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

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The α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ phosphors show two emission bands peaking at around 416 (blue) and 600 nm (orange), originating from the allowed f - d transition of Eu²⁺ and the forbidden 4T_1 - 6A_1 transition of Mn²⁺, respectively, under near ultraviolet (UV) excitation at 400 nm. Spectroscopy and fluorescence lifetime measurements demonstrate that energy transfer from Eu²⁺ to Mn²⁺ performs with transfer efficiency as high as 65% for Mn²⁺ 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 (α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ blue-orange phosphor and Ba₂SiO₄:Eu²⁺ 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 Ca₂P₂O₇:Eu²⁺ phosphors have extensive applications in the fields of luminescence and biomaterials due to its improved optical and biological characteristics.¹⁴ The blue-orange Ca₂P₂O₇:Eu²⁺, Mn²⁺ phosphor is also a good phosphor for lamp through the energy transfer from Eu²⁺ to Mn²⁺.¹⁵ However, most of them concern beta phase calcium pyrophosphates, while the applicability of Eu²⁺ and Mn²⁺ 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 α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ phosphor, besides a blue band of Eu²⁺, which has a strong orange band originating from the 4T_1 - 6A_1 transition of Mn²⁺ due to energy transfer between Eu²⁺ and Mn²⁺. The energy transfer and luminescent properties of the phosphors are investigated, as well as the optimal doping concentrations of Eu²⁺ and Mn²⁺. White LEDs are fabricated through combining near-UV chip with two phos-

phor blends of the green-poor α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ and a green Ba₂SiO₄:Eu²⁺ phosphor.¹⁰

Synthesis of the powder samples was conducted by using solid state reaction. The starting materials, analytical grade, CaHPO₄, MnCO₃, (NH₄)₂HPO₄, and Eu₂O₃ 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 Eu²⁺ was fixed at 4 mol %, while the Mn²⁺ concentrations were varied from 4 to 14 mol %. A green Ba₂SiO₄:0.03Eu²⁺ phosphor for mixing with α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ 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 Eu²⁺ and Mn²⁺ codoped α -Ca₂P₂O₇ 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 Eu²⁺ and Mn²⁺ ions do not cause any significant change in the host structure.

PL and PLE spectra of α -Ca₂P₂O₇:Eu²⁺, α -Ca₂P₂O₇:Mn²⁺, and α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ are presented in Fig. 2 by a comparable way. In Fig. 2(a), the Eu²⁺ singly doped sample exhibits a strong blue emission band centered

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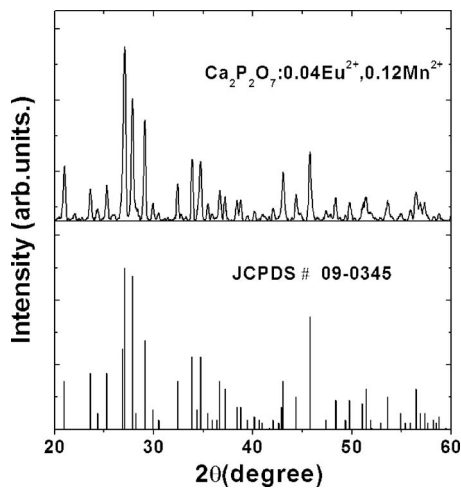


FIG. 1. XRD patterns of α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ samples and of Ref. 16.

at 416 nm with its PLE bands within UV and near-UV regions, originating from the $4f$ - $5d$ transition of Eu²⁺. In Fig. 2(b), the Mn²⁺ singly doped sample exhibits a weak orange emission band peaking at 600 nm due to the 4T_1 - 6A_1 transition of Mn²⁺ 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 Mn²⁺, respectively.¹⁷ The comparison of the PL spectrum of α -Ca₂P₂O₇:Eu²⁺ with the PLE spectrum of α -Ca₂P₂O₇:Mn²⁺ sample reveals a significant spectral overlap, indicating the possibility of energy transfer from Eu²⁺ to Mn²⁺ in α -Ca₂P₂O₇ host. As expected in Fig. 2(c), the emission spectrum of Eu²⁺ and Mn²⁺ codoped α -Ca₂P₂O₇ appears not only a strong blue band of Eu²⁺ but also a strong orange band of Mn²⁺. It is clearly shown that the PLE spectrum of

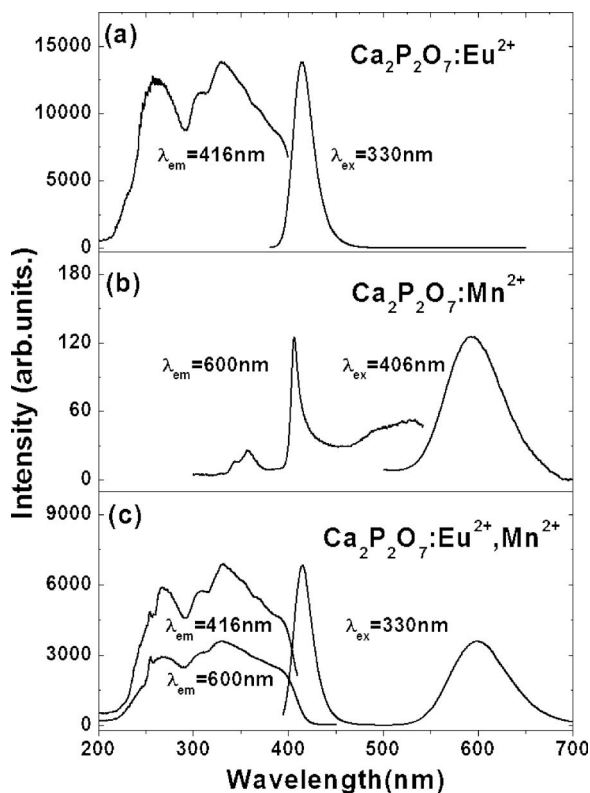


FIG. 2. PL and PLE spectra of α -Ca₂P₂O₇:Eu²⁺ (a), α -Ca₂P₂O₇:Mn²⁺, (b) and the α -Ca₂P₂O₇:Eu²⁺, Mn²⁺ (c).

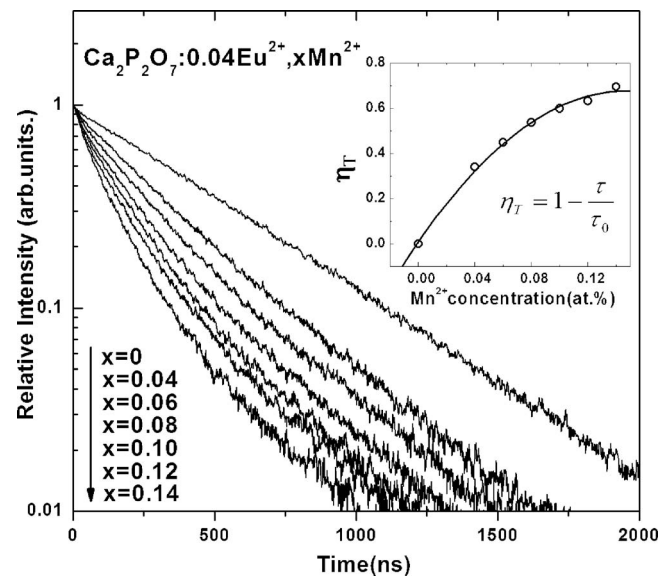


FIG. 3. Fluorescence lifetimes of Eu²⁺ in α -Ca₂P₂O₇:0.04Eu²⁺, xMn²⁺. Inset: the dependence of the energy transfer efficiency η_T in α -Ca₂P₂O₇:0.04Eu²⁺, xMn²⁺ on Mn²⁺ content x .

the orange band is consistent with that of the blue band of Eu²⁺, demonstrating effective energy transfer from Eu²⁺ to Mn²⁺. 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 % Eu²⁺ in α -Ca₂P₂O₇ with different Mn²⁺ concentrations. The fluorescence decays faster and trends to be nonexponential function with increasing Mn²⁺ concentrations, reflecting the characteristics of energy transfer between donors and acceptors.^{18,19} The energy transfer efficiency (η_T) for Eu²⁺ \rightarrow Mn²⁺ is calculated using the equation,

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

where τ and τ_0 are the fluorescence lifetimes of Eu²⁺ in α -Ca₂P₂O₇ with and without codoping of Mn²⁺, 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 Mn²⁺ concentrations, the energy transfer efficiencies (η_T) increase gradually and reach to as high as 70% for Mn²⁺ concentrations of 14 mol %. It is observed experimentally that the lifetimes of the orange band of Mn²⁺ are not shortened with increasing Mn²⁺ 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 Mn²⁺ is 12 mol % in α -Ca₂P₂O₇.

Figure 4(a) shows the emission spectra of α -Ca₂P₂O₇:0.04Eu²⁺, 0.12Mn²⁺ and Ba₂SiO₄:0.03Eu²⁺ phosphors¹⁰ under 400 nm excitation. The green emission band of Ba₂SiO₄:0.03Eu²⁺ phosphor peaking at 505 nm is complemented to the blue-orange α -Ca₂P₂O₇:0.04Eu²⁺, 0.12Mn²⁺ 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

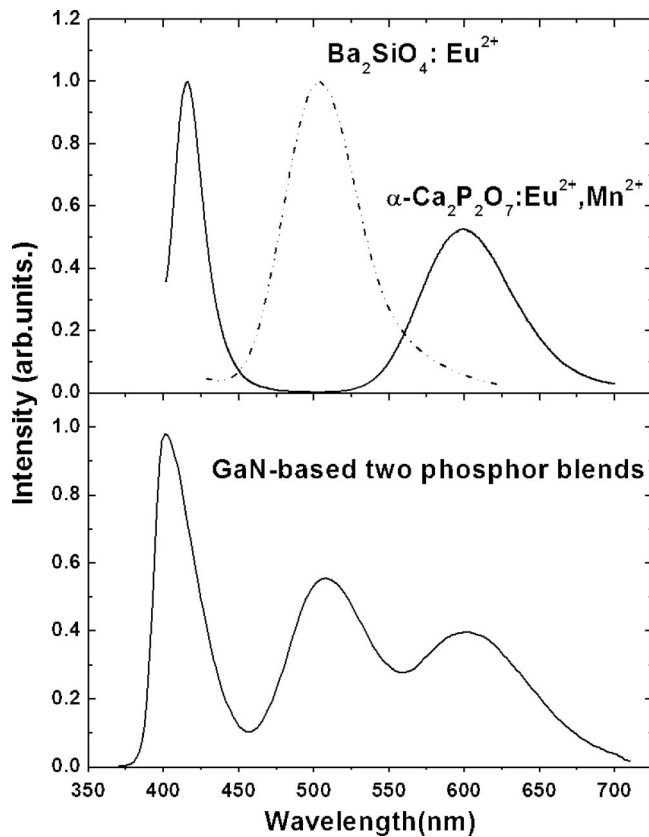


FIG. 4. Luminescence spectra of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}$, 0.12Mn^{2+} and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors (a) and the UV-pumped white LED with the blends of $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}$, 0.12Mn^{2+} and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$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

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

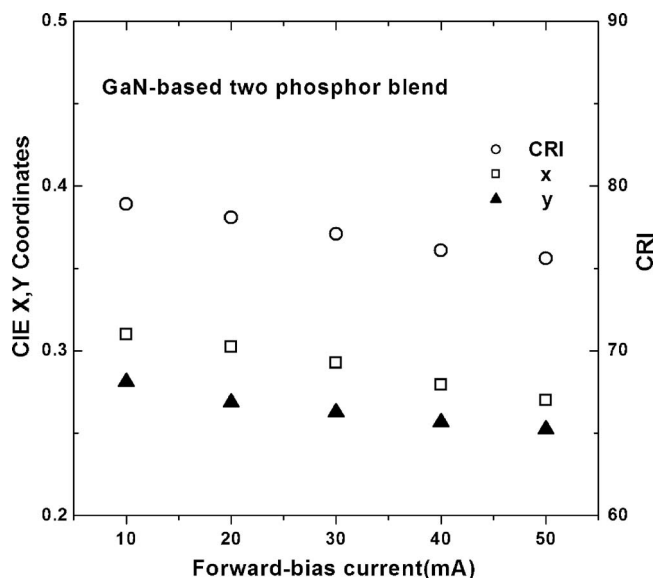


FIG. 5. CIE chromaticity coordinates and CRI of UV-pumped white LED with $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}$, 0.12Mn^{2+} and $\text{Ba}_2\text{SiO}_4:0.03\text{Eu}^{2+}$ phosphors with increasing forward-bias currents from 10 to 50 mA.

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 $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$, Mn^{2+} phosphors have been synthesized for application to white LEDs. The enhanced orange emission of Mn^{2+} is observed in $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$, 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 $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:0.04\text{Eu}^{2+}$, 0.12Mn^{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 $\alpha\text{-Ca}_2\text{P}_2\text{O}_7:\text{Eu}^{2+}$, Mn^{2+} phosphor can be a promising candidate phosphor for white LEDs.

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- ¹P. Schlotter, R. Schmidt, and J. Schneider, Appl. Phys. A: Mater. Sci. Process. **64**, 417 (1997).
- ²Toshio Nishida, Tomoyuki Ban, and Naoki Kobayashi, 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).