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Deep Red Emission of $Ca_{19}Ce(PO_4)_{14}$:Mn^{2+} Phosphor for Fluorescent Lamp and PDP Applications

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The unprecedented deep red-emitting phosphor, $Ca_{19}Ce(PO_4)_{14}$:Mn^{2+}, has been fabricated by a convenient solid-state method. A strong red emission centered at 637 nm corresponding to the 4T1(4G) → 6A1(6S) transition of Mn^{2+} is observed under 130–300 nm excitation. The chromaticity coordinates of optimized phosphor were found to be (0.69, 0.29). In addition, we have also made an attempt to observe strong red emission displayed by this phosphor for use as coating material on compact fluorescent lamps (CFLs). It is a promising candidate for application in CFLs as a red-emitting color converter.

Most applications that employ oxide red phosphors suffer from color purity problems. For example, a plasma display panel (PDP) does not generate a pure deep red color because the commission international de I'Eclairage (CIE) chromaticity coordinates of the most popularly used (Y,Gd)BO_3:Eu^{3+} red phosphor for PDP cannot reach the standard value (0.67, 0.33) specified by the national television standard committee (NTSC) and is, at best, around (0.65, 0.35). A similar problem is also now being addressed in the case of cold cathode fluorescent lamps (CCFLs) and light emitting diode lamps (LEDLs), which have been developed for use in back light units (BLUs) in liquid crystal displays (LCDs). In this regard, a deep red phosphor based on a Mn^{2+}-activated material was examined in the present investigation.

Luminescence due to Mn^{2+} is known to occur in a lot of inorganic compounds. Of these, several Mn^{2+}-doped materials are being used widely as fluorescent lamp phosphors, e.g., Zn_2SiO_4:Mn^{2+} (green)[1] and $BaAl_{12}O_{19}$:Mn^{2+} (green),[2] and cathode-ray tube (CRT) phosphors, e.g., ZnS:Mn^{2+} (orange),[3,4] $Zn_3(PO_4)_2$:Mn^{2+} (red),[5,6] and Zn_2SiO_4:Mn^{2+} (green).[1] Recently, Mn^{2+}-activated phosphates comprise a new class of red-emitting materials; $Zn(PO_3)_2$[7] and $BaMgP_2O_7$[8] are considered excellent phosphor materials for white-light LED application. However, few reports are available in the case of Mn^{2+} luminescence under VUV excitation. To the best of our knowledge, the luminescence properties of $Ca_{19}Ce(PO_4)_{14}$:Mn^{2+} have not been reported in the literature. In this study, we have first reported the unprecedented deep red-emitting phosphor. A red-light compact fluorescent lamp (RL-CFL) with the $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ phosphor has been fabricated and its performance was investigated.

In the present work, we have synthesized polycrystalline phosphors with compositions of $(Ca_{1-x}Mn_x)_{19}Ce(PO_4)_{14}$ by employing a solid-state reaction. The starting materials used were $CaCO_3$ (99.9%, Aldrich), CeO_2 (99.9%, Aldrich), $(NH_4)_2HPO_4$ (>99%, Merck), and MnO (99.99%, Aldrich). Stoichiometric amounts of reactants were first well ground and intimately mixed in the requisite proportions; all powder samples were sintered at 1400 °C for 8 h under an atmosphere. The products were then obtained by cooling down to room temperature in a furnace, ground, and pulverized for further measurements. The obtained product was then checked with X-ray diffraction (XRD) for impurity phases. The commercial CCFL phosphor Y_2O_3:Eu^{3+} (Kasei Optonix, Ltd., Kanagawa, Japan, catalog No. KX-YOX) and PDP phosphor (Y,Gd)BO_3:Eu^{3+} (Kasei Optonix, KX-504) served as references for comparison CIE chromaticity characteristics.

We verified the phase purity of the phosphor samples by powder X-ray diffraction (XRD) analysis with an advanced automatic diffractometer (Bruker AXS D8) with Cu K radiation ($\lambda = 1.5418$ Å) operating at 40 kV and 20 mA. The XRD profiles were collected in a range $10° < 2\theta < 80°$. Employing synchrotron radiation (SR) as a light source, we examined photoluminescence (PL) and the excitation (PLE) spectra excited with vacuum ultraviolet (VUV) radiation. The CIE chromaticity coordinates for all samples were determined by a Laiko DT-100 color analyzer equipped with a charge coupled device (CCD) detector (Laiko Co., Tokyo, Japan). The particle sizes for all samples were determined by HORIBA LA-920.

The XRD patterns of the $Ca_{19}Ce(PO_4)_{14}$ and the maximum efficiency activator conditions of $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ prepared by solid-state reaction at 1400 °C are shown in Figure 1. The diffraction peaks of these two products indicated that the samples had trigonal structures and in good agreement with the literature (JCPDS card No. 048-1129, space group *R*3*c*).[9]

The luminescence properties of the Mn^{2+}-doped $Ca_{19}Ce(PO_4)_{14}$ phosphors were then examined. The composition-optimized $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ sample is determined to be suitable for VUV excitation ($\lambda_{em} = 637$ nm), as displayed in Figure 2a. The excitation bands at 140–280 nm were attributed to host (PO_4^{3-} group) absorption.[10] Three absorption peaks of $Ca_{19}Ce(PO_4)_{14}$ host lattice are located at about 180, 230, and 250 nm, respectively. Figure 2b shows the emission spectrum of $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ ($\lambda_{ex} = 254$ nm). This emission at 637 nm is the characteristic emission of Mn^{2+} due to $^4T_1(^4G) \rightarrow {}^6A_1(^6S)$ transition.[11]

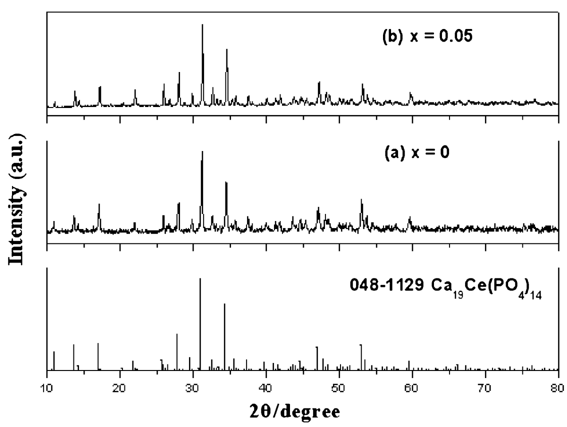

Figure 1. XRD patterns of $(Ca_{1-x}Mn_x)_{19}Ce(PO_4)_{14}$ consisting of (a) $x = 0$, (b) $x = 0.05$, and pure $Ca_{19}Ce(PO_4)_{14}$ (JCPDS file No. 048-1129).

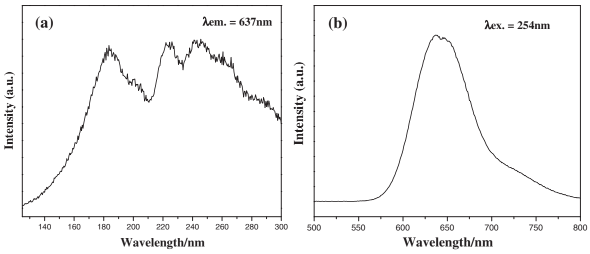

Figure 2. (a) PLE and (b) PL spectra of $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ phosphor ($\lambda_{em} = 637$ nm, $\lambda_{ex} = 254$ nm).

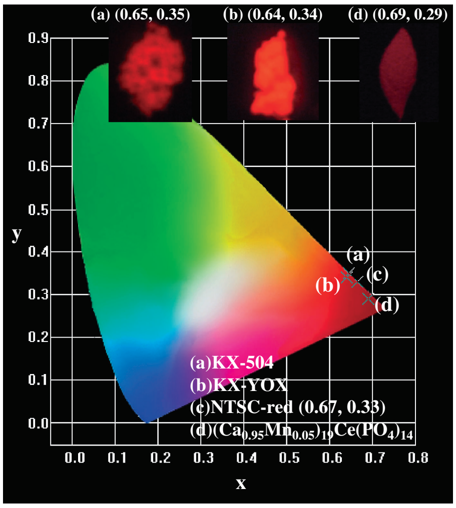

Figure 3. CIE chromaticity diagram for (a) KX-504, (b) KX-YOX, and (d) $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ excited at 254 nm. The inset shows those phosphor photos taken under 254 nm excitation in a UV box.

The CIE color chromaticity is shown in Figure 3. The inset shows $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ phosphor, $Y_2O_3:Eu^{3+}$ (KX-YOX) phosphor, and $(Y,Gd)BO_3:Eu^{3+}$ (KX-504) phosphor pictures under 254 nm excitation in a UV box. The chromaticity coordinates of optimized phosphors, $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$, KX-YOX, and KX-504, were found to be (0.69, 0.29), (0.64, 0.34), and (0.65, 0.35), respectively. This study shows $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ to have the best deep red chromaticity obtained to date under 254 nm excitation ensuring extended color realization.

In Table 1, the relative emission intensity of $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ is about 41% and 30% of that from KX-YOX ($\lambda_{ex} = 254$ nm) and KX-504 ($\lambda_{ex} = 172$ nm), respectively. The mean and median particle sizes of phosphors are summarized in Table 1.

Based on standard CFL technology, a low-pressure discharge lamp in which the envelope that contains argon and mercury is coiled into a helical configuration, our red-emitting $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ phosphor coating was provided on the interior surface of the envelope, and two tungsten electrodes were sealed into the ends of the envelope. The relative emission spectrum and luminous efficiency of RL-CFL under a power of 11 W were measured. The $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ phosphor layer exposed to ultraviolet irradiation absorbs the incipient radiation and emits visible red light with the main emission peak at around 637 nm as shown in Figure 4. The inset shows

Table 1. The comparison of particle size and relative PL emission intensity

Composition	Mean /μm	Median /μm	Relative emission intensity
KX-YOX	5.19	4.98	100% ($\lambda_{ex} = 254$ nm)
CCPO:Mn^{2+}	7.26	6.79	41% of KX-YOX ($\lambda_{ex} = 254$ nm) 30% of KX-504 ($\lambda_{ex} = 172$ nm)
KX-504	3.70	3.45	100% ($\lambda_{ex} = 172$ nm)

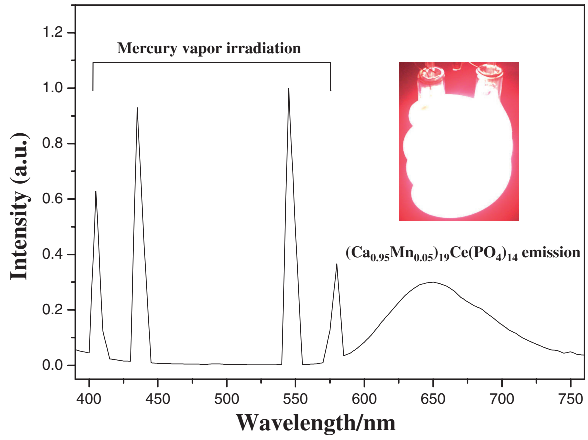

Figure 4. Luminescence spectrum of RL-CFL was fabricated using $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ phosphor. The inset shows the RL-CFL under a power of 11 W.

RL-CFL under a power of 11 W. The RL-CFL which used $(Ca_{0.95}Mn_{0.05})_{19}Ce(PO_4)_{14}$ phosphor emits about 16 lm W^{-1} under a power of 11 W. When commercial red phosphors ($Y_2O_3:Eu^{3+}$, KX-YOX) fabricated under the same RL-CFL conditions, luminescent efficiency was about 40 lm W^{-1} at 11 W.

In summary, new red phosphors based on Mn^{2+}-doped $Ca_{19}Ce(PO_4)_{14}$ were synthesized by a solid-state reaction, 1400 °C being the optimum sintering temperature for their preparation. These phosphors, which have a high color-rendering index, can be efficiently excited from 130 to 300 nm. Therefore, $Ca_{19}Ce(PO_4)_{14}:Mn^{2+}$ phosphors are potential candidates for the red-emitting phosphors of high-NTSC PDPs, high-NTSC LCDs (CCFLs as back light components), and high CRI fluorescent lamps for general lighting.

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