RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Rare-earth free narrow-band green-emitting $KAlSi_2O_6$: Mn^{2+} phosphor excited by blue light for LED-phosphor material

Xin Ding, Ge Zhu, Qian Wang, Yuhua Wang*

Key Laboratory of Special Function Materials and Structure Design, Ministry of Education, Department of Materials Science, School of Physical Science and Technology, Lanzhou University Lanzhou University, Tianshui South Road No. 222, Lanzhou, Gansu 730000, PR China

Abstract

A novel rare-earth free green-emitting $KAlSi_2O_6$: Mn^{2+} phosphor is synthesized by traditional solid-state reaction. The structure, photoluminescence and temperature-dependent properties are investigated. $KAlSi_2O_6$: Mn phosphor can emit green light peaking at 513 nm with narrow full-width at half-maximum of 30 nm upon 450 nm excitation. The quantum yields and Commission Internationale de I'Eclairage (CIE) color coordinates are 30.2% and (0.27, 0.64). The white LED is fabricated by $KAlSi_2O_6$: Mn and $CaAlSiN_3$: Eu (red phosphor) combined with blue LED chip. Its correlated color temperature, color coordinates, Ra and luminous efficiency are 4775 K, (0.35, 0.36), 85.1 and 110.2 lm/w, respectively. It is demonstrated that $KAlSi_2O_6$:Mn^{2+} phosphor as the potential material could be simulated to blue-LED for producing efficient white-light.

Keywords: Phosphors, Luminescence, Crystal structure

*Corresponding author at: Department of Materials Science, School of Physical Science and Technology, Lanzhou University, Lanzhou, 730000, PR China.

Tel.: +86 931 8912772; fax: +86 931 8913554.

Corresponding author' email: wyh@lzu.edu.cn

1. Introduction

White light-emitting diodes (w-LED), as promising candidates to replace conventional incandescent and fluorescent lamps, have received increasing attention in recent years due to their admirable merits of high luminous efficiency, low energy cost and robustness [1-3]. The current most widely used method to obtain w-LED is InGaN blue chip combined with yellow phosphor

(YAG: Ce) [4]. However, such design suffers some technical weaknesses in practical application. One of these problems is the hiatus in red components, which leads to high correlated color temperature (CCT) and low color rendering index (CRI) for the white light. Besides to this method, another kind of W-LEDs can be also fabricated by GaN-based blue chip combing with the green and red phosphors which can solve above problems. Some nitrides/oxynitrides green phosphors like $MSi_2O_2N_2$:Eu^{2+}, SiAlON: Eu^{2+} and Ba_2SiO_4: Eu^{2+} have been commercialized [5-7]. However, most of those phosphors are doped by rare-earth and their synthesis conditions are harsh which will lead to high production cost. As an alternative, the non-rare-earth Mn^{2+} doped phosphors offer some important advantages in these respects and thus have gained increased attention recently [8, 9]. As known to all, only Mn^{2+} in tetrahedron crystal field can it emit green light. Mn^{2+} is featured by the $3d^3$ electron configuration with electrons located in an outer orbit, which causes its optical property heavily affected by the matrix; in the other words, the green emitting wavelengths of spin-forbidden Mn^{2+}: forbidden d-d transition ($^4T_1 \rightarrow {}^6A_1$) can be affected by the crystal field conditions which can emit bright light [10].

In this work, a novel rare-earth free Mn-doped $KAlSi_2O_6$ (KAS) green phosphor excited by blue light is reported firstly. A phosphor with narrow green emission band and nice temperature properties is obtained. As the tetrahedrally coordinated, Al and Si are in the same crystal coordinate and occupy crystal position randomly. Relative appropriate radius and coordinate may provide suitable factor for Mn^{2+} occupying. The crystal phase formation, luminescence properties and thermal quenching properties are investigated.

2. Experimental Section

K_2CO_3 (99.9%), H_2SiO_3 (AR), $Al(OH)_3$ (AR) and $MnCO_3$ (99.99%) as the raw materials were stoichiometric and 2wt% NH_4F as the flux was also used in the synthesis process. These materials

were ground in an agate mortar and put a small amount of ethanol in it. The prepared samples were sintered at 800℃ for 2 h and 1420 ℃ for 6 h. When the material cooled, grinded them and got the samples. The phase formation and crystal structure were analyzed by the X-ray powder diffraction (XRD) (D2 PHASER X-ray Diffractometer, Germany) with graphite monochromator using Cu Kα radiation（λ = 1.54056 A), operating at 30 kV and 15 mA. The luminescent spectra were measured by Fluorolog R-3 Spectrophotometer.

3. Results and Discussion

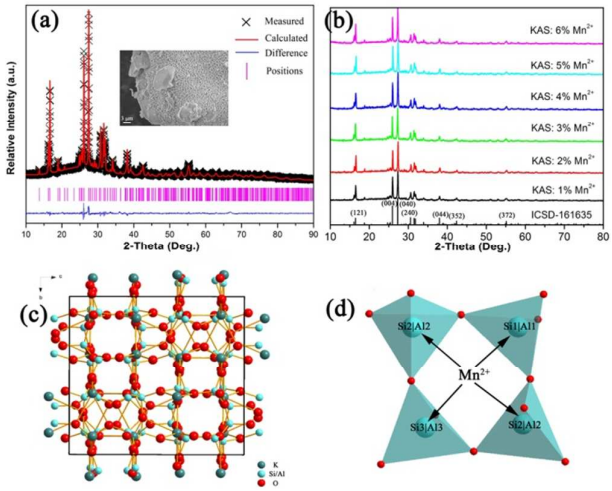

Figure 1 (a) Rietveld refinement of the powder XRD profile of KAS with its JCPDS. Inset shows the SEM micrograph of $KAlSi_2O_6$: 1%Mn^{2+} phosphor taken at a magnification of 1.50 kX. (b) XRD patterns of series KAS: *x*%Mn^{2+} and standard data. (c) Crystal structure of $KAlSi_2O_6$. (d) Coordination relationship of Si|Al-O and Mn^{2+} occupying situation.

In order to determine the real structure of the synthesized samples, ICSD-161638 ($KAlSi_2O_6$) is used as the standard data to refine KAS and structural refinement of XRD is made using GSAS program. Figure 1a illustrates the experimental and refined XRD patterns of KAS sample. By comparing the calculated data with the experimental spectra, we find that each peak is in good agreement. There is no impurity phase found in the samples, which reveals that it crystallizes in good single-phase. The calculated residual factor value is Rp = 7.43%, and Rwp = 8.55%. The appearance of $KAlSi_2O_6$ emerges homogeneous honeycomb morphology shown in the inset of

Figure 1a. XRD patterns of the as-prepared $KAlSi_2O_6$: $x\%Mn^{2+}$ ($1 \leq x \leq 6$) phosphors are given in Figure 1b. It can be seen that all of the diffraction peaks of the samples can be basically indexed to the standard data, suggesting that $KAlSi_2O_6$: $x\%Mn^{2+}$ with different Mn^{2+} concentration can be formed in the single-phased structure. $KAlSi_2O_6$ belongs to I 41/a (88) space group with tetragonal structure. Al and Si are in the same crystal coordinate and occupy crystal position randomly. Different Al/Si-O tetrahedrons are connected by total of angle connection of O [11]. According to ionic radius [12], Mn^{2+} may occupy Al/Si crystal site which is shown in Figure 1c and d.

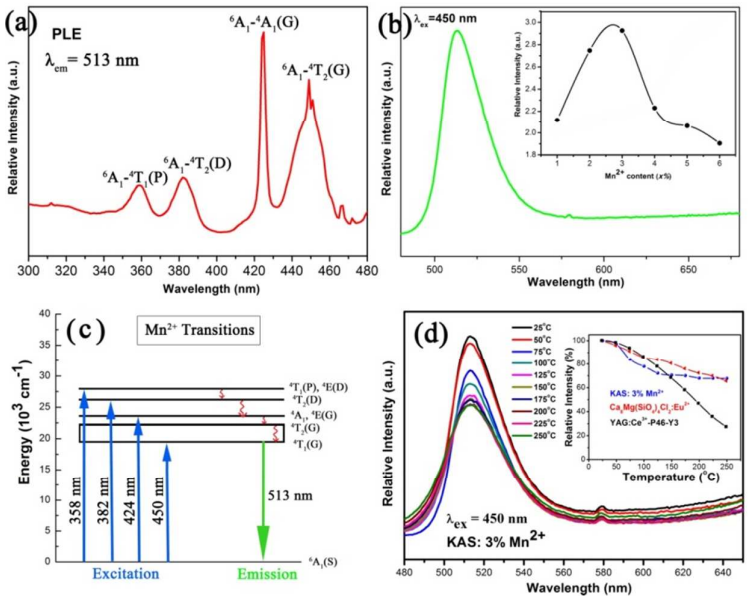

Figure 2 Photoluminescence excitation of KAS: Mn^{2+} (a); Photoluminescence emission spectra of KAS phosphors, inset: Dependence of emission intensity of KAS: $x\%Mn^{2+}$ phosphors on Mn^{2+} content (b); The excitation and emission transitions of Mn^{2+} ions (c); Temperature dependence of KAS: 3%Mn^{2+} PL properties, inset: contradistinction of KAS: 3%Mn^{2+}, YAG: Ce^{3+} (P46-Y3, yellow phosphor) and commercial $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+} (green phosphor).

Figure 2a shows the room-temperature photoluminescence (PL) excitation spectrum monitoring at 513 nm emission. The PL excitation shows five distinct peaks centered at 358, 382, 424, 450, and 465 nm that they are in good agreement with the well known Mn^{2+} absorption transitions [13]. Especially, it can match blue GaN chips well cause to its relative strong 450 nm absorption. The

PL emission spectra of $KAlSi_2O_6$: x%Mn^{2+} phosphor registered at 450nm excitation wavelengths are shown in Figure 2b. It can be easily seen that it is a green light emission peaking at 513 nm with full-width at half-maximum (FWHM) of 30 nm and the emission intensities have an obvious increasing trend with increasing Mn^{2+}concentration, and maximizes is at x% = 3%, then the emission intensity decreases. Since in $KAlSi_2O_6$, the Mn^{2+} is tetrahedron coordinated, it produces a single broad-band green emission centered at 513 nm which is attributed to spin forbidden d-d transition ($^4T_1 \rightarrow {}^6A_1$) of Mn^{2+} and the small FWHM (30 nm) can get high color purity. The excitation transitions of Mn^{2+} from ground level $^6A_1(^6S)$ to $^4E(^4D)$, $^4T_2(^4D)$, $[^4A_1(^4G)$, $^4E(^4G)]$, $^4T_2(^4G)$, and $^4T_1(^4G)$ excited levels are schematically shown in Figure 2c. The electron could be relaxed from these excited states to the $^4T_1(G)$ state by a non-radiative relaxation process and then transferred back to the ground state $^6A_1(S)$ emitting the characteristic green (513 nm) light. Temperature-dependent relative emission intensity upon 450 nm excitation of KAS: 3%Mn^{2+} is indicated in Figure 2d. It can be clearly seen that with temperature increasing, the emission intensity decreases gradually due to the non-radiative transition probability by thermal activation dependent on temperature. The integrated emission intensity of KAS: 3%Mn^{2+} is decreased to 67.6% (250 °C) compared with the initial value (25 °C), meanwhile, commercial $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+} (green phosphor) and YAG: Ce^{3+} (P46-Y3, yellow phosphor) are decreased to 65.3% and 27%. It indicates that the temperature-dependent properties of KAS: 3%Mn^{2+} are better than YAG: Ce^{3+} (P46-Y3, yellow phosphor) and similar with $Ca_8Mg(SiO_4)_4Cl_2$: Eu^{2+}.

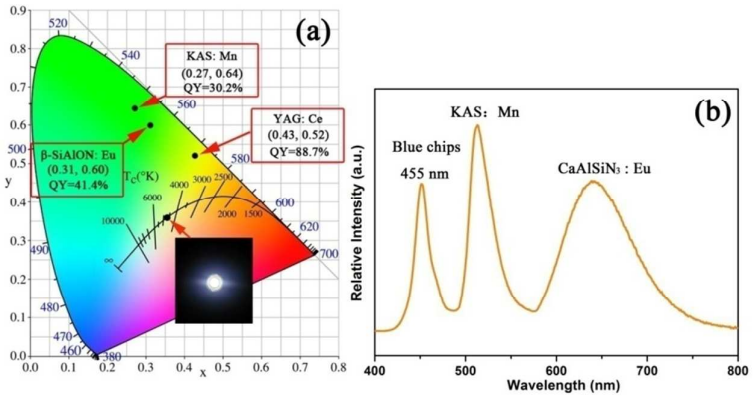

Figure 3 The CIE chromaticity coordinates and their respective quantum yields. The inset shows the phosphor simulated white light using blue (455 nm) LED (a); The PL spectrum of white light combined with blue chips, KAS: Mn and $CaAlSiN_3$: Eu.

The color coordinates are highly useful in determining the exact emission color and color purity of the sample, as per the chromaticity diagram of the Commission Internationale de I'Eclairage (CIE). The CIE color coordinates of KAS: $0.03Mn^{2+}$ phosphor were calculated to be x=0.27 and y=0.64 using equidistant wavelength method and are illustrated in the CIE chromaticity diagram as shown in Figure 3a. The color coordinates of KAS: Mn is much closer to standard green coordinates (0.21, 0.71). These values obtained are comparable to the coordinates (0.43, 0.52) and (0.31, 0.60) of commercially used YAG: Ce and β-SiAlON: Eu^{2+} (for green). The quantum yields are measured to be 41.4% at 460 nm, 30.2% at 450 nm, and 88.7% at 460 nm for β-SiAlON: Eu^{2+}, KAS: $0.03Mn^{2+}$, and YAG: Ce phosphors, respectively. The comparison of color coordinates to other yellow-green/green phosphors, this Mn doped phosphor exhibits high color purity, which enables to achieve a larger color gamut for devices. Furthermore, the relative strong absorption peaking at 450 nm can match with currently available blue-LED chips. To obtain warm white light, white light LED is fabricated by KAS: Mn phosphor blended with $CaAlSiN_3$: Eu red phosphor combined with blue-LED chip (~455 nm). Its emission spectrum is shown in Figure 3b. The chromaticity coordinates of this typical white LED is (0.35, 0.36) with CCT of 4775 K which is

shown in Figure 3a. The Ra and luminous efficiency is 85.1 and 110.2lm/w with drive voltage 3.2 V. It indicates that the narrow emission band and high color purity make the current sample a very attractive green phosphor for white LEDs.

4. Conclusions

In summary, we provide original insights for preparing a rare-earth free $KAlSi_2O_6$: Mn phosphor with comparable PL brightness levels useful for white-LEDs. This relatively inexpensive phosphor has an internal QY of 30.2% at 450 nm. It can emit green light peaking at 513 nm with FWHM = 30nm and nice color coordinates (0.27, 0.64). The integrated emission intensity of KAS: 3%Mn^{2+} is decreased to 67.6% (250 °C) of the initial value (25 °C). The chromaticity coordinates of fabricated white LED is (0.35, 0.36) with CCT of 4775 K. The Ra and luminous efficiency is 85.1 and 110.2 lm/w with drive voltage 3.2 V. It is demonstrated that $KAlSi_2O_6$:Mn^{2+} phosphor could be simulated to blue-LED for producing efficient white-light.

Acknowledgment

This work is supported by Specialized Research Fund for the Doctoral Program of Higher Education (no. 20120211130003), the National Natural Science Funds of China (Grant no. 51372105)

Reference

[1] S. Ye, F. Xiao, Y. X. Pan, Y. Y. Ma, Q.Y. Zhang, *Mater. Sci. Eng. R* 2010,**71**, 1

[2] C. C. Lin, R. S. Liu, *J. Phys. Chem. Lett.* 2011, **2**,1268

[3] A. Kitai, John Wiley & Sons, Ltd ISBN: 978-0-470-05818-3 (2008)

[4] P. F Smet, A. B. Parmentier, D. Poelman, 2011,**158 (6)**, R37

[5] K. Kimoto, R. J. Xie, Y. Matsui, K. Ishizuka, N. Hirosaki, *Appl. Phys. Lett.* 2009, **94**, 041908

[6] J. Botterman, K.V. Eeckhout, A. J. J. Bos, P. Dorenbos, P. F. Smet, *Opt. Mater. Exp.* 2012, **2**, 341

[7] M. A. Lim, J. K. Park, C. H. Kim, H. D. Park. *J. Mater. Sci. Lett.* 2003, **22**, 1351

[8] X. J. Wang, R. J. Xie, B. Dierre, T. Takeda, T. Suehiro, N. Hirosaki, et al. *Dalton Trans.* 2014, **43**, 6120

[9] D. Haranath, S. Mishra, S. Yadav, R. K. Sharma, L. M. Kandpal, N. Vijayan, M. K. Dalai, G. Sehgal, V. Shanker, *Appl. Phys. Lett.* 2012, **101**, 221905

[10] W. Lu, W. Z. Lv, Q. Zhao, M. M. Jiao, B. Q Hao, H. P. You, *Inorg. Chem.* 2014, **53**, 11985

[11] S. Goryainov, Phys. stat. sol. (a) 2005, **202 No. 3**, R25–R27

[12] R. D. Shannon. *Acta Cryst.* 1976, **A32**, 751

[13] C. M. Zhang, S. S. Huang, D. M. Yang, X. J. Kang, M. M. Shang, C. Peng, J. Lin, *J Mater. Chem*. 2010, **20**, 6674