

A Study on the Luminescent Properties of Praseodymium-Activated CaIn_2O_4 Phosphors

F. S. Kao and Teng-Ming Chen¹

Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30050, Taiwan

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The photoluminescent (PL) properties and decay lifetime of a series of unprecedented praseodymium-activated calcium in-dates ($\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$) have been investigated. The $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ ($x = 6.25 \times 10^{-4}$, 0.5%, 1%, and 2%) was found to exhibit orange emission under ultraviolet excitation. With different levels of Pr^{3+} doping, the X-ray diffraction profiles, photoluminescence spectra and fluorescence decay lifetime as a function of Pr^{3+} concentration, and chromatic characteristics of $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ with different x 's have been systematically investigated. The analysis of PL emission and excitation spectra, decay lifetime, and comparison of chromaticity coordinates and hues for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ are presented and their implications are discussed. © 2000 Academic Press

Key Words: Luminescence; $\text{CaIn}_2\text{O}_4:\text{Pr}^{3+}$; photoluminescence spectra; decay lifetime; chromaticity diagram.

1. INTRODUCTION

The development of displays has always been accompanied by improvements in the phosphors used. For example, the advent of color television depended on the development of efficient red phosphors (1). Great effort has been made to discover host materials as well as activators with high performance for phosphor applications. The progress in display technology will not be exploited to its full potential until the phosphors operating at required conditions have been synthesized. The requirements for various types of displays are different. For instance, the cathode ray tube phosphors have been optimized to endure the bombardment of high-voltage electron beams. In particular, for field emission display (FED) applications, in order to overcome the impediment of the space charge at the surface of conventional phosphors, intrinsically conducting materials must be adopted (2). Therefore, there has been an urgent need for the investigation of new phosphors for practical use. In this work, we investigated the possible combination

of a new host lattice and an efficient activator with high lumen equivalent and intrinsic conductivity.

The semiconducting CaIn_2O_4 with reported bandgap (E_g) of 3.9 eV was found to crystallize in an orthorhombic CaFe_2O_4 -type structure with space group $Pca2_1$ or $Pbcm$ (3). The lattice parameters have been reported to be $a = 9.70 \text{ \AA}$, $b = 11.30 \text{ \AA}$, and $c = 3.21 \text{ \AA}$ for CaIn_2O_4 (3). With the described properties it may possess the potential to serve as a candidate for new hosts in phosphor applications. The only disadvantage seems to be the high cost of source material In_2O_3 .

On the other hand, rare earth ions have been widely used as the activators for different host materials. Among these, trivalent praseodymium is known to exhibit very interesting prospects as an activator ion for luminescence and laser action, because its energy level contains several metastable multiplets such as $^3P_{0,1,2}$, 1D_2 , and 1G_4 (4). This provides many possibilities for pumping and lasing in several spectral regions, taking into account the large number of excitation and relaxation channels. It has been known that the emission color of Pr^{3+} depends strongly on the type of host lattice, the concentration, and the pumping conditions and it was reported to cover the spectral range from blue to red (5). The advantage of Pr^{3+} as a luminescent activator lies in the fact that the emission of Pr^{3+} -activated phosphors is known to be similar to that of Eu^{3+} which has long been known as an efficient red phosphor with great success in cathode ray tubes. For instance, in Pr^{3+} -activated CaTiO_3 ($\text{CaTiO}_3:\text{Pr}^{3+}$), a single bright red emission peaking at 613 nm was observed (6). Diallo *et al.* reported that $\text{CaTiO}_3:\text{Pr}^{3+}$ was excitable in a wide ultraviolet range and exhibited a unique red emission from the $\text{Pr}^{3+} \ ^1D_2$ level (7). Furthermore, a long-decay Pr^{3+} -activated phosphor ($\text{Ca}_{1-x}\text{M}_x\text{TiO}_3:\text{Pr}^{3+}$ ($M = \text{Zn}, \text{Mg}; 0 < x \leq 0.1$)) was reported to exhibit red phosphorescence emission at a wavelength (λ_{em}) of 614 nm and with a persistent afterglow for 30 to 60 sec (8).

Our work was motivated by the desire to understand the fluorescence behavior of Pr^{3+} -activated phosphors and, we hoped, to develop potentially efficient phosphors for practical applications.

¹To whom correspondence should be addressed. E-mail: tmchen@cc.nctu.edu.tw. Fax: 886 + 35723764.

During the past few years, several investigations on the luminescence of Pr^{3+} have been reported in the literature (5–10). However, to the best of our knowledge, no photoluminescence characterization of Pr^{3+} -activated CaIn_2O_4 ($\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$) has been reported so far. In the present work we report the results of our investigation on the luminescence spectra, possible radiative luminescent decay lifetime (τ_R), and chromatic characteristics of the unprecedented $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ as a function of Pr^{3+} activator concentrations.

2. EXPERIMENTAL

Polycrystalline $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ phases with $x = 0.0625\%$, 0.5%, 1%, and 2%, respectively, were synthesized by conventional solid-state reactions. The starting materials used for the phosphor preparation were of the highest purity commercially available. The stoichiometric constituent components of CaO , In_2O_3 (both from Aldrich Chemicals, U.S.A.) and Pr_2O_3 (from CERAC Inc., U.S.A.) were thoroughly mixed and finely ground together. The mixtures were first calcined at 550°C in the air for 6 h and then sintered at 1400°C for 24 h also in the air; however, no flux was used in the synthesis.

The phase purity and homogeneity of the as-prepared $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ samples were investigated by X-ray diffraction (XRD). The XRD profiles for Pr^{3+} -activated CaIn_2O_4 phases were collected by using a MAC Science MXP-3 automatic diffractometer using a graphite-monochromatized and Ni-filtered $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. Special caution was taken to make sure that none of the starting material nor any other allotropic form was present in the samples that could be identified in the XRD profiles. Only single-phase samples were used for this investigation.

The ambient temperature photoluminescence (PL) spectra (with λ_{exc} at 254 nm) in the spectral region of 350 to 800 nm and excitation spectra (with λ_{em} set at 613 nm) were measured at room temperature with use of a Spex Fluorolog-3 (Instruments S.A., Inc., U.S.A.) spectrofluorometer equipped with a 450-W xenon lamp as the excitation source. To eliminate the second-order emission of the source radiation, a UV-35 cutoff filter was used.

The measurements of decay lifetime (τ_R) for $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ phases were carried out by exciting the samples by using a Lamda Physik LPX150T excimer laser with ultraviolet wavelength of 248 nm and pulse duration of 0.1 sec; a Hamamatsu R928 type photomultiplier was used as a detector. The CIE chromaticity coordinates of $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ phases were measured to an accuracy of ± 0.001 in chromaticity coordinates (x, y) by using a Minolta CS-100 chromameter.

3. RESULTS AND DISCUSSION

The XRD profiles for $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ ($x = 0.0625\%$, 0.5%, 1%, and 2%) phases are shown in Fig. 1, respectively. The diffraction patterns for $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ phases were found to be exactly the same as that of CaIn_2O_4 reported in JCPDS Card No. 17-643. This observation indicates that pure crystalline CaIn_2O_4 was found in the as-prepared samples and no starting materials nor any other allotropic phase exists. However, no systematic shifting of diffraction peaks in the XRD profiles was observed as x increases and this observation can be attributed to the small amount of Pr^{3+} doped into the CaIn_2O_4 host lattice.

The Pr^{3+} concentration-dependent PL emission spectra for $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ phases shown in Fig. 2 were measured under 254-nm ultraviolet excitation at ambient temperature. A bright fluorescent orange color attributed to an $f \rightarrow f$ transition of praseodymium(III) was observed. In general, the photoluminescent properties of the four $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ samples with different x 's do not differ greatly from one another and no obvious red or blue shift was observed. Essentially, as indicated in Fig. 2, the PL spectra for the four $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ phases essentially consist of three groups of emissions, namely, blue, green, and red, peaking at 492.5 nm, 537 nm, and 605 nm, that were attributed to ${}^3P_0 \rightarrow {}^3H_4$, ${}^3P_1 \rightarrow {}^3H_5$, and ${}^1D_2 \rightarrow {}^3H_4$ transitions of Pr^{3+} , respectively. The emission spectra for $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ were found to be very similar to those of $\text{SrIn}_2\text{O}_4:\text{xPr}^{3+}$ reported by Kao *et al.* (9); the only difference is the relative luminescence intensity for peaks at three spectral regions (i.e., 492 nm, 537 nm, and 605–621 nm). In the previously reported $\text{SrIn}_2\text{O}_4:\text{xPr}^{3+}$ phases (9), the ratio of (integrated red band intensity)/(integrated blue band intensity + integrated green band intensity) is larger than that for $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ and, therefore, the $\text{SrIn}_2\text{O}_4:\text{xPr}^{3+}$ samples show red emission color but $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$

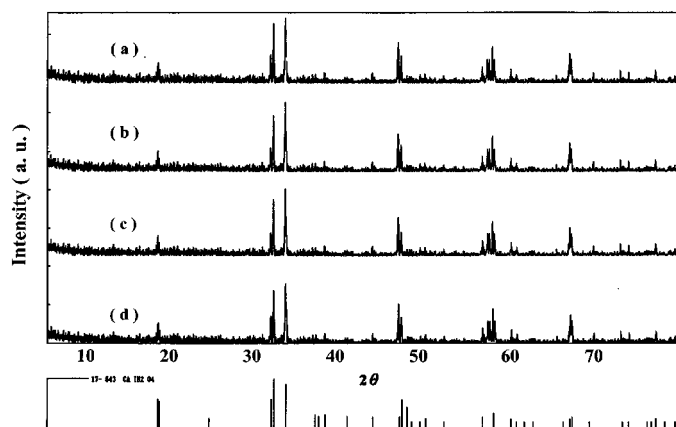


FIG. 1. XRD profiles for $\text{CaIn}_2\text{O}_4:\text{xPr}^{3+}$ phases with $x =$ (a) 6.25×10^{-4} , (b) 0.5%, (c) 1%, and (d) 2%, respectively.

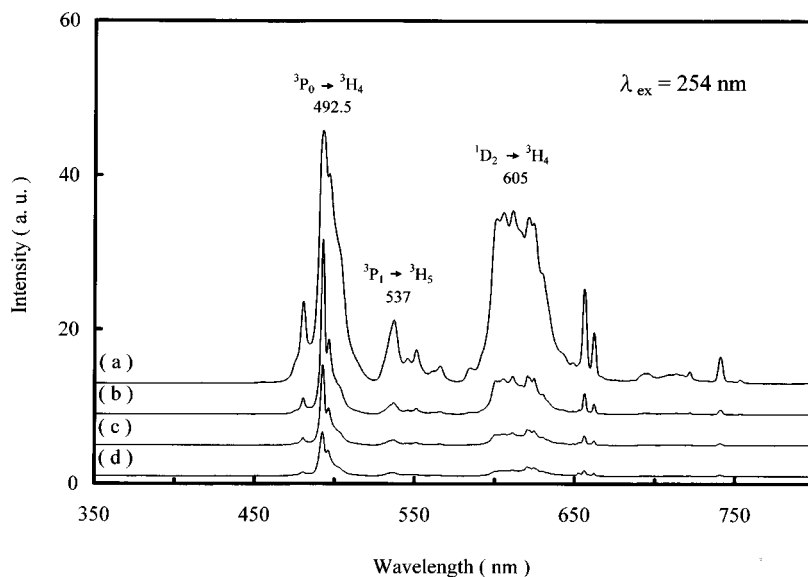


FIG. 2. PL emission spectra for Pr^{3+} -activated $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases with $x =$ (a) 6.25×10^{-4} , (b) 0.5%, (c) 1%, and (d) 2%, respectively.

orange. This observation may be attributed to the difference in crystal field strength that Pr^{3+} experiences in the two alkaline earth indiate host lattices.

As compared to the broadband feature of Pr^{3+} in some hosts such as $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (10), the fluorescence emission spectra attributed to Pr^{3+} for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ exhibit line features. The spectra shown in Fig. 2 also reveal that the width of emission peaks exhibits a considerable dependence on the activator content x . Hence, this observation indicates the strong effect of local crystal field on the energy level structure of Pr^{3+} . The splitting of the energy levels in the

crystal field was proposed to be responsible for the broadening of emission peaks (11).

In order to understand the energy levels involved in the energy absorption process, we have measured the photoluminescence excitation (PLE) spectrum of $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ ($x = 0.0625\%$) and the results are represented in Fig. 3. The spectrum yields the luminescence output with λ_{em} of 605 nm (the strongest emission) as a function of the exciting wavelength (λ_{exc}) and it allows us to construct an energy level scheme for Pr^{3+} in CaIn_2O_4 . The excitation spectrum consists of six peaks corresponding to the transitions from

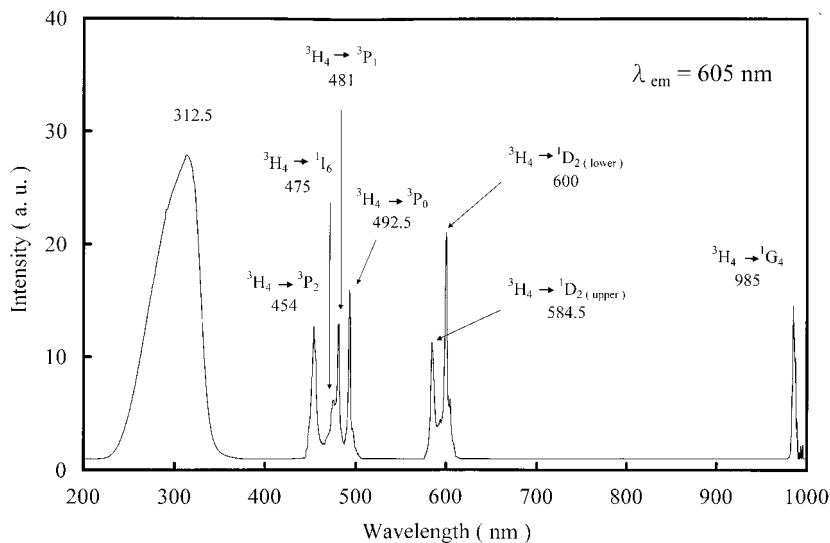


FIG. 3. PLE spectra for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ ($x = 6.25 \times 10^{-4}$) phase with $\lambda_{\text{em}} = 605$ nm.

the fundamental multiplet 3H_4 level to 1G_4 ($\lambda = 985$ nm), $^1D_{2(\text{lower})}$ ($\lambda = 600$ nm), $^1D_{2(\text{upper})}$ ($\lambda = 584.5$ nm), 3P_0 ($\lambda = 492.5$ nm), 3P_1 ($\lambda = 481$ nm), 1I_6 ($\lambda = 475$ nm), and 3P_2 ($\lambda = 454$ nm) in the far-infrared and visible spectral regions, respectively.

To examine the effect of luminescence quenching attributed to activator concentration on the PL emission intensity, we have tested different activator Pr^{3+} concentrations and optimized from 0.0625 atom% to 2 atom%. For accurate comparison of intensity, care was taken to maintain the excitation wavelength (λ_{exc}) and band slits for both excitation and emission monochromators of the spectrofluorometer strictly identical. The integrated fluorescence intensity is represented as a function of nominal Pr^{3+} concentration x and shown in Fig. 4. The correlation of PL intensity and x can be best fit according to the following equation,

$$I = -a \ln x + b,$$

where I is the PL intensity, a and b are scalar constants, and x is Pr^{3+} content (in atom %). The fitting parameters of a and b were found to be 22.4 and 20.0, respectively. A drastic decrease in the PL intensity by more than 1 order of magnitude was observed while Pr^{3+} concentration increased from 0.0625% to 2%. For the composition range investigated, the maximal PL emission intensity was observed in the sample of $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ with x of 0.0625%.

The lifetime or radiative decay time (τ_R) reported here is conventionally defined as the time required for the luminescence intensity to decay down to ca. 36.8% (or $1/e$) of its initial value (12). The observed luminescence decay lifetimes

TABLE 1
Observed Luminescence Decay Lifetime (τ_R) for
 $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ Phases

x (%)	τ_R (μsec)
0.0625	210
0.5	180
1	100
2	50

for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases are summarized in Table 1. The magnitude of τ_R for Pr^{3+} -activated CaIn_2O_4 phases with different Pr^{3+} contents was found to be in the range of 50–210 μsec which is comparable with that (i.e., 132 μsec) reported for $\text{CaTiO}_3:\text{Pr}^{3+}$ (7). Furthermore, a shortening of the lifetime with increasing Pr^{3+} content, presumably due to a concentration quenching effect, was also observed. The observed τ_R and the decay rate appear to meet the application requirement for CRT color televisions. As a matter of fact, not only fluorescence but also phosphorescent afterglow (for several seconds) of $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ ($x = 0.0625\%$) was actually observed by the naked eye under ultraviolet excitation. Investigations of phosphorescence properties for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases are currently in progress.

The observed PL emission spectra (Fig. 2) confirm the fact that blue and green emissions actually dominate the red for all polycrystalline $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phosphors investigated. Therefore, the fluorescence for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ observed is orange but not purely red, as compared to that for

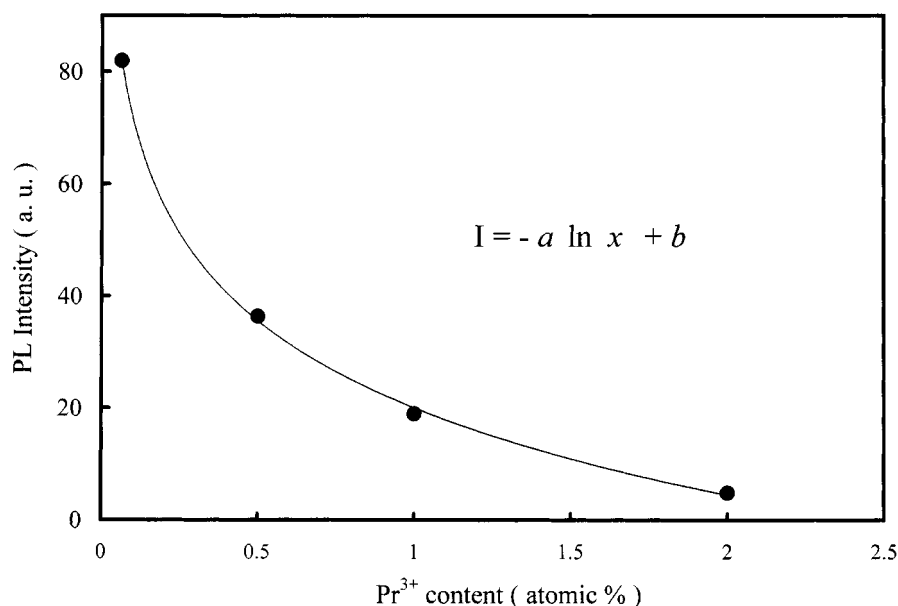


FIG. 4. Integrated PL emission intensity (solid circles) as a function of Pr^{3+} content for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases. The solid line represents the best-fit curve for experimental data.

TABLE 2
Chromaticity Coordinates and Relative Integrated Intensity Ratios for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ Phases

x (%)	Chromaticity coordinates	Ratio of integrated intensity ^a
0.0625	(0.544, 0.297)	0.69
0.5	(0.523, 0.295)	0.96
1	(0.447, 0.299)	1.24
2	(0.442, 0.301)	1.39

^a(Integrated intensity of blue band + integrated intensity of green band)/integrated of red band intensity.

$\text{SrIn}_2\text{O}_4:x\text{Pr}^{3+}$ (9). The orange color emission was analyzed and confirmed with the help of CIE (Commission Internationale de l'Eclairage) chromaticity coordinates and integrated intensity ratios, defined as (integrated blue band intensity + integrated green band intensity)/(integrated red band intensity). The chromaticity coordinates for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ denoted by (x, y) and measured with a chromameter are summarized in Table 2. The coordinates for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases were found to fall in the orange spectral region of the CIE chromaticity diagram represented in Fig. 5. It seems that the color coordinate x decreases linearly with increasing composition x . In general, the coordinate x is very sensitive to the relative ratio of intensity of the emissions in the blue (492 nm) and red (605 nm) regions observed in the PL spectra for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases with different x 's. We have noticed that concentration quenching of Pr^{3+} luminescence occurs at relatively low x and was already observed in the $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phase with x as low

as 6.25×10^{-4} , as compared to that (i.e., 0.2%) found in $\text{CaTiO}_3:\text{Pr}^{3+}$ reported by Diallo *et al.* (7). Since we are not sure whether the sample with $x = 6.25 \times 10^{-4}$ is really optimally doped in terms of emission intensity, it is difficult to predict the color trend for samples with x greater than 2%. However, for those with x less than 6.25×10^{-4} the linear correlation between coordinate x and composition x may still be valid.

In particular, the emissive color of $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ ($x = 6.25 \times 10^{-4}$) phase was found to be appreciably redder than that of samples with other compositions; this observation may be rationalized by the smaller integrated intensity ratios defined and represented in Table 2.

4. CONCLUSIONS

We have synthesized a series of unprecedented orange-emitting and Pr^{3+} -activated calcium indates (CaIn_2O_4) and investigated their photoluminescent properties. The PL emission spectra of $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases essentially exhibited three groups of emissions with λ_{em} peaking at 492.5 nm, 537 nm, and 605 nm, which are attributed to $^3P_0 \rightarrow ^3H_4$, $^3P_1 \rightarrow ^3H_5$, and $^2D_2 \rightarrow ^3H_4$ transitions of Pr^{3+} , respectively. The activator concentration quenching effect has been investigated and the optimal Pr^{3+} content was determined to be 6.25×10^{-4} for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases with $6.25 \times 10^{-4} \leq x \leq 2\%$. The decay lifetime was found to be in the range of 50–210 μsec for $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases, depending on x . On the other hand, the hue of orange-emitting $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$ phases with different x 's was compared to NTSC red, green, and blue, as indicated by the coordinates in the CIE chromaticity diagram.

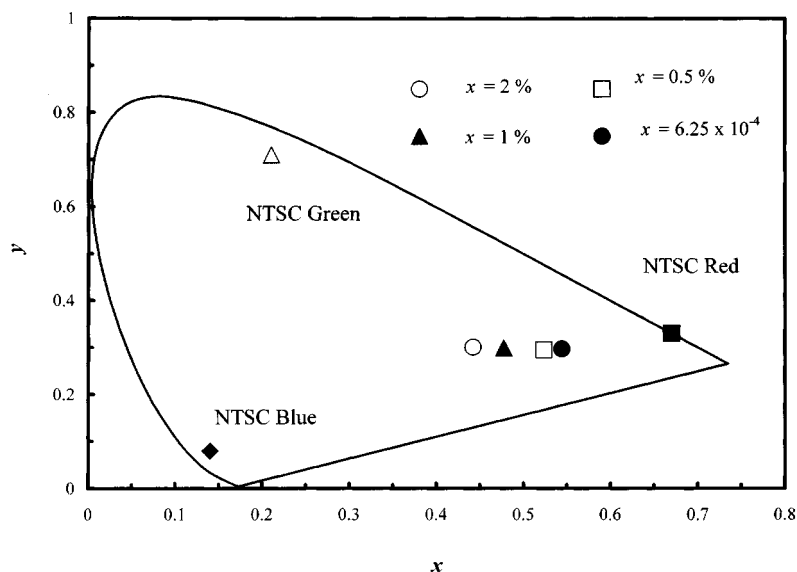


FIG. 5. Chromaticity diagram indicating the difference of hues of $\text{CaIn}_2\text{O}_4:x\text{Pr}^{3+}$, NTSC green, NTSC red, and NTSC blue phosphors (NTSC = National Television Standard Color).

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