{4+} concentration, two broad absorption bands appears at 200–425 nm and 425–580 nm, which is derived from the ${}^4A_2 \rightarrow {}^4T_1$ and ${}^4T_2$ transition of Mn^{4+}, respectively.

The PLE and PL spectra of CYA: $Mn^{4+}{}_{0.001}$ are showed in Figure 3. The PLE spectrum contains two broad bands at 250–420 nm and 420-550 nm, which can be attributed to ${}^4A_2 \rightarrow {}^4T_1$ and ${}^4T_2$ transition of Mn^{4+}, respectively. The PL spectra under the excitation at 335 nm, 370 nm and 460 nm exhibit a narrow band between 660 nm and 770 nm with a sharp peak at 710 nm, which is due to ${}^4E \rightarrow {}^4A_2$ transition of Mn^{4+}. It is to say this phosphor can be effectively excited by UV or blue LED chip and emits red light.

In order to further optimize the red emission of Mn^{4+} ion, the concentration dependent emission intensity of CYA: $Mn^{4+}{}_x$ (x = 0.001, 0.005, 0.01, 0.03, 0.05) is studied. It can be seen in Figure 4 that the emission intensity of Mn^{4+} ion at 710 nm initially increase, then reaches a maximum at x = 0.005 and decrease due to concentration

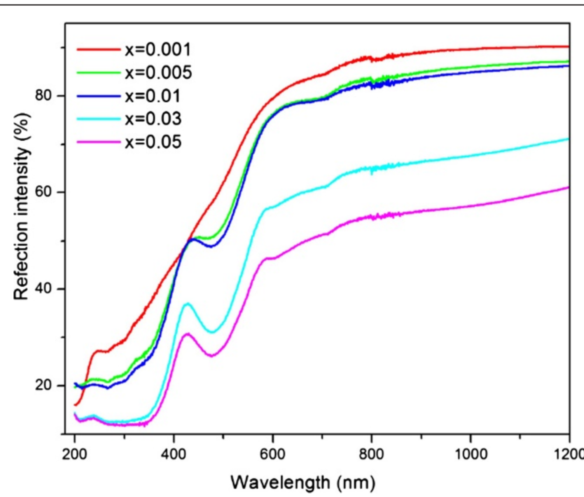

Figure 2 Powder DRS of CYA: $Mn^{4+}{}_x$ (x = 0.001, 0.005, 0.01, 0.03, 0.05).

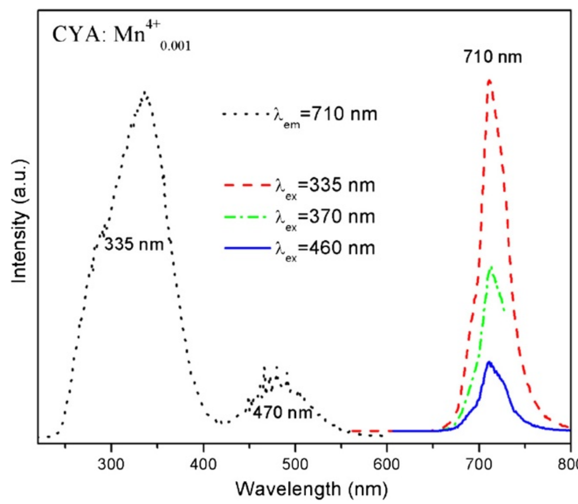

Figure 3 PLE and PL spectra of CYA: $Mn^{4+}{}_{0.001}$ (λ_{em} = 710 nm; λ_{ex} = 335 nm, 370 nm, 460 nm).

quenching. It is interesting that the chromaticity coordinates of CYA: $Mn^{4+}{}_x$ are almostly the same with the change of Mn^{4+} ion dopt content. The inset of Figure 4 gives the chromaticity coordinates of CYA: $Mn^{4+}{}_{0.005}$ under 370 nm excitation. The color purity of the point in spectrum locus is 100%. So the color purity of phosphor CYA: Mn^{4+} is near 100%.

The QE of phosphor $CaYAlO_4$: Mn^{4+} was recorded using an integrating sphere attached to the FSP920. QE is defined as the ratio of the number of emitted photons (I_{em}) to the number of absorbed photons (I_{abs}), and can be calculated by the following equation [22].

$$QE = I_{\mathrm{m}}/I_{\mathrm{abs}} = \int L_{\mathrm{s}} / \left(\int E_{\mathrm{R}} - \int E_{\mathrm{s}} \right) \tag{1}$$

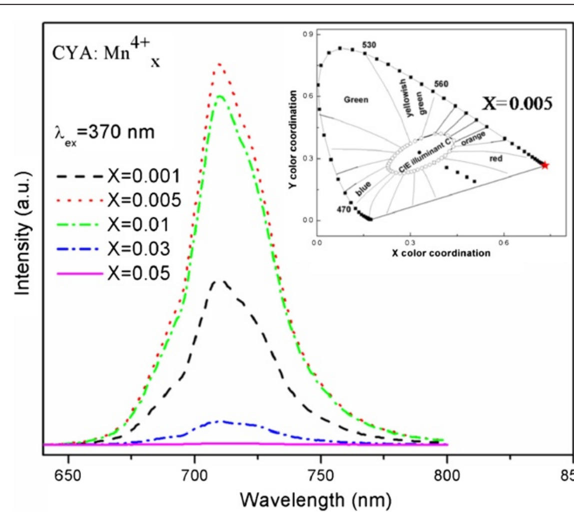

Figure 4 PLE spectra of CYA: $Mn^{4+}{}_x$(x = 0.001, 0.005, 0.01, 0.03, 0.05); Inset is chromaticity coordinates of CYA: $Mn^{4+}{}_{0.005}$ (λ_{ex} = 370 nm).

where E_R, E_S are the spectra of the excitation light without and with the sample in the integrating sphere, respectively, and L_S is the luminescence emission spectrum of the sample in the integrating sphere. The *QE* of the CYA: $Mn^{4+}{}_{0.005}$ was measured and calculated to be about 26% and 28% under 335 nm and 460 nm excitation, respectively.

The luminous efficiency of the radiation (LER) is an important parameter which shows how bright the radiation is perceived by the average human eye. Figure 5 shows the nonalized spectral eye sensitivity cures for photopic vision and spectrum of phosphor CYA: $Mn^{4+}{}_{0.005}$. It can be caculated from the emission sepctrum as: [23].

$$\mathrm{LER}(lm/w) = 683lm/w\cdot\frac{\int_{380nm}^{780nm} I(\lambda)V(\lambda)d\lambda}{\int_{380nm}^{780nm} I(\lambda)d\lambda}$$

Where *V (λ)* and *I (λ)* are eye sensitivity cure and phosphor emission spectrum respectively. The *LER* of the CYA: $Mn^{4+}{}_{0.005}$ is 3 lum/w which indicates the phosphor is too red for general lighting . However, it may be a promising phosphor for other artificial lighting applications, such as in plant photomorphogenesis [24].

For LEDs application, the thermal stability of phosphor is one of the important factors. Figure 6 shows the PL spectral ($\lambda_{ex} = 370$ nm) of CYA: $Mn^{4+}{}_{0.005}$ at the temperature range of 300–460 K. It illustrates that the position and shape of the emission spectra do not change with increasing temperature. The temperature-dependence of the integrated emission intensity for CYA: $Mn^{4+}{}_{0.005}$ is presented in the inset of Figure 6. It is clearly observed that the integrated emission intensity of CYA: $Mn^{4+}{}_{0.005}$ decreases as the temperature increases from 300 K to 460 K. The integrated emission intensity at 100 and 150°C remain about 70% and 50% when compared to room temperature. The above results mean this phoshor has a good thermal stability and is a candidate for pc-LEDs.

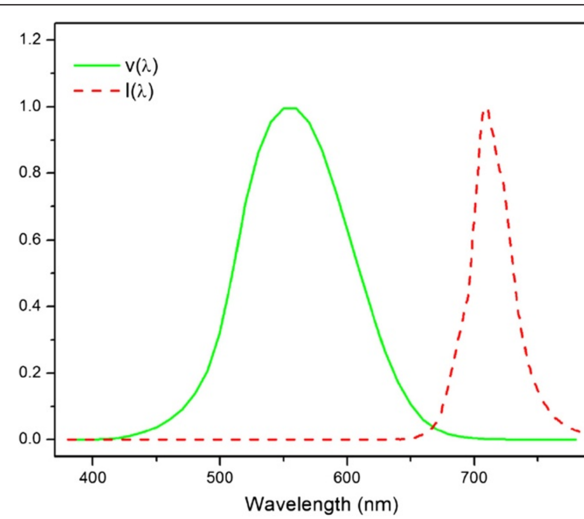

Figure 5 The normalized spectral eye sensitivity cures for photopic vision *V (λ)* and spectrum of phosphor CYA: $Mn^{4+}{}_{0.005}$ *I (λ)*.

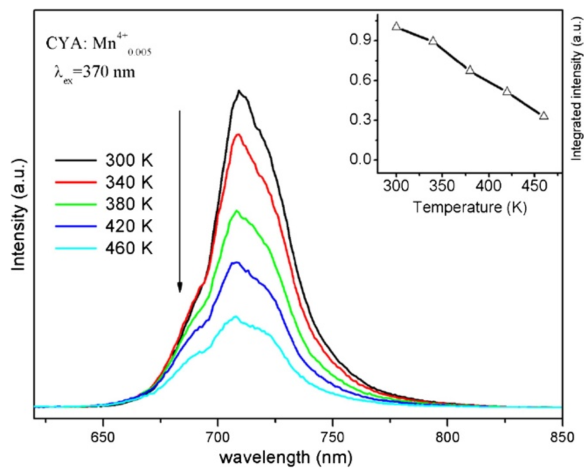

Figure 6 PL spectral ($\lambda_{ex} = 370$ nm) of CYA: $Mn^{4+}{}_{0.005}$ at the temperature range of 300–460 K. Inset shows temperature-dependent integrated emission intensity of CYA: $Mn^{4+}{}_{0.005}$.

Figure 7 shows the decay curves of Mn^{4+} $^4E \rightarrow {}^4A_2$ emission excited by 335 nm. The decay behavior can be expressed asfollows: [25].

$$I = A \exp(-t/t) + I_0 \tag{2}$$

where I and I_0 are emission intensity, A is constant, t is time and, τ is decay time for exponential component. For x = 0.001, 0.005, 0.01 all samples show a nearly single exponential decay behavior like CYA: $Mn^{4+}{}_{0.001}$ (the inset of Figure 7) and the life time is estimated to be 1.590 ms, 1.444 ms and 1.306 ms, respectively. When the Mn^{4+} concentration is further increased, the decay curves decrease more rapidly and become nonexponential. Such a fast decline of Mn^{4+} ^4E is due to the interaction or energy migration between Mn^{4+} ions. The same phenomenon was found in the decay curves of Mn^{4+} emission excited by 460 nm.

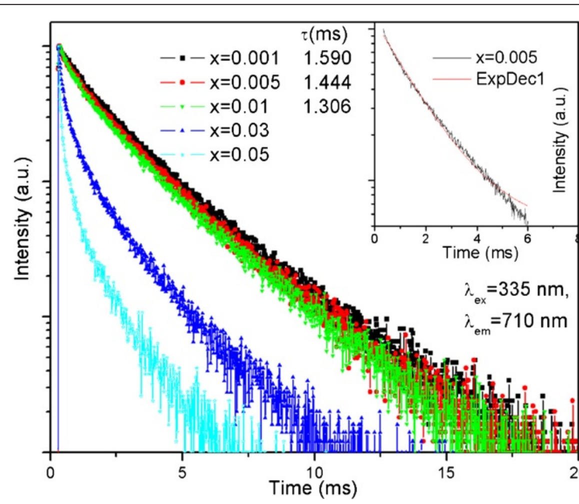

Figure 7 PL decay cure of CYA: $Mn^{4+}{}_x$ (x = 0.001, 0.005, 0.01, 0.03, 0.05); Inset shows the experiment curve (black line) and the fitted curve (red line).

Conclusion

In summary, a series of $CaYAlO_4$: Mn^{4+} red phosphors with good thermal stability were investigated. Mn^{4+} ion gives an intense red light at 710 nm with high color purity and intense broad absorption in UV and blue range. We demonstrate that it can be a useful red phosphor for LEDs, combined with blue (440 ~ 470 nm) InGaN and near (n)-UV (350 ~ 420 nm) GaN chip.

Abbreviations

LED: Light-emitting diode; PL: Photoluminescence; PLE: Photoluminescence excitation; CYA: CaYAlO4; CN: Coordination number; LERm: Luminous efficiency of the radiation.

Competing interests

The authors declare that they have no competing interests.

Authors' contribution

YC and MW carried out the experimental details and wrote the draft paper. JW, MW and CW designed the study and gave the discussion. All authors read and approved the final manuscript.

Acknowledgements

This work was financially supported by the "973" programs (2014CB643801), the NSFC (21271191), the Joint Funds of the National Natural Science Foundation of China and Guangdong Province (U1301242), the Doctoral Program of Higher Education of China (20130171130001), Teamwork Projects of Guangdong Natural Science Foundation (S2013030012842), Guangdong Provincial and Guangzhou Science & Technology Project (2012A080106005, 2013Y2-00118) and Guangdong Provincial Department of Science and Technology for Industrial applications of rare earth materials (2012B09000026).

Received: 6 May 2014 Accepted: 8 August 2014
Published: 27 August 2014

References

1. Mancic L, Marinkovic K, Marinkovic BA, Dramicanin M, Milosevic O: **YAG: Ce^{3+} nanostructured particles obtained via spray pyrolysis of polymeric precursor solution.** *J Eur Ceram Soc* 2010, **30**:577–582.
2. Li YX, Min YL, Zhou XZ, You XZ: **Coating and stability of YAG:Ce phosphor synthesized using inorganic–organic hybrid gel method.** *Chin J Inorg Chem* 2003, **19**:1169–1174.
3. Lu CH, Hong HC, Jaganathan R: **Sol–gel synthesis and photoluminescent properties of cerium-ion doped yttrium aluminium garnet powders.** *J Mater Chem* 2002, **12**:2525–2530.
4. Zhang M, Wang J, Zhang QH, Ding WJ, Su Q: **Optical properties of Ba_2SiO_4:Eu^{2+} phosphor for green light-emitting diode (LED).** *Mater Res Bull* 2007, **42**:33–39.
5. Geng DL, Shang MM, Zhang Y, Lian HZ, Lin J: **Color-tunable and white luminescence properties via energy transfer in single-phase $KNaCa_2$ $(PO_4)_2$: A (A = Ce^{3+}, Eu^{2+}, Tb^{3+}, Mn^{2+}, Sm^{3+}) phosphors.** *Inorg Chem* 2013, **52**:13708–13718.
6. Sun JG, Arunkumar P, Won BI: **A new blue-emitting oxohalide phosphor Sr_4OCl_6: Eu^{2+} for thermally stable, efficient white-light-emitting devices under near-UV.** *J Phys Chem C* 2014, **118**:2686–2692.
7. Sohn KS, Park DH, Cho SH, Kwak JS, Kim JS: **Computational evolutionary optimization of red phosphor for use in tricolor white LEDs.** *Chem Mater* 2006, **18**:1768–1772.
8. Shinde KN, Dhoble SJ: **A novel reddish-orange phosphor, $NaLi_2PO_4$: Eu^{3+}.** *Luminescence* 2013, **28**:93–96.
9. Zhou Z, Wang NF, Zhou N, He ZX, Liu S, Liu YN, Tian ZW, Mao ZY, Hintzen HT: **High colour purity single-phased full colour emitting white LED phosphor $Sr_2V_2O_7$: Eu^{3+}.** *J Phys D* 2013, **46**:035104–035110.
10. Mo FW, Zhou LY, Pang Q, Gong FZ, Liang ZJ: **Potential red-emitting $NaGd(MO_4)_2$: R (M = W, Mo, R = Eu^{3+}, Sm^{3+}, Bi^{3+}) phosphors for white light emitting diodes applications.** *Ceram Int* 2012, **38**:6289–6294.
11. Xiao Q, Zhou QT, Li M: **Synthesis and photoluminescence properties of Sm^{3+}-doped $CaWO_4$ nanoparticles.** *J Lumin* 2010, **130**:1092–1094.
12. Zhang SM, Zhu B, Zhou SF, Qiu JR: **Orange-red upconversion luminescence of Sm^{3+}-doped ZnO-B_2O_3-SiO_2 glass by infrared femtosecond laser irradiation.** *J Soc Inf Display* 2009, **17**:507–510.
13. Li YQ, Van Steen JEJ, Van Krevel JWH, Botty G, Delsing ACA, Disalvo FJ, De With G, Hintzen HT: **Luminescence properties of red-emitting $M_2Si_5N_8$:Eu^{2+} (M = Ca, Sr, Ba) LED conversion phosphors.** *J Alloys Compd* 2006, **417**:273–279.
14. Xie RJ, Hirosaki N: **Silicon-based oxynitride and nitride phosphors for white LEDs-A review.** *Sci Technol Adv Mat* 2007, **8**:588–600.
15. Xie RJ, Hirosaki N, Li YQ, Takeda T: **Rare-earth activated nitride phosphors: synthesis, luminescence and applications.** *Mater* 2010, **3**:3777–3793.
16. Yusuke A, Sadao A: **Optical transitions and internal vibronic frequencies of MnF_6^{2-} Ions in Cs_2SiF_6 and Cs_2GeF_6 red phosphors.** *J Electrochem Soc* 2011, **158**:J179–J183.
17. Paulusz AG: **Efficient Mn () emission in fluorine coordination.** *J Electrochem Soc* 1973, **120**:942–947.
18. Yusuke A, Toru T, Sadao A: **Photoluminescent properties of $K_2SnF_6H_2O$: Mn^{4+} red phosphor.** *Opt Mater* 2010, **32**:1095–1101.
19. Murata T, Tanoue T, Iwasaki M, Morinaga K, Hase T: **Fluorescence properties of Mn^{4+} in $CaAl_{12}O_{19}$ compounds as red-emitting phosphor.** *J Lumin* 2005, **114**:207–212.

20. Lv S, Zhu Z, Wang Y, You Z, Li J, Tu C: **Spectroscopic investigations of Ho^{3+}/Er^{3+}: CaYAlO4 and Eu^{3+}/Er^{3+}: $CaYAlO_4$ crystalsfor2.7 µm emission.** *J Lumin* 2013, **144:**117–121.
21. Shannon RD: **Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides.** *Acta Crystallogr* 1976, **A32:**751–767.
22. Zhang XJ, Huang L, Pan FJ, Wu MM, Wang J, Chen Y, Su Q: **Highly thermally stable single-component white-emitting silicate glass for organic-resin-free white-light-emitting diodes.** *ACS Appl Mater Interfaces* 2014, **6:**2709–2717.
23. Smet PF, Parmentier AB, Dirk P: **Selecting conversion phosphors for white light-emitting diodes.** *J Electrochem Soc* 2011, **158:**R37–R54.
24. Akvilė Z, Skirmantė B, Artūras Z, Pranciškus V, Aivaras K, Pranciškus V, Aivaras K: **Sol–gel synthesized far-red chromium-doped garnet phosphors for phosphor-conversion light-emitting need of plants.** *Appl Optics* 2014, **53:**907–914.
25. Lu J, Huang YL, Tao Y, Sec HJ: **Spectroscopic parameters of Ce^{3+} ion doped $Na_2CaMg\ (PO_4)_2$ phosphor.** *J Alloy Compd* 2010, **500:**134–137.

doi:10.1186/s40539-014-0015-4
Cite this article as: Chen *et al.*: A high color purity red emitting phosphor $CaYAlO_4$:Mn^{4+} for LEDs. *Journal of Solid State Lighting* 2014 **1**:15.