Photoluminescence Optimization of $\text{Ca}_3(\text{PO}_4)_2:\text{Eu}^{3+}$ Phosphors By Crystallinity Improvement And Charge Compensation

D.H. KIM

Sejong University

J.W. PI

Sejong University

G.W. JUNG

Sejong University

J.S. KIM

Pukyong National University

K. Park (✉ kspark@sejong.ac.kr)

Sejong University

Research Article

Keywords: crystal structure, phosphor, photoluminescence, $\text{Ca}_3(\text{PO}_4)_2:\text{Eu}^{3+}$, synthesis

Posted Date: August 25th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-809996/v1>

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Abstract

In this study, in order to improve the photoluminescence properties of $\text{Ca}_3(\text{PO}_4)_2:\text{Eu}^{3+}$ phosphors, alkali metal ions (Li^+ , Na^+ , and K^+) were doped into the $\text{Ca}_{2.91}(\text{PO}_4)_2:\text{Eu}^{3+}$ phosphors, and the effects of alkali metal ions on the structural and optical properties were investigated. The alkali metal ions significantly enhanced the emission intensity and improved the emission color quality because they induced the charge balance, improved the crystalline quality, and stabilized the crystal structure, namely, the alkali metal ions in $\text{Ca}_3(\text{PO}_4)_2:\text{Tb}^{3+}$ acted as both charge compensators and fluxes. Of the alkali metal ions used, Li^+ was an optimal cation to improve the emission intensity and color purity. The $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor showed a 40% stronger red emission intensity than that of the $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. We demonstrate that incorporating alkali metal ions, especially Li^+ , is important to improve the emission intensity and color purity.

Introduction

Nowadays, phosphor-converted white light-emitting diodes (pc-WLEDs) have received significant attention in the solid-state lighting area due to their high photoluminescence (PL) efficiency, long operational lifetime, low power consumption, high reliability, and environment-friendliness [1–7]. The pc-WLEDs are mainly fabricated by using blue LED chips coated with $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ yellow-emitting phosphors, but its low color rendering index ($\text{CRI} < 70$) and high correlated color temperature ($\text{CCT} > 7000 \text{ K}$) are insufficient for efficient pc-WLEDs, which result from the color deficiency in red spectral region [8]. Therefore, another effective method to overcome the aforementioned problems is to combine near-ultraviolet (NUV) LED chips with a mixture of red, green, and blue phosphors [7]. However, red-emitting $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ phosphors exhibit a much lower emission efficiency in comparison with blue and green phosphors, and it is unstable due to the release of sulfide gas [9]. As a result, a new red-emitting compound should be developed for efficient pc-WLEDs.

Among many inorganic host materials, phosphates, such as $\text{Ca}_3(\text{PO}_4)_2$, $\text{Ca}_8\text{MgR}(\text{PO}_4)_7$ ($\text{R} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Lu}, \text{Y}$), $\text{Ca}_8\text{ZnEu}(\text{PO}_4)_7$, $\text{Ca}_9\text{Gd}(\text{PO}_4)_7$, $\text{Sr}_8\text{ZnSc}(\text{PO}_4)_7$, $\text{Sr}_8\text{MgLn}(\text{PO}_4)_7$, and $\text{Ca}_{8.5}\text{Pb}_{0.5}\text{Eu}(\text{PO}_4)_7$, have been studied as host materials of phosphors due to their high thermal stability, high stabilization of the ionic charge in the lattice, easy synthesis, and low material cost [10–17]. In particular, tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is a highly promising host material owing to its strong absorption in the near-UV region and its high chemical, physical, and thermal stability [16]. The rare-earth ion doped $\text{Ca}_3(\text{PO}_4)_2$ phosphors are recommended as a potential candidate for pc-WLEDs and solid-state lighting devices [16–20].

Traditionally, oxide based phosphors doped with trivalent rare-earth ions have been synthesized by the solid-state reaction method. The method requires a high reaction temperature, a long reaction time, and a milling process to obtain a fine size and pure phase. Therefore, previous researchers synthesized oxide based phosphors through wet-chemical methods, including the sol-gel based Pechini process [21], hydrothermal synthesis [22], solution combustion [23], sol-gel [24], spray pyrolysis [25], polyol [26], and co-precipitation [27]. In particular, the sol-gel based Pechini method has been regarded as a promising technique for preparing high-quality of multi-component metal oxide materials due to high purity products, simple apparatus, cost-effectiveness, and low processing temperature [21]. In the present study, $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.10$) phosphors were prepared by the sol-gel based Pechini method, and then the effects of the Eu^{3+} concentration on the structural and optical properties were investigated.

Substituting a trivalent Eu^{3+} ion for a divalent Ca^{2+} ion in $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors induces a charge unbalance and creates crystal defects, such as V_{Ca} or O_i , in order to maintain a charge balance [28]. The crystal defects act as sites for non-radiative recombination, thereby degrading PL properties [29]. Therefore, alkali metal ions such as Li^+ , Na^+ , and K^+ as charge compensators are doped to $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors. Substituting a Eu^{3+} ion and a monovalent alkali metal ion (Li^+ , Na^+ , and K^+) for two divalent Ca^{2+} ions creates an oxygen vacancy ($\text{V}_{\text{O}}^{\bullet\bullet}$) or interstitial M^+ (M_i^+) defect [29]. The ($\text{V}_{\text{O}}^{\bullet\bullet}$) or (M_i^+) defect reacts with the V_{Ca} and O_i defects, thereby removing the non-radiative recombination sites caused by the V_{Ca} and O_i defects and improving PL properties. In this work, to further improve the PL properties of Eu^{3+} -activated $\text{Ca}_3(\text{PO}_4)_2$ phosphors, $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors were prepared by the sol-gel based Pechini method. Subsequently, the effects of alkali metal ions (Li^+ , Na^+ , and K^+) on the structural and optical properties were systematically investigated using X-ray diffraction (XRD), XRD Rietveld refinement, X-ray photoelectron spectroscopy (XPS), UV-Vis-NIR spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, and photoluminescence (PL) spectroscopy.

Experimental

$\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors were synthesized by the sol-gel based Pechini method. $\text{Ca}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, Eu_2O_3 , LiNO_3 , NaNO_3 , KNO_3 , and polyethylene glycol (PEG) 400 were used as raw materials.

Eu_2O_3 was dissolved in HNO_3 to form $\text{Eu}(\text{NO}_3)_3$. The prepared solutions were well-mixed with a magnetic stirrer for 3 h to form a transparent solution (sol). The obtained sol was heated at 80°C for 24 h with constant agitation to provide the desired condition of gel formation. The gel was oven-dried at 300°C for 12 h, and then annealed at 1200°C for 3 h in ambient atmosphere, followed by natural cooling to room temperature.

A combination of several analytical techniques was used to characterize the structural and optical properties of the prepared $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors, including X-ray diffraction (XRD), XRD Rietveld refinement, X-ray photoelectron spectroscopy (XPS), UV-visible-near infrared (UV-Vis-NIR) spectroscopy, Fourier-transform infrared (FT-IR) spectroscopy, and PL spectroscopy. The crystal structure was investigated with an X-ray diffractometer (XPert-PRO, PANalytical, Netherlands). The obtained XRD patterns were refined using Fullprof suite software and the crystallography information file of $\beta\text{-Ca}_3(\text{PO}_4)_2$ (ICSD No. 82123). The overall concentrations of Li, Na, and K elements in $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors were investigated by an inductively coupled plasma-optical emission spectroscopy system (OPTIMA 8300, PerkinElmer, USA). The XPS, UV-Vis-NIR diffuse reflectance, and FT-IR spectra at room temperature were collected with an XPS spectrophotometer (K-alpha, Thermo VG, UK), a UV-Vis-NIR spectrophotometer (Varian Cary 5000, Agilent, USA), and a FT-IR spectrometer (Thermo-Nicolet spectrometer), respectively. The PL spectra of the prepared phosphors were recorded with a fluorescence spectrometer (FS-2, Scinco Co., Korea) at room temperature. The internal quantum efficiency (IQE) was measured with an integrating sphere-attached fluorescence spectrophotometer (DARSA PRO-5200 System, PSI Co., Korea) equipped with a 200 W xenon lamp as an excitation light source. The Commission International de l'Eclairage (CIE) chromaticity coordinates (x, y) were calculated from the obtained emission spectra by using the CIE calculator. The CCT and color purity were also calculated using the obtained CIE chromaticity coordinate (x, y) data.

Results And Discussion

Figure 1(A) exhibits the XRD diagrams of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) phosphors. All XRD peaks are well in agreement with the standard ICSD No. 82123 of $\beta\text{-Ca}_3(\text{PO}_4)_2$. $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors have a rhombohedral unit cell (space group $R\bar{3}c$) [17]. The incorporation of Eu^{3+} does not significantly influence the crystal structure of $\text{Ca}_3(\text{PO}_4)_2$. No diffraction peaks derived from raw materials and impurities, such as Eu_2O_3 and CaO , are detected. This suggests that the Eu^{3+} ions occupy the Ca^{2+} sites in the host lattice, and the prepared $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors form a single phase.

The XRD diagrams of $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors are presented in Fig. 1(B) along with $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor for comparison. $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ phosphors show similar XRD patterns to those of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors, except for the intensity of XRD peaks. $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ phosphors have the rhombohedral unit cell, as in $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors. The doped Li^+ , Na^+ , and K^+ ions occupy the Ca^{2+} sites without changing the crystal structure of $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. The full width at half maximum (FWHM) of $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ phosphors appears narrower than that of $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. This is because the alkali metal ions act as fluxes, so they significantly improves the crystallinity of the phosphors due to enhanced diffusions in the solid-state reaction and crystallization process [30–33].

The crystallinity of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ phosphors is related to the FWHM of the XRD peaks, which is given in Table 1. The FWHM of the XRD peaks in $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors first decreases with increasing Eu^{3+} concentration, reaching a minimum at $x = 0.09$, and then increases with further increasing its concentration. For the $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ phosphors, the magnitude of FWHM in the (0 2 10) and (2 2 0) XRD peaks follows the order of $\text{K}^+ > \text{Na}^+ > \text{Li}^+$. For example, the magnitudes of FWHM in the (0 2 10) XRD peak for $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor and Li^+ -, Na^+ -, and K^+ -doped phosphors are 0.141, 0.115, 0.120, 0.129, respectively. The Li^+ -doped phosphor shows the narrowest FWHM, indicating excellent crystallinity. The diffraction peaks corresponding to the alkali metal ions and impurities are not observed. This indicates that the alkali metal ions do not affect the crystal structure and are effectively incorporated on the Ca^{2+} sites in the host lattice. The overall concentration of Li, Na, and K elements in $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors is lower than its initial nominal composition, as represented in Table 2, which is attributed to the evaporation of LiNO_3 , NaNO_3 , and KNO_3 during the annealing process. It is thus necessary to add an excess LiNO_3 , NaNO_3 , and KNO_3 to the starting materials in order to compensate for Li, Na, and K losses.

Table 1
FWHM of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$,
 0.09M^+ (M = Li, Na, and K) phosphors.

		FWHM	
		(0 2 10)	(2 2 0)
$\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphor	$x = 0.06$	0.158	0.154
	$x = 0.07$	0.147	0.147
	$x = 0.08$	0.146	0.147
	$x = 0.09$	0.141	0.145
	$x = 0.10$	0.145	0.150
$\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09M^+ phosphor	M = Li	0.115	0.127
	M = Na	0.120	0.130
	M = K	0.129	0.139

Table 2
 Li^+ , Na^+ , and K^+ concentrations of $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09M^+ (M = Li, Na, and K) phosphors.

	Li^+ concentration (mol)		Na^+ concentration (mol)		K^+ concentration (mol)	
	Nominal	Measured	Nominal	Measured	Nominal	Measured
$\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09Li^+	0.090	0.078	–	–	–	–
$\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09Na^+	–	–	0.090	0.074	–	–
$\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09K^+	–	–	–	–	0.090	0.067

To analyze the crystal structure of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09M^+ (M = Li, Na, and K) phosphors in detail, XRD Rietveld refined data are obtained using the Fullprof program. For the XRD refinement, the structural information of rhombohedral β - $\text{Ca}_3(\text{PO}_4)_2$ (ICSD No. 82123) is used as a reference. Figure 2 represents the XRD Rietveld refined profiles of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.09$) phosphors, showing the observed and calculated diffraction profiles, the difference between the two profiles, and the positions of the calculated diffraction profiles. The XRD Rietveld refined profiles of $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09M^+ phosphors are quite similar to those of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors (Supplementary Figs. S1 – S3). The crystallographic data and reliability factors of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09M^+ phosphors are summarized in Table 3.

Table 3. Crystallographic data and reliability factors of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.09$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, 0.09M^+ (M = Li, Na, and K) phosphors.

	$\text{Ca}_{3-x}(\text{PO}_4)_2 \cdot x\text{Eu}^{3+}$				$\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}, 0.09\text{M}^+$		
	$x = 0.06$	$x = 0.07$	$x = 0.08$	$x = 0.09$	$\text{M}^+ = \text{Li}^+$	$\text{M}^+ = \text{Na}^+$	$\text{M}^+ = \text{K}^+$
Crystal structure	Rhombohedral	Rhombohedral	Rhombohedral	Rhombohedral	Rhombohedral	Rhombohedral	Rhombohedral
Space group	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>	<i>R3c</i>
Lattice parameters	10.4509	10.4506	10.4499	10.4489	10.4365	10.4520	10.4564
<i>a</i> (Å)	10.4509	10.4506	10.4499	10.4489	10.4365	10.4520	10.4564
<i>b</i> (Å)	37.4338	37.4332	37.4292	37.4283	37.4155	37.4092	37.3925
<i>c</i> (Å)	90.0	90.0	90.0	90.0	90.0	90.0	90.0
$\alpha = \beta$ (°)	120.0	120.0	120.0	120.0	120.0	120.0	120.0
γ (°)	3540.8	3540.5	3539.7	3538.9	3529.3	3539.2	3540.6
Volume (Å ³)							
Reliability factors							
R_{wp} (%)	4.78	5.67	6.94	6.82	8.39	6.37	5.89
R_{exp} (%)	4.71	4.98	6.83	5.42	4.90	5.05	5.38
χ^2	1.03	1.30	1.03	1.59	2.93	1.59	1.20

The crystal structure of $\text{Ca}_{2.94}(\text{PO}_4)_2 \cdot 0.06\text{Eu}^{3+}$, drawn by the VESTA (Visualization for Electronic and Structural Analysis) program and XRD Rietveld refinement data, is shown in Fig. 3. The crystal structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ consists of five Ca atoms, three P atoms, and ten O atoms. Ca atoms are located at five crystallographic sites, Ca(1) – Ca(5). The coordination numbers of Ca(1), Ca(2), Ca(3), Ca(4), and Ca(5) atoms are 7, 8, 8, 3, and 6, respectively. Ca(4) is three – fold coordinated with oxygen atoms, and the Ca(4)O_3 polyhedron has a planar shape. In addition, P atoms are located at three crystallographic sites, i.e., P(1), P(2), and P(3). All P atoms are four – fold coordinated with oxygen atoms. The Eu^{3+} ions enter into three Ca sites, i.e., Ca(1), Ca(2), and Ca(3) sites, and the Li^+ , Na^+ , and K^+ ions enter into the Ca(4) site. In spite of the incorporation of the higher Eu^{3+} concentrations and the alkali metal ions, no obvious change in the crystal structure is noticed (Supplementary Figs. S4 – S9).

Figures 4(A) and (B) show the lattice parameters (*a*, *c*) and unit cell volume of $\text{Ca}_{3-x}(\text{PO}_4)_2 \cdot x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.09$) and $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$, 0.09M^+ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors, respectively. The Eu^{3+} substitution leads to a decrease in the unit cell volume because the ionic radius of Eu^{3+} ion (1.065 Å for coordination number (CN) = 8) is smaller than that of Ca^{2+} ion (1.12 Å for CN = 8) [10,34 – 36], indicating that the Eu^{3+} ions are successfully incorporated into the host lattice. The lattice parameters *a* and *c* follow the orders of $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ and of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$, respectively. The atomic coordinate, isotropic thermal parameter (B_{iso}), and occupancy factor of $\text{Ca}_{2.94}(\text{PO}_4)_2 \cdot 0.06\text{Eu}^{3+}$ phosphor, obtained from the XRD Rietveld refinement, are given in Table 4. The occupancy factors of Ca(5), P, and O atoms are 1.0. The Ca(4) atom among the Ca(1) – Ca(5) atoms has the lowest occupancy factor (0.4948), thereby forming the vacancies of Ca(4) atom at 6*a* site [37]. Furthermore, the isotropic thermal parameter of the Ca(4) atom (2.4753 Å²) is much larger than that of other Ca atoms. The high vacancy of Ca(4) atom at 6*a* site yields a large isotropic thermal parameter and unstable crystal structure [37]. The atomic coordinate, isotropic thermal parameter (B_{iso}), and occupancy factor of $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$, 0.09M^+ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors are similar to those of $\text{Ca}_{2.94}(\text{PO}_4)_2 \cdot 0.06\text{Eu}^{3+}$ phosphor (Supplementary Tables S1 – S3).

Table 4

Atomic coordinate, isotropic thermal parameter (B_{iso}), and occupancy of $\text{Ca}_{2.94}(\text{PO}_4)_2 \cdot 0.06\text{Eu}^{3+}$ phosphor obtained from the XRD Rietveld refinement.

Atomic coordinates					Isotropic thermal parameter	Occupancy
Atom	Site	x	y	z	$B_{\text{iso}} (\text{\AA}^2)$	
Ca(1)	18b	0.7234	0.8577	0.1660	0.2479	0.9779
Eu(1)	18b	0.7234	0.8577	0.1660	0.2479	0.0221
Ca(2)	18b	0.6182	0.8210	-0.0335	0.3348	0.9758
Eu(2)	18b	0.6182	0.8210	-0.0335	0.3348	0.0242
Ca(3)	18b	0.7293	0.8528	0.0610	0.9104	0.9783
Eu(3)	18b	0.7293	0.8528	0.0610	0.9104	0.0217
Ca(4)	6a	0.0000	0.0000	-0.0855	2.4753	0.4948
Ca(5)	6a	0.0000	0.0000	0.7340	0.7904	1.0000
P(1)	6a	0.0000	0.0000	0.0000	1.0486	1.0000
P(2)	18b	0.6863	0.8612	0.8691	0.9917	1.0000
P(3)	18b	0.6511	0.8473	0.7673	0.2463	1.0000
O(1)	18b	0.7255	-0.0955	-0.0909	0.9649	1.0000
O(2)	18b	0.7639	0.7782	0.8546	0.5187	1.0000
O(3)	18b	0.7318	0.0090	0.8471	0.1398	1.0000
O(4)	18b	0.5164	0.7614	0.8602	0.6838	1.0000
O(5)	18b	0.5986	-0.0508	0.7793	0.0837	1.0000
O(6)	18b	0.5722	0.6876	0.7826	0.4406	1.0000
O(7)	18b	0.0833	0.9012	0.7781	0.4832	1.0000
O(8)	18b	0.6342	0.8278	0.7270	0.1350	1.0000
O(9)	18b	0.0103	0.8618	-0.0109	1.3825	1.0000
O(10)	6a	0.0000	0.0000	0.0399	0.8298	1.0000

Table 5 shows the Ca – O and P – O lengths in $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ phosphor. The Ca(1) – O, Ca(2) – O, Ca(3) – O, and Ca(5) – O lengths are in the ranges of 2.3489 – 2.5479 Å, 2.3070 – 2.8001 Å, 2.4015 – 2.7265 Å, and 2.2441 – 2.3345 Å, respectively, and the Ca(4) – O length is 2.5301 Å. The P(1) – O, P(2) – O, and P(3) – O lengths are in the ranges of 1.4938 – 1.5551 Å, 1.5535 – 1.5980 Å, and 1.4906 – 1.5668 Å, respectively. The Ca – O and P – O lengths in $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$, 0.09M^+ (M = Li, Na, and K) phosphors are shown in Supplementary Tables S4 – S6. The average Ca – O and P – O lengths in $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$, 0.09M^+ (M = Li, Na, and K) phosphors, calculated by Table 5 and Supplementary Tables S4 – S6, are shown in Table 6. To better understand the effect of alkali metal ions on the average Ca(1 – 5) – O lengths, the Ca(1 – 5) – O lengths in $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$, 0.09M^+ (M = Li, Na, and K) phosphors are represented in Fig. 5(A). The incorporation of alkali metal ions hardly influences the Ca(1) – O, Ca(2) – O, Ca(3) – O, and Ca(5) – O lengths, but significantly influences the Ca(4) – O length. The largest and smallest Ca – O lengths of the phosphors appear in Ca(3) – O and Ca(5) – O bonds, respectively.

Table 5
Ca – O and P – O lengths in Ca_{2.91}(PO₄)₂·0.09Eu³⁺ phosphor.

Ca – O and P – O bonds			Bond length (Å)
Ca – O [†]	Ca(1) – O	Ca(1) – O(3)	2.5479
		Ca(1) – O(4)	2.4304
		Ca(1) – O(4)	2.4394
		Ca(1) – O(5)	2.4025
		Ca(1) – O(6)	2.3489
		Ca(1) – O(8)	2.4223
		Ca(1) – O(9)	2.4414
	Ca(2) – O	Ca(2) – O(1)	2.3781
		Ca(2) – O(2)	2.4334
		Ca(2) – O(3)	2.3070
		Ca(2) – O(5)	2.6691
		Ca(2) – O(6)	2.8001
		Ca(2) – O(7)	2.4056
		Ca(2) – O(7)	2.4074
		Ca(2) – O(9)	2.3382
	Ca(3) – O	Ca(3) – O(1)	2.7265
		Ca(3) – O(2)	2.5974
		Ca(3) – O(3)	2.4059
		Ca(3) – O(5)	2.4015
		Ca(3) – O(6)	2.4456
		Ca(3) – O(8)	2.6197
		Ca(3) – O(8)	2.5794
		Ca(3) – O(10)	2.5768
	Ca(4) – O	Ca(4) – O(1)	2.5301
	Ca(5) – O	Ca(5) – O(4)	2.2441
		Ca(5) – O(7)	2.3345
P – O	P(1) – O	P(1) – O(9)	1.5551
		P(1) – O(10)	1.4938
	P(2) – O	P(2) – O(1)	1.5576
		P(2) – O(2)	1.5535
		P(2) – O(3)	1.5980
		P(2) – O(4)	1.5809
	P(3) – O	P(3) – O(5)	1.4906
		P(3) – O(6)	1.5541
		P(3) – O(7)	1.5668

[†]The distances of Eu(1) – O, Eu(2) – O, and Eu(3) – O equal to those of Ca(1) – O, Ca(2) – O, and Ca(3) – O, respectively.

Ca – O and P – O bonds	Bond length (Å)
P(3) – O(8)	1.5234
†The distances of Eu(1) – O, Eu(2) – O, and Eu(3) – O equal to those of Ca(1) – O, Ca(2) – O, and Ca(3) – O, respectively.	

Table 6

Average Ca – O and P – O lengths in $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}, 0.09\text{M}^+$ (M = Li, Na, and K) phosphors.†

	$\text{Ca}_{2.91}\text{Eu}_{0.09}(\text{PO}_4)_2$	$\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}, 0.09\text{M}^+$		
		M = Li	M = Na	M = K
Average Ca(1) – O length (Å)	2.4333	2.4593	2.4313	2.4300
Average Ca(2) – O length (Å)	2.4674	2.4759	2.4774	2.4780
Average Ca(3) – O length (Å)	2.5441	2.5315	2.5439	2.5426
Average Ca(4) – O length (Å)	2.5301	2.4771	2.4855	2.5107
Average Ca(5) – O length (Å)	2.2893	2.2979	2.2920	2.2804
Average P(1) – O length (Å)	1.5398	1.5266	1.5293	1.5234
Average P(2) – O length (Å)	1.5725	1.5625	1.5528	1.5612
Average P(3) – O length (Å)	1.5337	1.5088	1.5174	1.5568
†The distances of Eu(1) – O, Eu(2) – O, Eu(3) – O, and M – O equal to those of Ca(1) – O, Ca(2) – O, Ca(3) – O, and Ca(4) – O, respectively.				

The relationship between the average Ca(1 – 5) – O length and the coordination number of Ca atom is plotted in Fig. 5(B). The expected Ca(1 – 5) – O length d , indicated by a solid line, is obtained by the following formula: $d = r_{\text{Ca}} + r_{\text{O}}$, where r_{Ca} and r_{O} are the radii of Ca^{2+} and O^{2-} ions, respectively. The radii of Ca^{2+} ion with coordination numbers of 6, 7, and 8 are 1.00, 1.06, and 1.12, respectively, and that of O^{2-} ion is 1.38 Å [34]. The linear solid line is obtained by extrapolating the Ca(1 – 3) – O lengths expected from the ionic radii of Ca and O [34]. The expected Ca–O length linearly increases with increasing the coordination number of Ca atom. The average Ca(1) – O, Ca(2) – O, and Ca(3) – O lengths calculated by the XRD refinements in this study are similar to the expected Ca – O length, but the average Ca(4) – O length calculated here is significantly larger compared with the expected Ca – O length. The large difference between the expected Ca(4) – O length and the calculated Ca(4) – O length induces an unstable crystal structure. It is important to note that the calculated Ca(4) – O length approaches the expected Ca(4) – O length through the incorporation of alkali metal ions. This indicates that the alkali metal ions allow the crystal structure to stabilize. Of the alkali metal ions used, Li^+ is the most effective ion for stabilizing the crystal structure.

Figure 6(A) shows the XPS survey spectra of $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}, 0.09\text{M}^+$ (M = Li, Na, and K) phosphors along with $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ phosphor for comparison. The sharp peaks in Fig. 6(A) are indexed in accordance with the Ca, P, Eu, and O elements and its orbital. This figure reveals that the Ca, P, Eu, and O elements exist in the phosphors. Figures 6(B) and (C) exhibit the high – resolution XPS spectra of Ca and P elements, respectively, in the phosphors. The XPS spectra of Ca $2p$ consist of two distinct peaks, Ca $2p_{1/2}$ and Ca $2p_{3/2}$ (Fig. 6(B)) [38]. The binding energies of Ca $2p_{1/2}$ and Ca $2p_{3/2}$ peaks for the phosphors are summarized in Table 7. The difference between the binding energies of Ca $2p_{1/2}$ and Ca $2p_{3/2}$ peaks for all the phosphors is 3.5 eV. The XPS spectra of P $2p$ are also composed of P $2p_{1/2}$ and P $2p_{3/2}$ (Fig. 6(C)) [38]. The binding energies of P $2p_{1/2}$ and P $2p_{3/2}$ peaks for the phosphors are given in Table 7. The difference between the binding energies of P $2p_{1/2}$ and P $2p_{3/2}$ peaks for all phosphors is 0.8 eV, except for K^+ -doped phosphor, which has a binding energy of 0.9. Figures 6(D) – (F) show the high – resolution XPS spectra of Li, Na, and K elements, respectively, for $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}, 0.09\text{M}^+$ (M = Li, Na, and K) phosphors, confirming the presence of Li, Na, and K elements [39 – 41]. The binding energies of Li $1s$ and Na $1s$ for the Li^+ - and Na^+ -doped phosphors are 55.3 and 1072.1 eV, respectively [39, 40]. The binding energies of K $2p_{1/2}$ and K $2p_{3/2}$ for the K^+ -doped phosphor are 296.0 and 292.9 eV, respectively, and the difference between the binding energies of K $2p_{1/2}$ and K $2p_{3/2}$ is 3.1 eV [41].

Table 7
Binding energies of Ca, P, Li, Na, K, Eu, and O elements obtained from the high – resolution XPS spectra.

		Ca _{2.91} Eu _{0.09} (PO ₄) ₂	Ca _{2.82} (PO ₄) ₂ :0.09Eu ³⁺ , 0.09M ⁺		
			M = Li	M ⁺ = Na	M ⁺ = K
Binding energies of Ca (eV)	Ca 2p _{1/2} (E ₁)	350.7	350.8	350.8	350.7
	Ca 2p _{3/2} (E ₂)	347.2	347.3	347.3	347.2
	$\Delta E (E_1 - E_2)$	3.5	3.5	3.5	3.5
Binding energies of P (eV)	P 2p _{1/2} (E ₃)	133.8	133.9	133.9	133.9
	P 2p _{3/2} (E ₄)	133.0	133.1	133.1	133.0
	$\Delta E (E_3 - E_4)$	0.8	0.8	0.8	0.9
Binding energies of charge compensators (eV)	Li 1s	–	55.3	–	–
	Na 1s	–	–	1072.1	–
	K 2p _{1/2} (E ₅)	–	–	–	296.0
	K 2p _{3/2} (E ₆)	–	–	–	292.9
	$\Delta E (E_5 - E_6)$	–	–	–	3.1
Binding energies of Eu (eV)	Eu 3d _{3/2} (E ₇)	1164.9	1165.1	1164.9	1164.7
	Eu 3d _{5/2} (E ₈)	1135.0	1135.2	1135.0	1134.8
	$\Delta E (E_7 - E_8)$	29.9	29.9	29.9	29.9
Binding energies of O (eV)	O 1s in Eu – O	529.6	529.8	529.7	529.5
	O 1s in (PO ₄) ^{3–}	530.9	531.0	531.0	530.9
	O 1s in Ca – O	531.8	532.0	531.9	531.8
	Absorbed H ₂ O	533.6	533.6	533.5	533.5

To investigate the chemical states of Eu ion, the high – resolution XPS spectra of Eu 3d_{3/2} and Eu 3d_{5/2} for Ca_{2.91}(PO₄)₂:0.09Eu³⁺ and Ca_{2.82}(PO₄)₂:0.09Eu³⁺, 0.09M⁺ (M = Li, Na, and K) phosphors are obtained, as shown in Fig. 7. The binding energies of Eu 3d_{3/2} peaks for Ca_{2.82}(PO₄)₂:0.09Eu³⁺ phosphor and Li⁺–, Na⁺–, and K⁺–doped phosphors are 1164.9, 1165.1, 1164.9, and 1164.7 eV, respectively, and those of Eu 3d_{5/2} are 1135.0, 1135.2, 1135.0, and 1134.8 eV, respectively [42, 43]. These results indicate that the binding energy of Eu 3d_{3/2} and Eu 3d_{5/2} in the alkali metal ion–contained phosphors follows the order of Li⁺ > Na⁺ > K⁺. The difference between the binding energies of Eu 3d_{3/2} and Eu 3d_{5/2} for all alkali metal ion–contained phosphors is 29.9 eV, irrespective of the alkali metal ions used. This confirms that Eu ions in Ca_{2.82}(PO₄)₂:0.09Eu³⁺, 0.09M⁺ phosphors exist as Eu³⁺ ions [42, 43].

Figure 8 exhibits the high – resolution XPS spectra of O 1s for Ca_{2.91}(PO₄)₂:0.09Eu³⁺ and Ca_{2.82}(PO₄)₂:0.09Eu³⁺, 0.09M⁺ (M = Li, Na, and K) phosphors. The four distinct O 1s peaks are deconvoluted using Gaussian functions, which are attributed to the presence of (PO₄)^{3–}, Ca – O, Eu – O, and H₂O absorbed from humidity [38,44 – 46]. The binding energies of O 1s related to the (PO₄)^{3–}, Ca – O, Eu – O, and absorbed H₂O are given in Table 7. The binding energy of O 1s follows the order of absorbed H₂O > Ca – O > (PO₄)^{3–} > Eu – O.

The optical absorption and band–gap energy of the prepared phosphors are investigated using the UV–Vis–NIR spectroscopy. Figure 9 shows the UV–Vis–NIR diffuse reflectance spectra of Ca_{3–x}(PO₄)₂:xEu³⁺ (x = 0.06 and 0.09) and Ca_{2.82}(PO₄)₂:0.09Eu³⁺, 0.09M⁺ (M = Li, Na, and K) phosphors. The diffuse reflectance significantly increases with increasing wavelength from 250 to 320 nm. The reflectance spectra exhibit strong absorption bands at 200 to 260 nm and characteristic absorption peaks at 362, 383, 394, 416, 465, 526, and 534 nm are due to the ⁷F₀→⁵D₄, ⁷F₀→⁵L₇, ⁷F₀→⁵L₆, ⁷F₀→⁵D₃, ⁷F₀→⁵D₂, ⁷F₁→⁵D₁ and ⁷F₀→⁵D₁ transitions of Eu³⁺ ions, respectively [47, 48]. Clearly, the Li⁺ ions lead to an increase in absorbance due to increased transition probability.

$\text{Ca}_3(\text{PO}_4)_2$ is a direct band-gap material, and its band-gap energy can be estimated by the obtained UV-Vis-NIR diffuse reflectance spectra and Wood and Tauc's relation [49]. The relationship between $(ah\nu)^2$ and photon energy $(h\nu)$ for $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x = 0.06$ and 0.09) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors are shown in Figs. 10(A) and (B), respectively. In these figures, a is the absorption coefficient, h is the Plank constant, and ν is the frequency. The band-gap energies of $x = 0.06$ and 0.09 phosphors are 4.64 and 4.60 eV, respectively, and those of Li^+ -, Na^+ -, and K^+ -doped phosphors are 4.41 , 4.51 , and 4.54 eV, respectively. These results indicate that the band-gap energy of $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor decreases by adding the alkali metal ions due to the improved crystallinity, and that of the alkali metal ion-contained phosphors follows the order of $\text{K}^+ > \text{Na}^+ > \text{Li}^+$. A similar trend was reported in $\text{CaZrO}_3:\text{Eu}^{3+}, \text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors [48]. The band-gap energies of $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphor and Li^+ -, Na^+ -, and K^+ -doped $\text{CaZrO}_3:\text{Eu}^{3+}$ phosphors were 4.35 , 4.25 , 4.33 and 4.34 eV, respectively.

To analyze the chemical structure of the major functional groups in $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($x = 0.06$ and 0.09) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors, its FT-IR spectra in the infrared region (range of $4000 - 400 \text{ cm}^{-1}$) are obtained, as shown in Fig. 11. The weak absorption bands at 727 and 1210 cm^{-1} , marked with "▼", are assigned to the presence of $(\text{P}_2\text{O}_7)^{4-}$, in particular the P-O-P bonds [50]. The absorption bands at $1300 - 1500 \text{ cm}^{-1}$ are attributed to the presence of $(\text{CO}_3)^{2-}$ [51 - 53], which comes from the CO_2 that combined into the crystal structure during dissolving, stirring, reaction, and annealing, and that at 1751 cm^{-1} is attributed to the vibration of CH and C = O bonds [54]. The absorption bands at 2010 and 3432 cm^{-1} , marked with "▽", are attributed to the vibration of OH group, which comes from the covering of water on the surface of the phosphors [51,52,54 - 58]. The absorption bands at 2858 and 2929 cm^{-1} are associated with the symmetric and asymmetric stretching vibrations of $(\text{CH}_2)^-$ group, respectively [56]. The absorption peaks at 2300 and 2400 cm^{-1} correspond to the vibration of CO_2 group [58]. In particular, the vibrations of $(\text{PO}_4)^{3-}$ group yields several absorption bands at $500 - 1150 \text{ cm}^{-1}$. The absorption bands at 537 and 604 cm^{-1} are attributed to the ν_4 vibration of $(\text{PO}_4)^{3-}$, and those at $930 - 1150 \text{ cm}^{-1}$ are associated with the ν_1 and ν_3 vibrations of $(\text{PO}_4)^{3-}$ [55, 59, 60]. These characteristic vibration modes confirm the formation of $\beta\text{-Ca}_3(\text{PO}_4)_2$ -based phosphors. The obtained FT-IR spectra show that in spite of change in Eu^{3+} concentration and the incorporation of the alkali metal ions, no significant change in FT-IR spectra is observed. This means that the chemical structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ is hardly affected by the Eu^{3+} concentration and the incorporation of the alkali metal ions, and the prepared phosphors have good crystallinity without the formation of crystal defects and impurities. The crystal defects and impurities yield the splitting and shifting of characteristic bands.

The PL excitation spectra of $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.10$) phosphors ($\lambda_{\text{em}} = 614 \text{ nm}$) are displayed in Fig. 12(A). The excitation spectra consist of a broad excitation band in the range of 225 to 315 nm with a maximum intensity at 270 nm and several sharp excitation peaks at 365 , 384 , 397 , 418 , and 466 nm [61]. The broad excitation band at 270 nm , which corresponds to the charge transfer band (CTB), is attributed to the electron transfer from the negative oxygen ion ($2p^6$) to the partially filled $4f^7$ state of Eu^{3+} ion [62]. The presence of the CTB indicates that the energy can be transferred from the $\text{Ca}_3(\text{PO}_4)_2$ host to the Eu^{3+} ions [63]. The sharp excitation peaks at 365 , 384 , 397 , 418 , and 466 nm are caused by the $^7\text{F}_0 \rightarrow ^5\text{D}_4$, $^7\text{F}_0 \rightarrow ^5\text{L}_7$, $^7\text{F}_0 \rightarrow ^5\text{L}_6$, $^7\text{F}_0 \rightarrow ^5\text{D}_3$, and $^7\text{F}_0 \rightarrow ^5\text{D}_2$ transitions of the Eu^{3+} ions [61]. The strongest excitation peak among the excitation peaks is located at 397 nm , which matches well with the emission wavelength of the near-UV LEDs. This means that the $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors can be effectively excited by the near-UV LEDs.

The CTB corresponds to allowed transition, whereas the $4f - 4f$ peaks correspond to forbidden transition. As a result, in general, the intensity of CTB is much stronger than that of $4f - 4f$ peaks, as shown in commercial $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ [64, 65] and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ [66] phosphors and other $\text{LaBO}_3:\text{Eu}^{3+}$ [67], $\text{CaWO}_4:\text{Eu}^{3+}$ [68], $\text{MgWO}_4:\text{Eu}^{3+}$ [69] phosphors. However, the intensity of CTB for the studied phosphors is weaker than that of $4f - 4f$ peaks. This could be explained by the strong potential field of the anion O^{2-} sites around the Eu^{3+} ion, which increases the energy required to transfer an electron from the O^{2-} ion to the Eu^{3+} ion and decreases the intensity of CTB [70]. G. Blasse [70] reported that the CTB is closely related to the potential field of anion O^{2-} ions. The strong potential field shifts the CTB towards higher energy region and decreases the intensity of the CTB. A similar phenomenon was found in Eu^{3+} doped calcium phosphate phosphors, such as $\text{Ca}_9\text{R}(\text{PO}_4)_7$ ($\text{R} = \text{Al}, \text{Lu}$): Eu^{3+} [71], $\text{Ca}_3(\text{PO}_4)_2:\text{Eu}^{3+}$ [72, 73], $\text{Ca}_{19}\text{Mg}_2(\text{PO}_4)_{14}:\text{Eu}^{3+}$ [74], $\text{Ca}_8\text{MgLu}(\text{PO}_4)_7:\text{Eu}^{3+}$ [75], $\text{Ca}_8\text{MgBi}(\text{PO}_4)_7:\text{Eu}^{3+}$ [76], $\text{Ca}_8\text{MgR}(\text{PO}_4)_7$ ($\text{R} = \text{La}, \text{Gd}, \text{Y}$): Eu^{3+} [77], $\text{KNaCa}_2(\text{PO}_4)_2:\text{Eu}^{3+}$ [78], and $\text{Ca}_8\text{ZnLa}(\text{PO}_4)_7:\text{Eu}^{3+}$ [79]. The intensity of the CTB and the $4f - 4f$ peaks from Eu^{3+} ions increases with increasing Eu^{3+} concentration up to 0.09 . Increasing the Eu^{3+} concentration above this value decreases the intensity of the CTB and the $4f - 4f$ peaks. The alkali metal ion-free $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors yield a charge unbalance, thereby creating crystal defects and degrading PL excitation intensities.

To improve the PL properties of $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors, alkali metal ions (Li^+ , Na^+ , and K^+) are doped into the $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor, which shows the strongest excitation intensity among the alkali metal ion-free phosphors. The excitation spectra of alkali metal

ion-contained $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors ($\lambda_{\text{em}} = 614 \text{ nm}$) are presented in Fig. 12(B). The excitation spectrum of the alkali metal ion-free $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor is also provided for comparison. The alkali metal ion-contained phosphors show significantly higher excitation intensity than that of the alkali metal ion-free $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. The excitation intensity of the alkali metal ion-contained phosphors increases in the sequence of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

Figure 13(A) exhibits the emission spectra of $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.10$) phosphors under 397 nm excitation. All phosphors show similar spectral characteristics with emission peaks from the $^5\text{D}_1 \rightarrow ^7\text{F}_J$ ($J = 1 \text{ and } 2$) and $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3, \text{ and } 4$) transitions of Eu^{3+} ions. The emission peaks from the $^5\text{D}_1 \rightarrow ^7\text{F}_1$ and $^5\text{D}_1 \rightarrow ^7\text{F}_2$ transitions are observed at 536 and 556 nm, respectively [80, 81], which are attributed to the fast non-radiative relaxation of the excited $^5\text{D}_1$ state by multiphonon interaction [82]. In addition, four main emission peaks are located at 592, 614, 652, and 699 nm, which are attributed to the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3, \text{ and } 4$) transitions of Eu^{3+} ions in the phosphors, respectively [83, 84]. The strongest emission peak, corresponding to the red light emission, is located at 614 nm, which is attributed to the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} . The transition occurs dominantly when the Eu^{3+} ions are located at a low-symmetry local site without an inversion center [15]. The emission intensity caused by the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (614 nm) is significantly stronger than that by the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (592 nm), corresponding to the orange light emission. This indicates that the Eu^{3+} in $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors prefers the non-centro-symmetric site in the lattice, and the phosphors emit red color.

As shown in the inset of Fig. 13(A), the emission intensity increases with increasing Eu^{3+} concentration up to 0.09 due to the increased luminescent centers, and then decreases with further increasing the Eu^{3+} concentration as a result of the concentration quenching of Eu^{3+} ions [85]. The concentration quenching of emission is mainly caused by the non-radiative energy transfer between the neighboring Eu^{3+} ions. When the Eu^{3+} concentration exceeds the critical value, non-radiative relaxation occurs, thereby decreasing the emission intensity. On the basis of Blasse's theory [86], the critical energy transfer distance (R_0) for the concentration quenching in $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors can be calculated using the following formula [87]: $R_0 = 2[(3V)/(4\pi x_c N)]^{1/3}$, where V is the volume of the unit cell, x_c is the critical concentration of the Eu^{3+} , and N is the number of cations in the unit cell. By using the $x_c = 0.09$, $N = 21$, and $V = 3538.9 \text{ \AA}^3$, the critical energy transfer distance (R_0) of Eu^{3+} in the $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors is calculated to be 15.29 Å. The calculated R_0 of Eu^{3+} is larger than 5 Å required for exchange interaction. This indicates that the electric multipolar interaction is responsible for the concentration quenching in $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors [88 – 90].

The emission spectra of alkali metal ion-contained $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ phosphors ($\lambda_{\text{ex}} = 397 \text{ nm}$) are displayed in Fig. 13(B) along with the alkali metal ion-free $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor for comparison. The emission intensity is remarkably enhanced by incorporating the alkali metal ions because they act as both charge compensators and fluxes, namely, they induce the charge balance, improve the crystalline quality, and stabilize the crystal structure. It is thus important to incorporate a monovalent alkali metal ion into the $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. The emission intensity from the electric dipole transition (614 nm) increases in the sequence of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$. These results strongly suggest that the emission intensity of the alkali metal ion-contained phosphors is related to the crystallinity and structural stability. The $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor shows good crystallinity and stable crystal structure. The $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor shows a 40% stronger red emission intensity than that of the alkali metal ion-free $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. A similar behavior was reported in Li^+ -doped $\text{Sr}_3(\text{PO}_4)_2:\text{R}^{3+}$, Li^+ ($\text{R} = \text{Eu}, \text{Sm}$) phosphors [90]. Cheng et al. [90] synthesized red-emitting $\text{Sr}_3(\text{PO}_4)_2:\text{R}^{3+}$, Li^+ ($\text{R} = \text{Eu}, \text{Sm}$) phosphors through a solid-state reaction. The PL properties of $\text{Sr}_3(\text{PO}_4)_2:\text{R}^{3+}$, Li^+ phosphors were substantially improved by the incorporation of Li^+ ions. Moreover, the IQE values of the prepared $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$, $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$, $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Na}^+$, and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{K}^+$ phosphors under the excitation wavelength of 397 nm are 18.5%, 38.3%, 27.7%, and 18.9%, respectively. Of the prepared phosphors, the $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor has the largest IQE.

Figure 14 shows the luminescent decay curves of $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors ($\lambda_{\text{ex}} = 397 \text{ nm}$ and $\lambda_{\text{em}} = 614 \text{ nm}$). All decay curves follow a single exponential function [71]: $I(t) = I_0 \exp(-t/\tau)$, where I is the emission intensity at time t , I_0 is the emission intensity at $t = 0$, and τ is the lifetime of the Eu^{3+} . The lifetime of all phosphors is determined to be 1.62 ms. No significant change in lifetime with the incorporation of the alkali metal ions is observed. This indicates that the incorporation and type of alkali metal ions hardly affect the lifetime.

To investigate the photometric characteristics of $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors, the color performance such as CIE chromaticity coordinate (x, y), CCT, and color purity are obtained using its corresponding

emission spectra. The CIE chromaticity diagrams of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) phosphors are shown in Fig. 15(A). The CIE chromaticity coordinates of alkali metal ion-free $x = 0.06, 0.07, 0.08, 0.09$, and 0.10 phosphors are (0.6422, 0.3571), (0.6426, 0.3567), (0.6435, 0.3559), (0.6438, 0.3557), and (0.6432, 0.3562), respectively (Table 8). The x - and y -coordinates of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors are located at red light region. The x -coordinates of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors become larger with increasing Eu^{3+} concentration from 0.06 to 0.09 and then decreases with further increasing the Eu^{3+} concentration. In contrast, the values of the y -coordinate with increasing Eu^{3+} concentration show an opposite trend to those of the x -coordinate. The $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor emits the purest red color, and its coordinate (x, y) is (0.6438, 0.3557).

Table 8
CIE chromaticity coordinate (x, y), CCT, and color purity of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li, Na, and K}$) phosphors.

		CIE coordinate (x, y)		CCT (K)	Color purity (%)
		x	y		
$\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphor	$x = 0.06$	0.6422	0.3571	2304	99.3
	$x = 0.07$	0.6426	0.3567	2315	99.4
	$x = 0.08$	0.6435	0.3559	2342	99.6
	$x = 0.09$	0.6438	0.3557	2351	99.7
	$x = 0.10$	0.6432	0.3562	2333	99.5
$\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ phosphor	$\text{M} = \text{Li}$	0.6447	0.3548	2380	99.7
	$\text{M} = \text{Na}$	0.6445	0.3550	2374	99.6
	$\text{M} = \text{K}$	0.6441	0.3554	2360	99.5

The CIE chromaticity diagrams of $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li, Na, and K}$) phosphors are shown in Fig. 15(B). The CIE chromaticity coordinates of Li^+ -, Na^+ -, and K^+ -doped phosphors are (0.6447, 0.3548), (0.6445, 0.3550), and (0.6441, 0.3554), respectively (Table 8). The x -coordinate of the alkali metal ion-contained phosphors is larger than that of the alkali metal ion-free $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor, and the y -coordinate of the alkali metal ion-contained phosphors is smaller than that of the alkali metal ion-free $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. These results indicate that the incorporation of the alkali metal ions improves the red color purity. In particular, the CIE coordinate of the Li^+ -doped phosphor, (0.6447, 0.3548), is close to that of the commercial $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ (0.655, 0.345) and $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ (0.624, 0.337) phosphors and of the NTSC standard red value (0.670, 0.330) [91].

The CCT of phosphors is an important factor in measuring the color temperature of light emitted from phosphors. The CCT values of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li, Na, and K}$) phosphors are calculated by the obtained CIE coordinate (x, y) data and McCamy empirical expression [92–94]: $\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5514.31$, where $n = (x - x_c) / (y - y_c)$, and the chromaticity epicenter is located at $x_c = 0.3320$ and $y_c = 0.1858$. The CCT values of alkali metal ion-free $x = 0.06, 0.07, 0.08, 0.09$, and 0.10 phosphors are 2304 K, 2315 K, 2342 K, 2351 K, and 2333 K, respectively, and the incorporation of alkali metal ions slightly increases the CCT (Table 8). The calculated CCT of the studied phosphors indicates warm light emission, which is suitable for relaxation and comfort at restaurants, bedrooms, and libraries.

The color purities of alkali metal ion-free $x = 0.06, 0.07, 0.08, 0.09$, and 0.10 phosphors, calculated using the obtained CIE coordinate (x, y) data, are as high as 99.3%, 99.4%, 99.6%, 99.7%, and 99.5%, respectively (Table 8), indicating very high color purity. In addition, the color purities of Li^+ -, Na^+ -, and K^+ -doped phosphors are as high as 99.7%, 99.6%, and 99.5%, respectively. The color purity of $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor is higher than that of the previously reported red phosphors. The color purities of $\text{Sr}_2\text{SiO}_4:\text{Eu}^{3+}$, $\text{Ca}_3\text{Gd}(\text{AlO})_3(\text{BO}_3)_4:\text{Eu}^{3+}$, $\text{Y}_2\text{LuCaGaAl}_2\text{SiO}_{12}:\text{Eu}^{3+}$, and $\text{LaNaCaGa}_3\text{PZrO}_{12}:\text{Eu}^{3+}$ phosphors were 97%, 94%, 80%, and 89.9%, respectively [92,95–97]. Clearly, the studied $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor possesses excellent color purity.

Conclusions

$\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ ($0.06 \leq x \leq 0.10$) and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li, Na, and K}$) phosphors formed the rhombohedral unit cell. Alkali metal ions (Li^+ , Na^+ , and K^+) occupied the Ca^{2+} sites in the $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor without disturbing the crystal structure. All

phosphors showed sharp emission peaks at 592, 614, 652, and 699 nm due to the $^5D_0 \rightarrow ^7F_J$ ($J = 1, 2, 3, \text{ and } 4$) transitions of Eu^{3+} , respectively. The alkali metal ions significantly enhanced the emission intensity and improved the emission color quality because they acted as both charge compensators and fluxes. Of the alkali metal ions used, Li^+ was an optimal cation to improve the emission intensity and color purity. The $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor showed a 40% stronger red emission intensity than that of the $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor. The CIE chromaticity coordinate (x, y), color purity, and correlated color temperature of the $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{Li}^+$ phosphor were (0.6447, 0.3548), 99.7%, and 2380 K, respectively.

Declarations

Acknowledgment

We also acknowledge the financial support by the Human Resources Development of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry & Energy (No. 20184030202260).

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Figures

Figure 1

XRD diagrams of (A) $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors with $x =$ (a) 0.06, (b) 0.07, (c) 0.08, (d) 0.09, and (e) 0.10 and of (B) $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ (M = (a) Li, (b) Na, and (c) K) and (d) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphors.

Figure 2

XRD Rietveld refined profiles of $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors with $x =$ (A) 0.06, (B) 0.07, (C) 0.08, and (D) 0.09.

Figure 3

Crystal structure of $\text{Ca}_{2.94}(\text{PO}_4)_2:0.06\text{Eu}^{3+}$ drawn by the VESTA program and XRD Rietveld refinement data.

Figure 4

Lattice parameters (a , c) and unit cell volume of (A) $\text{Ca}_{3-x}(\text{PO}_4)_2 \cdot x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.09$) and (B) $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+} \cdot 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) phosphors. Note that “none” in (B) corresponds to $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ phosphor.

Figure 5

Relationships between (A) average Ca-O length and alkali metal ion and between (B) average Ca-O length and coordination number of Ca^{2+} for $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+} \cdot 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$) phosphors. Note that “none” in (A) and (B) corresponds to $\text{Ca}_{2.91}(\text{PO}_4)_2 \cdot 0.09\text{Eu}^{3+}$ phosphor.

Figure 6

(A) XPS survey spectra of (a) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ (M = (b) Li, (c) Na, and (d) K) phosphors. High-resolution XPS spectra of (B) Ca and (C) P elements in (a) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ (M = (b) Li, (c) Na, and (d) K) phosphors. High-resolution XPS spectra of (D) Li, (E) Na, and (F) K elements in $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ (M = Li, Na, and K) phosphors.

Figure 7

High-resolution XPS spectra of Eu element in (A) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}$ ($\text{M} =$ (B) Li, (C) Na, and (D) K) phosphors. Note that “▼” indicates satellite peak.

Figure 8

High-resolution XPS spectra of O element in (A) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}$ ($\text{M} =$ (B) Li, (C) Na, and (D) K) phosphors.

Figure 9

UV-Vis-NIR diffuse reflectance spectra of (A, B) $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors ($x = 0.06$ and 0.09) and of (C, D) $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M}^+ = \text{Li}^+, \text{Na}^+, \text{and K}^+$) phosphors.

Figure 10

Relationship between $(\alpha h\nu)^2$ and photon energy ($h\nu$) for (A) $\text{Ca}_{3-x}(\text{PO}_4)_2:\text{xEu}^{3+}$ phosphors ($x = 0.06$ and 0.09) and (B) $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors.

Figure 11

FT-IR spectra of (A) $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors ($x = 0.06$ and 0.09) and (B) $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors.

Figure 12

Excitation spectra of (A) $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ ($0.06 \leq x \leq 0.10$) phosphors and (B) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M} = \text{Li}, \text{Na}, \text{and K}$) phosphors monitored at a wavelength of 614 nm . Note that “none” in (B) corresponds to $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor.

Figure 13

Emission spectra of (A) $\text{Ca}_{3-x}(\text{PO}_4)_2:xEu^{3+}$ ($0.06 \leq x \leq 0.10$) phosphors and (B) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09M^+$ ($M = \text{Li}, \text{Na}, \text{and K}$) phosphors under 397 nm excitation. Note that “none” in (B) corresponds to $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ phosphor.

Figure 14

Luminescent decay curves of (A) $\text{Ca}_{2.91}(\text{PO}_4)_2:0.09\text{Eu}^{3+}$ and $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09M^+$ ($M =$ (B) Li, (C) Na, and (D) K) phosphors ($\lambda_{\text{ex}} = 397 \text{ nm}$ and $\lambda_{\text{em}} = 614 \text{ nm}$).

Fig. 15. CIE chromaticity diagrams of (A) $\text{Ca}_{3-x}(\text{PO}_4)_2:x\text{Eu}^{3+}$ phosphors with $x = (\bullet) 0.06$,

$(\blacksquare) 0.07$, $(\blacklozenge) 0.08$, $(\blacktriangle) 0.09$, and $(\blacktriangledown) 0.10$ and of (B) $\text{Ca}_{2.82}(\text{PO}_4)_2:0.09\text{Eu}^{3+}, 0.09\text{M}^+$ ($\text{M}^+ =$

$(\bullet) \text{Li}^+$, $(\blacksquare) \text{Na}^+$, and $(\blacklozenge) \text{K}^+$) phosphors under 397 nm excitation.

Figure 15

"See image above for figure legend."

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