

Enhancement of Photoluminescence and Color Purity of CaTiO₃:Eu Phosphor by Li Doping

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High color purity red phosphors of $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_xLi_xTiO_3$ ($0 < x \leq 0.3$) are synthesized via a solid-state reaction method. The red emission photoluminescence intensity and color purity are enhanced by the incorporation of Li $^+$ into CaTiO_3:Eu $^{3+}$. The Li $^+$ doping increases the emission probability from 5D_0 state, increases photoluminescence intensity by 1.6 times, increases color purity to 92.1%, and shortens the decay time. With increasing Eu $^{3+}$ and Li $^+$ content, the color coordinates approach the ideal red chromaticity values, coming closer than commercial $Y_2O_2S:Eu^{3+}$ red phosphor.

I. Introduction

T HE development of flat panel displays (FPDs) has seen great growth in the last decade. White-light-emitting diodes (WLEDs) have attracted a lot of attention in recent years due to their numerous applications, such as backlights in liquid crystal displays (LCDs), automotive headlights, and general illumination. The development of phosphor materials that can enhance the luminescence and efficiency of WLEDs is essential for the FPD industry. The most commonly used commercial WLEDs, which use a blue LED chip with $Y_3Al_5O_{12}:Ce^{3+}$ yellow phosphor powder,^{1,2} have a low color rendering index (CRI) and thus require a red phosphor. Furthermore, blue- and UV-chip-excited RGB color phosphors also require a high color-purity red phosphor.

Titanate $(TiO_3^{2^-})$ -based ceramics systems have unique optical, thermal, electrical, and mechanical properties,³ which can be exploited to fabricate promising phosphor materials. The idiosyncratic deformation of the perovskite structure influences the luminescence behavior of titanate.⁴ According to Kyomen,⁵ the *f*-*f* transition would be increased due to the lowering of the point symmetry at the alkaline-earth site in (Ca, Sr, Ba) TiO_3:Pr³⁺. The component CaTiO_3:Pr³⁺ with an orthorhombic structure has better photoluminescence intensity than that of the other two components (BaTiO_3 and SrTiO_3 with tetragonal and cubic structures, respectively). The Ca-TiO₃ was thus chosen as the host in the present study. Table I summarizes recent studies related to titanate phosphors.

A promising phosphor material, $CaTiO_3:Pr^{3+}$ red phosphor used for field emission displays (FEDs) was first reported in 1994.⁶ The CaTiO_3:Pr³⁺ with high color purity and a low voltage excitation compared to those of commercial $Y_2O_3:Eu^{3+}$ phosphor was later developed.⁷ However, the excitation spectrum of CaTiO_3:Pr³⁺ has a narrow peak near 335 nm,^{8,9} which limits its application in the field of LEDs. Therefore, the present study improves the excitation characteristics by

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replacing Pr^{3+} with Eu^{3+} in CaTiO₃:Pr³⁺, which can be excited by UV as well as blue light to increase the usability of the phosphor.¹⁰ According to previous studies,^{11,12} photoluminescence can be improved by doping Li⁺ into the host. Since few titanate-related phosphor studies have been conducted, the present study focuses on the synthesis of CaTiO₃ red phosphor doped with both Eu³⁺ and Li⁺. The characteristics and performance of the phosphor are investigated and discussed.

II. Experimental Procedure

The synthesis of CaTiO₃ phosphors doped with trivalent europium (Eu³⁺) and monovalent lithium (Li⁺) was carried out via a solid-state reaction method. The raw materials, CaCO₃ (Mallinckrodt, Hazelwood, MO, 99.99%), TiO₂ (Showa, Tokyo, Japan, 99.9%), Eu₂O₃ (Alfa Aesar, Ward Hill, MA, 99.99%), and Li₂CO₃ (Mallinckrodt, 99%), were well mixed with alcohol (99%) stoichiometrically, and then dried in the oven at 80°C. The dried mixture was allowed to react in the furnace at 1300°C for 8 h in an air atmosphere with a heating rate of 5°C/min.

The crystal structure of samples was confirmed using X-ray diffractometry (XRD, Rigaku D/max VIII, Tokyo, Japan) with Cu- K_{α} ($\lambda = 1.54056$ Å) radiation operated at 30 kV and 20 mA. Photoluminescence (PL) spectra and excitation (PLE) spectra were acquired using a fluorescence spectrophotometer (Hitachi F-7000, Tokyo, Japan) equipped with a 150-W xenon lamp as the excitation source. The quantum efficiency was measured using an integrating sphere coated with BaSO₄ installed in the fluorescence spectrophotometer. The photoluminescence decay time was recorded using the fluorescence spectrophotometer with a pulsed xenon lamp. Fourier transform infrared (FTIR) spectra were obtained using a Jasco FTIR-200E spectrometer with the KBr pellet technique. All results were measured at room temperature and atmospheric pressure.

III. Results and Discussion

(1) XRD Characteristics

The perovskite CaTiO₃ formed during sintering at 1300°C for 8 h belongs to the orthorhombic structure. In this structure, a Ca²⁺ ion is at the center of a cubic unit cell surrounded by twelve O²⁻ ions, and Ti⁴⁺ ions are at the corners of the cubic unit cell surrounded by six O²⁻ ions in the cube-octahedral coordination.¹³ The XRD patterns for the Ca_{1-3/2x}Eu_xTiO₃ (CET) and Ca_{1-2x}Eu_xLi_xTiO₃ (CELT) series are shown in Fig. 1. The results are consistent with JCPDS Card No. 22-0153 (cell parameters: a = 5.440 Å, b = 7.643 Å, and c = 5.381 Å). An impurity phase of Eu₂Ti₂O₇ appears when the Eu³⁺ content is greater than 10 mol% (x = 0.1) in the CET series [see Fig. 1(a)]. The impurity phase disappears when a commensurate amount of Li⁺ is added [see Fig. 1(b)].

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Table I. Summary of Titanate-Related Research

Host	Activator	Process	Excitation/emission	Year
(Ba,Sr)TiO ₃	Eu ³⁺	Solid-state reaction (1200°C for 2 h)	465 nm/617, 667, and 695 nm	2004 ²⁵
CaTiO ₃	Pr ³⁺	Solid-state reaction (600°C–1000°C for 2 h)	330 nm/614 nm	2007 ²⁶
BaTiO ₃	Pr ³⁺	Solid-state reaction (1300°C for 2 h)	360 and 300 nm/600 and 616 nm	2008 ²⁷
CaTiO ₃	Eu ³⁺	Solid-state reaction (1300°C–1600°C for 4 h)	400 nm/618 nm	2009 ²⁸
CaTiO ₃	Eu ³⁺ , Li ⁺	Solid-state reaction (1300°C for 8 h)	397 and 466 nm/590, 594, and 616 nm	This study



Fig. 1. XRD patterns of (a) $Ca_{1-3/2x}Eu_xTiO_3$ and (b) $Ca_{1-2x}Eu_xLi_xTiO_3$ sintered at 1300°C for 8 h.

The unit-cell parameters of CET and CELT were determined using Program Unit Cell software (T.J.B. Holland, S.A.T. Redfern, Department of Earth Sciences, Cambridge, U.K., 1995); the calculation results are shown in Table II and Fig. 2. In the CET series [see Fig. 2(a)], the values of these parameters slightly decrease with increasing x; the lowest values were obtained for x = 0.15. This indicates that the maximum content of Eu^{3^+} was around 15 mol% in CaTiO₃ under sintering at 1300°C for 8 h. The parameter values decrease with increasing x (equal amounts of Eu^{3^+} and Li^+) in the CELT series [see Fig. 2(b)]. Since Eu^{3^+} (0.947 Å) and Ca^{2^+} (0.99 Å) have similar atomic radii, Eu^{3^+} can substitute the Ca^{2^+} site smoothly. However, the Li^+ radius (0.76 Å) is smaller than that of Ca^{2^+} , and thus co-doped Li^+ decreases the cell volume. Li^+ is not only a charge compensator, but it also plays the role of flux, which can enhance the crystallinity and increase the partial solid solubility of Eu^{3^+} in the Ca-TiO₃ host.

Figure 3 shows the SEM images of CET and CELT (x = 0.15) synthesized via the solid-state reaction method. Comparing the surface morphology of these two samples, it can be seen that the particles of CET are fine and spherical-like, whereas the particles of CET are large and irregular. The average particle sizes of CET and CELT are around 3 and 5 µm, respectively. This reveals that the particle size increased after Li⁺ was doped into CaTiO₃: Eu. Thus, Li⁺ doping enhances the crystallinity and the growth of CaTiO₃ particles, as shown in the XRD and SEM results.

(2) Photoluminescence and Quantum Efficiency

Figure 4 shows the PL and PLE spectra of the CET and CELT series (x = 0.15) for 397 and 466 nm excitation wavelengths and 594 and 616 nm emission wavelengths. The PL/ PLE spectra of CEL and CELT are similar. There was no change in the emission peak position after doping with Li^+ in CET. The schematic energy level of Eu^{3+} in CaTiO₃ illus-trating the emissions of Eu^{3+} is shown in Fig. 5. From the PLE spectra in Fig. 4(a), the excitation bands of CEL and CELT samples centered at 361, 386, 397, 416, and 466 nm are due to the ${}^7F_0 \rightarrow {}^5D_4$, ${}^7F_0 \rightarrow {}^5L_7$, ${}^7F_0 \rightarrow {}^5L_6$, ${}^7F_0 \rightarrow {}^5D_3$, and ${}^7F_0 \rightarrow {}^5D_2$ electron transitions of Eu³⁺, respectively. In the PL spectra [shown in Fig. 4(b)], the emission peaks at 590, 594, and 616 nm can be attributed to the energy relaxation of ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{1}$ (590, 594 nm) and ${}^{5}\text{D}_{0} \rightarrow {}^{7}\text{F}_{2}$.¹⁴ The narrow band was attributed to the characteristic electron shielding effect in trivalent rare-earth ions (Eu³⁺). From the PL/PLE spectra, the optimal excitation and the strongest emission wavelengths are 397 and 616 nm, respectively. The PLE spectra reveal that the as-prepared phosphors are suitable for being excited by near-UV and blue light. Furthermore, the PL spectra show that regardless of the excitation source, the energy transfer process is always from the higher energy level to the ${}^{5}D_{0}$ energy level through

Table II. Unit-Cell Parameters of $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_xLi_xTiO_3$ for various x values

		Ca ₁₋₃	$_{z/2x}Eu_{x}TiO_{3}$		Ca _{1-2x} Eu _x Li _x TiO ₃						
x	a (Å)	b (Å)	<i>c</i> (Å)	Volume (Å ³)	a (Å)	b (Å)	<i>c</i> (Å)	Volume (Å ³)			
0	5.4402	7.6454	5.3704	223.3650	5.4402	7.6454	5.3704	223.3650			
0.01	5.4417	7.645	5.3694	223.3777	5.4392	7.6437	5.3695	223.2385			
0.05	5.4408	7.6438	5.3685	223.2676	5.4427	7.6424	5.3655	223.1819			
0.1	5.4381	7.6423	5.3659	223.0038	5.438	7.6426	5.3658	223.0035			
0.15	5.4315	7.6424	5.3669	222.7788	5.4242	7.639	5.3404	221.2777			
0.2	5.4327	7.6452	5.3656	222.8546	5.4219	7.6249	5.3261	220.1905			
0.3	5.4309	7.6461	5.3639	222.7339	5.4233	7.6144	5.3179	219.6024			



Fig. 2. Unit-cell parameters of (a) $Ca_{1-3/2x}Eu_xTiO_3$ and (b) $Ca_{1-2x}Eu_xLi_xTiO_3$ for various x values.



Fig. 3. SEM images of (a) $Ca_{1-3/2x}Eu_xTiO_3$ and (b) $Ca_{1-2x}Eu_xLi_xTiO_3$ (x = 0.15).

the multi-phonon relaxation process, and then they start to emit lights.

It has been reported that the ratio of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ to ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ can represent the asymmetry ratio (*R*) around Eu³⁺, and this asymmetry structure site can benefit photoluminescence. The asymmetry ratio is expressed as¹⁵:

$$R = \frac{I({}^{5}\mathrm{D}_{0} - {}^{7}\mathrm{F}_{2})}{I({}^{5}\mathrm{D}_{0} - {}^{7}\mathrm{F}_{1})}.$$
 (1)

The ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition belongs to the electric dipole transition, which can be influenced by the asymmetry

around the activator. In contrast, the ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transition belongs to the magnetic dipole transition, which is not influenced by the environment. According to the calculation results of Eq. (1), the asymmetry ratio of the Eu³⁺ site is about 2 (R=2), which means that the electric dipole transition is twice as strong as the magnetic dipole transition. With increased doping content, the symmetry of the local environment of Eu³⁺ decreases, which strengthens the transition from energy level ${}^{5}D_{0}$ to energy level ${}^{7}F_{1}$, and thus leads to stronger red emission and higher color purity.

Figure 6 shows the integrated emission intensity for CET and CELT under 397 and 466 nm excitations. The intensities indicate that concentration quenching occurs as x approaches 0.15. For both excitation wavelengths, the CELT series has a much higher photoluminescence emission intensity than that of the CET series. This is due to the charge imbalance caused by Eu³⁺ substituting the Ca²⁺ sites; Ca vacancies are required for charge neutrality. However, an excessive number of vacancies makes the structure unstable and reduces the photoluminescence intensity. According to Liu,¹⁶ Ca^{2+} vacancies are not favorable for the emission of the Eu^{3+} activator because of the fact that the energy transfer from Eu³⁺ to the vacancies is more efficient, and hence a certain number of vacancies will affect the photoluminescence intensity. In the CET system, for maintaining charge neutrality, the doped Eu³⁺ induces Ca vacancies, which can be expressed as:

$$3Ca_{Ca}^{\times} + 2Eu_{Eu}^{\times} \rightarrow 2Eu_{Ca}^{\cdot} + V_{Ca}^{\prime\prime}$$
⁽²⁾

To eliminate the Ca vacancies and the impurity phase,¹⁷ the charge compensation method is used here to improve crystallinity. A possible approach for compensating the valance and decreasing the number of Ca vacancies is doping Li⁺. The process can be expressed as:

$$2Ca_{Ca}^{\times} + Eu_{Eu}^{\times} + Li_{Li}^{\times} \rightarrow Eu_{Ca}^{\cdot} + Li_{Ca}^{\prime}$$
(3)

Based on the above results, we propose that the concentration quenching which occurs in CET is caused by the redundant defects (including Ca vacancies and the impurity phase), which lead to a large energy loss between Eu^{3+} and vacan-



Fig. 4. (a) PLE and (b) PL spectra of $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_xLi_xTiO_3$ (x = 0.15) for various excitation and emission wavelengths.



Fig. 5. Schematic energy levels of Eu^{3+} in the CaTiO₃ host.



Fig. 6. Integrated emission intensity of $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_xLi_xTiO_3$ for various x values ($0 < x \le 0.3$).

cies. In CELT, Li⁺ doping increases the partial solid solubility of Eu^{3+} in CaTiO₃. With increasing Eu^{3+} content, the distance between Eu^{3+} ions decreases. Thus, the concentration quenching occurred due to the energy loss from nonradiation between Eu^{3+} .

The absorption coefficient (A) and quantum efficiency (η) were estimated using the following equations¹⁸ (details of the calculation method can be found elsewhere¹⁹):

$$A = \frac{\int \lambda [E(\lambda) - R(\lambda)] d\lambda}{\int \lambda E(\lambda) d(\lambda)}$$
(4)

$$\eta = \frac{\int \lambda P(\lambda) d\lambda}{\int \lambda [E(\lambda) - R(\lambda)] d\lambda}$$
(5)

where $E(\lambda)$, $R(\lambda)$, and $P(\lambda)$ are the light intensity per unit wavelength in the spectra of excitation, reflectance, and emission of the phosphor, respectively. The calculation results of A and η with excitation at 397 and 466 nm for the CET and CELT series are shown in Table III (the A and η values of commercial YAG:Ce yellow phosphor measured using our instrument are 84.7% and 73.2%, respectively). The results suggest that A increases with increasing Eu³ and Li⁺ content. Furthermore, η increases with increasing Eu^{3+} and Li^+ content up to x = 0.15 (quenching concentration), and then starts to decrease. A and η are higher for both the CET and CELT series under 397 nm excitation than under 466 nm excitation. In the as-prepared phosphors, the optimal value of η is 19.9%, which in the CELT series was obtained at x = 0.15. The optimal value of A is 59.6%, which in the CELT series was obtained at x = 0.30. The value of η in this system is not satisfactory, it may be derived from the value of A which is not high enough. However, this could be further improved through the modification technique. According to the literature, 20,21 modification of the surface of particles, enhancement uniformity, and doping with other elements (such as: Sm^{3+} , etc.)

Table III. Properties of $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_xLi_xTiO_3$ for Various x Values

	$Ca_{1-3/2x}Eu_{x}TiO_{3} \\$								$Ca_{1-2x}Eu_xLi_xTiO_3$							
	at 397 nm		at 466 nm			CIE			at 397 nm		at 466 nm			CIE		C D
x	A (%)	η (%)	A (%)	η (%)	$\tau \ (ms)$	х	у	(%)	A (%)	η (%)	A (%)	η (%)	$\tau \ (ms)$	х	у	(%)
0.01	28.7	1.9	17.2	1.0	0.79	0.615	0.385	83.8	36.5	2.0	21.2	1.3	0.78	0.629	0.371	86.8
0.05	32.3	6.8	21.5	2.5	0.78	0.642	0.358	89.7	42.5	8.3	29.8	3.0	0.77	0.643	0.356	89.9
0.1	37.3	10.6	23.1	3.8	0.76	0.646	0.353	90.6	49.2	13.8	34.1	5.9	0.76	0.649	0.351	91.4
0.15	39.6	14.1	23.7	6.8	0.75	0.648	0.351	91.1	51.7	19.9	35.0	9.4	0.70	0.651	0.349	91.8
0.2	44.1	12.7	25.6	6.3	0.71	0.648	0.351	91.1	52.4	18.5	35.5	8.9	0.63	0.652	0.348	92.1
0.3	47.1	7.3	26.6	4.2	0.61	0.648	0.352	91.2	59.6	11.2	41.4	6.8	0.41	0.652	0.348	92.1

C.P., color purity; τ , decay time; A, absorption coefficient; η , quantum efficiency.



Fig. 7. FTIR spectra of $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_xLi_xTiO_3$ (x = 0.15).

can be used to enhance the photoluminescence intensity and efficiency.

(3) FTIR Spectra and Multi-Phonon Process

To further investigate the enhanced luminescent intensity due to Li^+ doping, the FTIR spectra of CET and CELT (x = 0.15) are presented in Fig. 7. The FTIR spectra were used to obtain the phonon energy of vibrational modes in the host. The phonon energies at 577 and 442 cm⁻¹ are attributed to the characteristics of alkaline titanates and the Ti–O bond vibration of (TiO₃)^{2–} groups, respectively.²² After Li⁺ doping, higher energy phonons appear at 716 cm⁻¹. From the PL results [shown in Fig. 4(b)], regardless of the excitation to ⁵L₆ or ⁵D₂ of Eu³⁺, the energy in ⁵L₆ or ⁵D₂ can be relaxed to ⁵D₀ of Eu³⁺, and then the phonons start to emit light. The energy relaxation process from the Eu³⁺ excited state to the Eu³⁺ ⁵D₀ state is called multi-phonon relaxation process, which is also a kind of non-radiative transition. The non-radiative transition rate of the multi-phonon relaxation process as a function of temperature can be expressed by¹⁶:



Fig. 8. Natural logarithm of the normalized emission intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (616 nm) versus the decay time under an excitation of 397 nm for (a) Ca_{1-3/2}xEu_xTiO₃ and (b) Ca₁₋₂xEu_xLi_xTiO₃.

$$W(T) = W(0)(n+1)^{p}$$
(6)

where W(T) is the rate at temperature T, $n = [\exp(h\nu/kT) - 1]^{-1}$, $p = \Delta E/h\nu$ is the number of phonons, ΔE is the energy difference between the levels involved, and $h\nu$ is the phonon energy. W(0) is temperature-independent and large



Fig. 9. CIE chromaticity coordinates of $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_xLi_xTiO_3$, and photographs of as-prepared samples excited by various light sources.

for high phonon energy or low p. W(0) can be expressed by:¹⁶

$$W(0) = \beta \exp[-(\Delta E - 2hv)\alpha]$$
⁽⁷⁾

where α and β are constants, and ν is the highest available vibration frequency of the surroundings of the rare-earth ions.

According to the above formula, the multi-phonon relaxation rate is related to the highest available vibration frequency of the host. The multi-phonon relaxation rate increases with higher phonon energy of vibrational mode in the host. To calculate the number of phonons that participated in the process of multi-phonon relaxation, the energy difference between the levels involved was divided by the phonon energy of the highest available vibration frequency.¹⁴ The rate of multi-phonon relaxation from the Eu excited state to the $Eu^{3+5}D_0$ state step by step (as shown in Fig. 5) is correlated with the highest available vibration frequency of the host (716 cm^{-1}). Thus, with a higher available vibration frequency of the host, fewer phonons participated in the process of multi-phonon relaxation from the Eu^{3+} excited state to the Eu^{3+} 5D_0 state. This increased the multi-phonon relaxation rate, increasing the emission probability as well as PL intensity from energy level ${}^{5}D_{0}$ to the ground state.

In this study, a higher vibration frequency of the host appears at 716 cm⁻¹ after Li⁺ doping. This makes fewer phonons participate in the multi-phonon relaxation process from the Eu³⁺ excited state to the Eu³⁺ ⁵D₀ state, leading to a higher multi-phonon relaxation rate, a higher emission probability from ⁵D₀ state, and thus a stronger intensity from ⁵D₀ state, as shown in Fig. 5.

Figure 8 shows the natural logarithm of the normalized emission intensity of ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ (616 nm) versus the decay time under an excitation of 397 nm for CET and CELT. The decay time results can be well fitted with the following single exponential decay function²³:

$$I = I_0 \exp(\frac{-t}{\tau}) \tag{8}$$

where I_0 is the initial emission intensity at t = 0 and τ is the decay time. The decay times of CET and CELT were evaluated using Eq. (8); the results are shown in Table III. The decay times decrease with increasing x. The photoluminescence decay time of the phosphor (τ) is affected by the radiative decay time, non-radiative rate, and energy transfer rate, which can be expressed by¹⁴:

$$(1/\tau) = A_{\rm r} + A_{\rm nr} + P_{\rm t} \tag{9}$$

where A_r is the radiative transition rate ($A_r = (1/\tau_0)$), A_{nr} is the non-radiative transition rate due to multi-phonon relaxation, and P_t is the transfer rate due to energy transfer.

The Li⁺ doping leads to fewer phonons participating in the multi-phonon relaxation process from the Eu³⁺ excited state to the Eu³⁺ ⁵D₀ state, leading to a higher multi-phonon relaxation rate, a higher emission probability, and intensity from energy level ⁵D₀, and a higher radiative transition rate. According to Eq. (9), the luminescence decay time of the phosphor is affected by the radiative decay time, non-radiative rate, and energy transfer rate. The non-radiative rate of multi-phonon relaxation and the radiative transition rate are inversely proportional to the radiative decay time of the donor ions. The luminescence decay time decreases with increasing Li⁺ content.

(4) Color Purity

Figure 9 shows the Commission Internationale de l'Éclairage (CIE) color coordinates of the CET and CELT specimens, and photographs of as-prepared samples excited by various light sources. From the CIE results, with increasing Eu³⁺ and Li⁺ content, the color coordinates of CET and CELT approach the ideal red chromaticity (0.67, 0.33) for the National Television Standard Committee (NTSC) system (as shown in the inset of Fig. 9). When the co-doping content of Eu^{3+} and Li^+ is over 15 mol%, the CIE color coordinates are closer to the ideal red chromaticity than those of the commercial $Y_2O_2S:Eu^{3+}$ red phosphor. To investigate the effect of the incorporation of Li⁺ on color purity, the color purity was calculated using²⁴:

Color purity =
$$\frac{\sqrt{(x_{\rm s} - x_i)^2 + (y_{\rm s} - y_i)^2}}{\sqrt{(x_{\rm d} - x_i)^2 + (y_{\rm d} - y_i)^2}} \times 100\%$$
 (10)

where (x_d, y_d) are the coordinates of the dominant wavelength, (x_s, y_s) are the coordinates of a sample point, and (x_i, y_s) y_i) are the coordinates of the illuminant point. In this study, $(x_d, y_d) = (0.68, 0.32)$ and $(x_i, y_i) = (0.3101, 0.3162)$ for the dominant wavelength at 616 nm.

The calculation results shown in Table III indicate that Li⁺ affects the color purity, which can be improved to 92.1%. These results show that $Ca_{1-2x}Eu_xLi_xTiO_3$ red phosphors with high color purity have promising application in solid-state lighting devices fabricated with UV (InGaN) or blue (GaN) chips.

IV. Conclusions

Using the solid-state reaction method, $Ca_{1-3/2x}Eu_xTiO_3$ and $Ca_{1-2x}Eu_{x}Li_{x}TiO_{3}$ red phosphors with bright red emission and high color purity were synthesized. The $Ca_{1-3/2x}Eu_xTiO_3$ powder phosphors exhibited a main red emission peak centered at 616 nm under 397 nm UV light excitation. The photoluminescence intensity was increased by 1.6 times and the color purity was increased to 92.1% with Li⁺ doping. These improvements can be attributed to two effects: (i) the compensation of charges, which decreases the number of Ca vacancies and (ii) leads to a higher emission probability from ${}^{5}D_{0}$ state and stronger red emission. Thus, $Ca_{1-2x}Eu_xLi_xTiO_3$ powder phosphors can be regarded as a promising red phosphor material which is applicable to solidstate lighting devices when coupled with UV or blue chips.

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