

White light emitting diode by using α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ phosphor

Zhendong Hao, Jiahua Zhang, Xia Zhang, Xiaoyuan Sun, Yongshi Luo et al.

Citation: *Appl. Phys. Lett.* **90**, 261113 (2007); doi: 10.1063/1.2752725

View online: <http://dx.doi.org/10.1063/1.2752725>

View Table of Contents: <http://apl.aip.org/resource/1/APPLAB/v90/i26>

Published by the [American Institute of Physics](#).

Related Articles

An earth-isolated optically coupled wideband high voltage probe powered by ambient light
Rev. Sci. Instrum. **83**, 104703 (2012)

Organic light-emitting diodes with direct contact-printed red, green, blue, and white light-emitting layers
APL: Org. Electron. Photonics **5**, 228 (2012)

Organic light-emitting diodes with direct contact-printed red, green, blue, and white light-emitting layers
Appl. Phys. Lett. **101**, 153304 (2012)

Analysis of parasitic cyan luminescence occurring in GaInN blue light-emitting diodes
J. Appl. Phys. **112**, 074512 (2012)

Gallium nitride-based light-emitting diodes with embedded air voids grown on Ar-implanted AlN/sapphire substrate
Appl. Phys. Lett. **101**, 151103 (2012)

Additional information on *Appl. Phys. Lett.*

Journal Homepage: <http://apl.aip.org/>

Journal Information: http://apl.aip.org/about/about_the_journal

Top downloads: http://apl.aip.org/features/most_downloaded

Information for Authors: <http://apl.aip.org/authors>

ADVERTISEMENT



AMERICAN
PHYSICAL
SOCIETY'S
OPEN ACCESS
JOURNAL

PRX

Committed to
Excellence

Physical Review X
prx.aps.org

White light emitting diode by using $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ phosphor

Zhendong Hao, Jiahua Zhang,^{a)} Xia Zhang, Xiaoyuan Sun, Yongshi Luo, and Shaozhe Lu
Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics
and Physics (CIOMP), Chinese Academy of Sciences, 16 Eastern South Lake Road, Changchun 130033,
China and Graduate School of Chinese Academy of Sciences, Beijing, 100039, China

Xiao-jun Wang

CIOMP, Chinese Academy of Sciences, Changchun 130033, China and Department of Physics, Georgia
Southern University, Statesboro, Georgia 30460

(Received 13 May 2007; accepted 3 June 2007; published online 27 June 2007)

The $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ phosphors show two emission bands peaking at around 416 (blue) and 600 nm (orange), originating from the allowed $f\text{-}d$ transition of Eu^{2+} and the forbidden ${}^4T_1\text{-}{}^6A_1$ transition of Mn^{2+} , respectively, under near ultraviolet (UV) excitation at 400 nm. Spectroscopy and fluorescence lifetime measurements demonstrate that energy transfer from Eu^{2+} to Mn^{2+} performs with transfer efficiency as high as 65% for Mn^{2+} concentration of 12 mol %. The authors have fabricated a white light emitting diode (LED) through the integration of GaN near-UV chip and two phosphor blends ($\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ blue-orange phosphor and $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ green phosphor) into a single package. The white LED shows color rendering index of 78, luminescent efficiency of 9 lm/W, and low color point variation against forward-bias currents. © 2007 American Institute of Physics. [DOI: 10.1063/1.2752725]

The white light emitting diode (LED) have received increasing interests in recent years for its promising applications on solid state lighting.¹⁻³ There are basically two approaches for generating white light using LEDs.⁴ The first approach is to mix the light of different colors emitted from different LED chips. Another approach is to mix the emission from a blue or near-ultraviolet (UV) LED with a longer wavelength light downconverted from the LED emission using phosphors.⁵⁻⁸ In a near-UV chip white LED, the visible components of the white light are generated only by phosphors, exhibiting low color point variation against the forward-bias currents. Some yellow, green, and blue emitting phosphors as good candidates for near-UV chip excitation have been reported.⁹⁻¹² However, there are very few inorganic red or orange phosphors with environmental stability and nontoxicity for this type of white LEDs.¹³

The blue $\text{Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$ phosphors have extensive applications in the fields of luminescence and biomaterials due to its improved optical and biological characteristics.¹⁴ The blue-orange $\text{Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ phosphor is also a good phosphor for lamp through the energy transfer from Eu^{2+} to Mn^{2+} .¹⁵ However, most of them concern beta phase calcium pyrophosphates, while the applicability of Eu^{2+} and Mn^{2+} codoped alpha phase calcium pyrophosphates to a tricolor conversion phosphor excited by near-UV LED has not been demonstrated. In this letter, we represent the blue-orange $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ phosphor, besides a blue band of Eu^{2+} , which has a strong orange band originating from the ${}^4T_1\text{-}{}^6A_1$ transition of Mn^{2+} due to energy transfer between Eu^{2+} and Mn^{2+} . The energy transfer and luminescent properties of the phosphors are investigated, as well as the optimal doping concentrations of Eu^{2+} and Mn^{2+} . White LEDs are fabricated through combining near-UV chip with two phos-

phor blends of the green-poor $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ and a green $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$ phosphor.¹⁰

Synthesis of the powder samples was conducted by using solid state reaction. The starting materials, analytical grade, CaHPO_4 , MnCO_3 , $(\text{NH}_4)_2\text{HPO}_4$, and Eu_2O_3 were homogenized by an agate mortar, pestled for 1 h and placed in a crucible with a lid. The crucible was preheated at 600 °C for 1 h, cooled down, ground, and put into crucible again which was buried by carbon sticks and sintered at 1250 °C for 2 h in CO reducing atmosphere. The concentration of Eu^{2+} was fixed at 4 mol %, while the Mn^{2+} concentrations were varied from 4 to 14 mol %. A green $\text{Ba}_2\text{SiO}_4\text{:0.03Eu}^{2+}$ phosphor for mixing with $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ was synthesized by the process, as described in Ref. 10. The structure of sintered samples was identified by x-ray powder diffractometer (XRD) (Rigaku D/M AX-2500 V). The measurements of photoluminescence (PL) and photoluminescence excitation (PLE) spectra were performed by using a Hitachi F4500 fluorescent spectrometer. In fluorescence lifetime measurements, the third harmonic (355 nm) of a Nd doped yttrium aluminum garnet laser (Spectra-Physics, GCR 130) was used as an excitation source, and the signals were detected with a Tektronix digital oscilloscope (TDS 3052). The chromaticity coordinates and color rendering indices (CRIs) as well as the correlated color temperature (T_c) in kelvins of the fabricated white LED were obtained using PR-705 SpectraScan spectroradiometer.

XRD patterns of Eu^{2+} and Mn^{2+} codoped $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$ are shown in Fig. 1. All the peaks are indexed based on monoclinic structure and match well with those in Ref. 16, JCPDS card 09-0345, indicating that the obtained samples are single phase and the codoped Eu^{2+} and Mn^{2+} ions do not cause any significant change in the host structure.

PL and PLE spectra of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}$, $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Mn}^{2+}$, and $\alpha\text{-Ca}_2\text{P}_2\text{O}_7\text{:Eu}^{2+}, \text{Mn}^{2+}$ are presented in Fig. 2 by a comparable way. In Fig. 2(a), the Eu^{2+} singly doped sample exhibits a strong blue emission band centered

^{a)} Author to whom correspondence should be addressed; FAX: +86-431-617-6317; electronic mail: zhangjh@ciomp.ac.cn

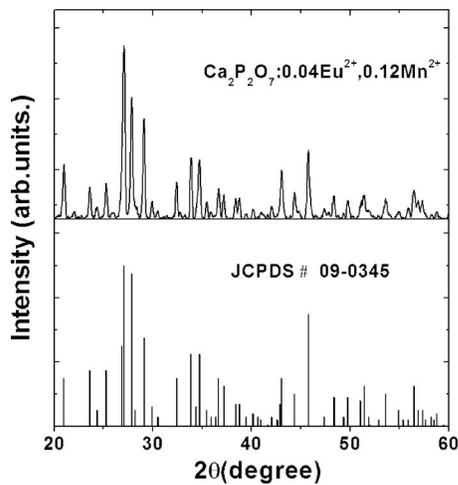


FIG. 1. XRD patterns of α - $\text{Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ samples and of Ref. 16.

at 416 nm with its PLE bands within UV and near-UV regions, originating from the $4f$ - $5d$ transition of Eu^{2+} . In Fig. 2(b), the Mn^{2+} singly doped sample exhibits a weak orange emission band peaking at 600 nm due to the 4T_1 - 6A_1 transition of Mn^{2+} with its PLE peaks at 355 and 406 nm, corresponding to the forbidden transitions from the ground state ${}^6A_1({}^6S)$ to ${}^4T_2({}^4D)$ and $[{}^4A_1({}^4G), {}^4E({}^4G)]$ levels of Mn^{2+} , respectively.¹⁷ The comparison of the PL spectrum of α - $\text{Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$ with the PLE spectrum of α - $\text{Ca}_2\text{P}_2\text{O}_7:\text{Mn}^{2+}$ sample reveals a significant spectral overlap, indicating the possibility of energy transfer from Eu^{2+} to Mn^{2+} in α - $\text{Ca}_2\text{P}_2\text{O}_7$ host. As expected in Fig. 2(c), the emission spectrum of Eu^{2+} and Mn^{2+} codoped α - $\text{Ca}_2\text{P}_2\text{O}_7$ appears not only a strong blue band of Eu^{2+} but also a strong orange band of Mn^{2+} . It is clearly shown that the PLE spectrum of

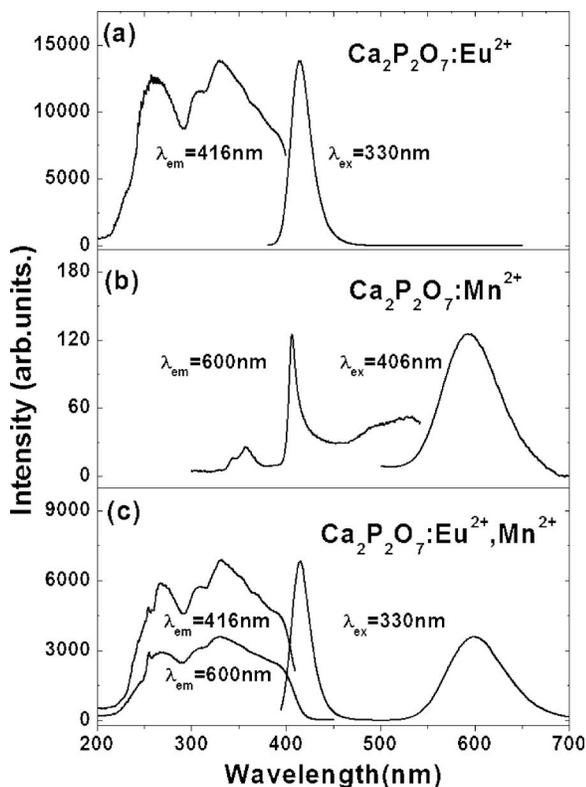


FIG. 2. PL and PLE spectra of α - $\text{Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$ (a), α - $\text{Ca}_2\text{P}_2\text{O}_7:\text{Mn}^{2+}$, (b) and the α - $\text{Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ (c).

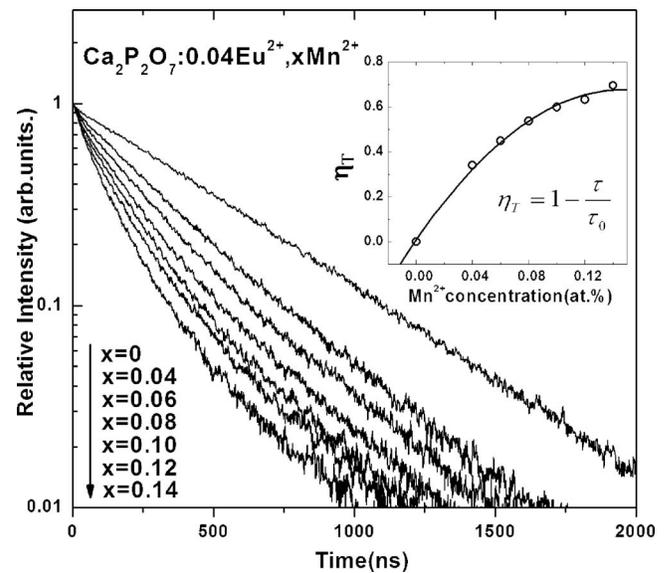


FIG. 3. Fluorescence lifetimes of Eu^{2+} in α - $\text{Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, x\text{Mn}^{2+}$. Inset: the dependence of the energy transfer efficiency η_T in α - $\text{Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, x\text{Mn}^{2+}$ on Mn^{2+} content x .

the orange band is consistent with that of the blue band of Eu^{2+} , demonstrating effective energy transfer from Eu^{2+} to Mn^{2+} . The PLE spectrum covers the spectral region of 225–425 nm, implying that the doubly doped phosphor is suitable to near-UV LED excitation.

Figure 3 shows the fluorescence transients of the blue band of 4 mol % Eu^{2+} in α - $\text{Ca}_2\text{P}_2\text{O}_7$ with different Mn^{2+} concentrations. The fluorescence decays faster and trends to be nonexponential function with increasing Mn^{2+} concentrations, reflecting the characteristics of energy transfer between donors and acceptors.^{18,19} The energy transfer efficiency (η_T) for $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ is calculated using the equation,

$$\eta_T = 1 - \tau/\tau_0,$$

where τ and τ_0 are the fluorescence lifetimes of Eu^{2+} in α - $\text{Ca}_2\text{P}_2\text{O}_7$ with and without codoping of Mn^{2+} , respectively. The values of the lifetimes are obtained by integrating the decay curves, of which the initial intensities are normalized. The results are plotted in the inset of Fig. 3. With increasing Mn^{2+} concentrations, the energy transfer efficiencies (η_T) increase gradually and reach to as high as 70% for Mn^{2+} concentrations of 14 mol %. It is observed experimentally that the lifetimes of the orange band of Mn^{2+} are not shortened with increasing Mn^{2+} concentration up to 12 mol %, at which the energy transfer efficiency is 65% and the strongest intensity of the orange band is achieved, implying that the quenching concentration of Mn^{2+} is 12 mol % in α - $\text{Ca}_2\text{P}_2\text{O}_7$.

Figure 4(a) shows the emission spectra of α - $\text{Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors¹⁰ under 400 nm excitation. The green emission band of $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphor peaking at 505 nm is complemented to the blue-orange α - $\text{Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ phosphor, so that it is expected to fabricate white LEDs with a mixture of the two phosphors. Figure 4(b) shows the emission spectrum of the fabricated white LED under 20 mA forward-bias currents. Obviously, the spectrum exhibits the emission colors of the two phosphor blends. The asymmetry of the 400 nm band is caused by overlapping

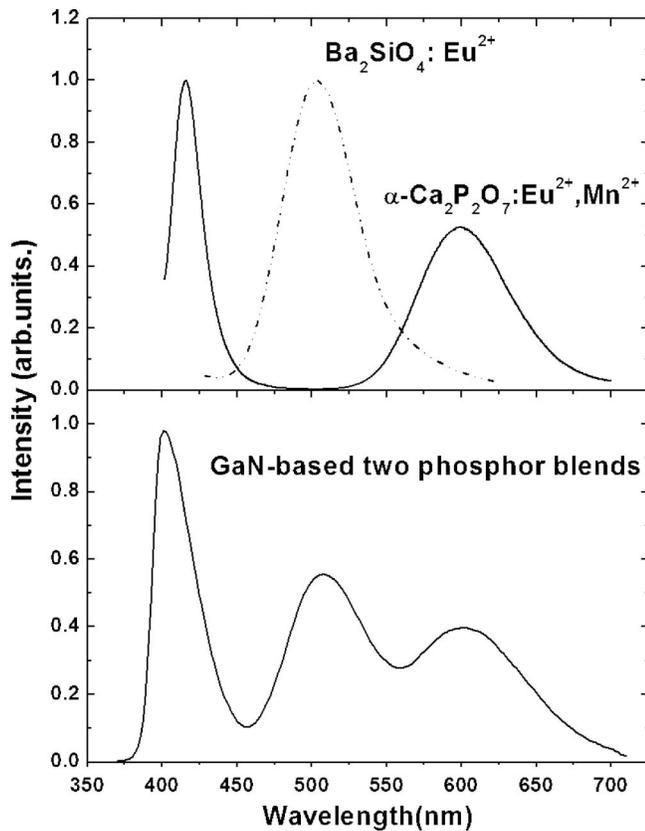


FIG. 4. Luminescence spectra of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors (a) and the UV-pumped white LED with the blends of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors under the forward-bias currents of 20 mA (b).

with the 416 nm emission band of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ phosphor.

The chromaticity coordinates on Commission Internationale de l'Eclairage (CIE) 1931 and CRIs of the fabricated white LED as a function of forward-bias currents are depicted in Fig. 5. With increasing applied currents from 10 to 50 mA, the variation of both the CIE chromaticity co-

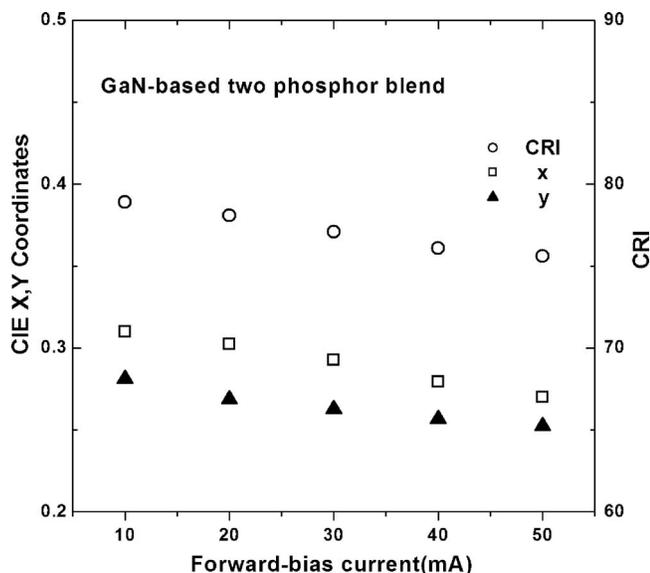


FIG. 5. CIE chromaticity coordinates and CRI of UV-pumped white LED with $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors with increasing forward-bias currents from 10 to 50 mA.

ordinates and CRIs is less than 10%, indicating lower color point variation of UV chip based white LED compared with the blue chip.²⁰ When the forward-bias current is 20 mA, the CIE coordinates are $x=0.27$ and $y=0.30$; the CRI is 78 and the luminous efficiency is 9 lm/W; the correlated color temperature (T_c) is 10 465 K. The CIE coordinates and the correlated color temperature indicate that the LED emission shows bluish white due to the weak spectral content of the orange light. However, by tuning the weight ratio of two phosphors, increasing the orange emission intensity, the warm white LED can be expected to obtain and we have experimentally obtained evidence for the possibility of further improvements in the CIE coordinates and the correlated color temperature.

In conclusion, the single-phased $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ phosphors have been synthesized for application to white LEDs. The enhanced orange emission of Mn^{2+} is observed in $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ upon UV excitation due to the energy transfer from Eu^{2+} to Mn^{2+} . The energy transfer efficiency can be as high as 65%. The white LED integrating 400-nm-emitted chip with the mixture of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}, 0.12\text{Mn}^{2+}$ blue-orange phosphor and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ green phosphor is realized and the results show a color rendering index of 78 and a good luminescent efficiency of 9 lm/W. The present letter indicates that the $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}, \text{Mn}^{2+}$ phosphor can be a promising candidate phosphor for white LEDs.

This work is financially supported by the MOST of China (2006CB601104 and 2006AA03A138) and by the National Natural Science Foundation of China (10574128 and 10504031).

- ¹P. Schlotter, R. Schmidt, and J. Schneider, Appl. Phys. A: Mater. Sci. Process. **64**, 417 (1997).
- ²Toshio Nishida, Tomoyuki Ban, and Naoki Kobayashic, Appl. Phys. Lett. **82**, 3817 (2003).
- ³Ho Seong Jang and Duk Young Jeon, Appl. Phys. Lett. **90**, 041906 (2007).
- ⁴E. F. Schubert and J. K. Kim, Science **308**, 1274 (2005).
- ⁵S. Nakamura, Proc. SPIE **3002**, 26 (1997).
- ⁶M. S. Shur and A. Zukauskas, Proc. IEEE **93**, 1691 (2005).
- ⁷J. K. Park, M. A. Lim, C. H. Kim, H. D. Park, J. T. Park, and S. Y. Choi, Appl. Phys. Lett. **82**, 683 (2003).
- ⁸J. S. Kim, P. E. Jeon, J. C. Choi, H. L. Park, S. I. Mho, and G. C. Kim, Appl. Phys. Lett. **84**, 2931 (2004).
- ⁹Weijia Ding, Jing Wang, Mei Zhang, Qihong Zhang, and Qiang Su, Chem. Phys. Lett. **435**, 301 (2007).
- ¹⁰Mei Zhang, Jing Wang, Qihong Zhang, Weijia Ding, and Qiang Su, Mater. Res. Bull. **42**, 33 (2007).
- ¹¹Naoto Hirotsaki, Rong-Jun Xie, Koji Kimoto, Takashi Sekiguchi, Yoshinobu Yamamoto, Takayuki Suehiro, and Mamoru Mitomo, Appl. Phys. Lett. **86**, 211905 (2005).
- ¹²Z. C. Wu, J. X. Shi, J. Wang, M. L. Gong, and Q. Su, J. Solid State Chem. **179**, 2356 (2006).
- ¹³Weijia Ding, Jing Wang, Mei Zhang, Qihong Zhang, and Qiang Su, J. Solid State Chem. **179**, 3394 (2006).
- ¹⁴A. Doat, F. Pelle, and A. Lebugle, J. Solid State Chem. **178**, 2354 (2005).
- ¹⁵W. M. Yen and M. J. Weber, *Inorganic Phosphor* (CRC, New York, 2004), Section 4, p. 494.
- ¹⁶JCPDS File No. 09-0345.
- ¹⁷Woan-Jen Yang, Liyang Luo, Teng-Ming Chen, and Niann-Shia Wang, Chem. Mater. **17**, 3883 (2005).
- ¹⁸M. M. Broer, D. L. Huber, W. M. Yen, and W. K. Zwicker, Phys. Rev. Lett. **49**, 394 (1982).
- ¹⁹M. M. Broer, D. L. Huber, W. M. Yen, and W. K. Zwicker, Phys. Rev. B **29**, 2382 (1984).
- ²⁰J. S. Kim, P. E. Jeon, W. N. Kim, J. C. Choi, H. L. Park, and G. C. Kim, Mater. Res. Soc. Symp. Proc. **817**, L9.4.1 (2004).