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A Study on the Luminescent Properties of Red-Emitting Praseodymium-Activated $SrIn_2O_4$ Phosphors

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The photoluminescent (PL) properties of new red-emitting praseodymium-activated strontium indates have been investigated. A series of $SrIn_2O_4$:$x$$Pr^{3+}$ ($x = 6.25 \times 10^{-4}$, 0.5%, 2%, and 4%) phases were synthesized and found to exhibit red emission. With different levels of Pr^{3+} doping, the absolute brightness, CIE chromatic characteristics, PL and cathodoluminescence spectra, and luminescence decay lifetime (τ_R) for $SrIn_2O_4$:$x$$Pr^{3+}$ have been systematically investigated. The results are reported and their implications are discussed. © 2001 Academic Press

Key Words: **luminescence; $SrIn_2O_4$:xPr; photoluminescence spectra; cathodoluminescence spectra; decay curve; chromaticity diagram.**

1. INTRODUCTION

The development of displays has always been accompanied by improvements in the phosphors used. For example, the advent of the present color television was dependent on the development of an efficient red phosphor (1). Display technology will not be exploited to its full potential until the phosphors that operate under the required conditions are synthesized. For instance, cathode ray phosphors have been optimized to endure the bombardment of high-voltage electron beams. In particular, for FED applications intrinsically conducting materials were generally adopted as the host lattice of low-voltage phosphor (2) to prevent the buildup of space charges at the surface of phosphors at low-voltage excitation. Therefore, there has been an urgent need to investigate new phosphors with good high-voltage performance and decent intrinsic electrical conductivity for practical uses. In this work, we investigated the possible combination of a new host lattice and a red-emitting activator with luminescence lying inside the eye sensitivity curve and having a high lumen equivalent.

Semiconducting $SrIn_2O_4$ with a reported bandgap (E_g) of 3.6 eV was found to crystallize in an orthorhombic $CaFe_2O_4$-type structure with space group *Pnam* and the lattice parameters $a = 9.83$ Å, $b = 11.50$ Å, and $c = 3.27$ Å (3). There exist a few unoccupied cation sites in the lattice of $SrIn_2O_4$ and this offers a great potential for cation substitutions. It is known that luminescence is related to the presence of defects and, thus, the unoccupied sites in the lattice must have an influence on the luminescence properties of phosphors. As far as we are concerned, no previous work on phosphors with $SrIn_2O_4$ as a host lattice has been reported in the literature.

On the other hand, trivalent praseodymium has been known to exhibit a very interesting luminescence as an activator ion, since its energy level contains several metastable multiplets $^3P_{0,1,2}$, $^1D_2$, and $^1G_4$ that offer the possibility of efficient emissions such as red (from the $^1D_2$ level), green (from the $^3P_0$ level), blue (from the $^1S_0$ level), and ultraviolet (from the $4f5d$ state) between the blue and the red spectral regions (4). Furthermore, the emission color of Pr^{3+} strongly depends on the structure of the host lattice, the concentration of activators, and the excitation conditions. The spectra of red-emitting Pr^{3+} phosphors were reported to be similar to those of Eu^{3+}-activated phosphors that have been used as red phosphors in cathode ray tubes with great success. For instance, Cho *et al.* (5) reported that in Pr^{3+}-activated $CaTiO_3$ crystals, an intense emission peaking at 613 nm was observed in the photoluminescence spectra and characteristics of low-voltage excitation were also investigated. Diallo *et al.* reported that $CaTiO_3$:Pr^{3+} was excitable in a wide ultraviolet range and exhibited a unique red emission from the Pr^{3+} $^1D_2$ level (6). Zhang *et al.* presented the results of studies on the dynamic spectroscopic properties of the excited states and discussed the effect of the $(Sr_xBa_{1-x})Nb_2O_6$ host lattice on the luminescence of Pr^{3+} (7).

Motivated by the investigations described above, we have begun investigations on the luminescent properties of Pr^{3+}-activated $SrIn_2O_4$ phases as potential phosphors. In this work we report our results on the luminescent

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properties, apparent decay lifetime, and chromatic characteristics of $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ with different activator concentrations.

2. EXPERIMENTAL

Polycrystalline $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ phases with $x = 6.25 \times 10^{-4}$, 0.5%, 2%, and 4% were synthesized by conventional solid state reactions. Stoichiometric amounts of source materials $SrCO_3$, In_2O_3, and Pr_2O_3 (all from Aldrich Chemicals Co., Milwaukee, WI) were thoroughly mixed and finely ground together. The mixture was first calcined at 550°C in air for 6 h and then sintered at 1200°C for 24 h also in the air; however, no flux was used in this work.

The phase purity and homogeneity of the as-prepared $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ samples were investigated by X-ray diffraction (XRD). The XRD profiles for Pr^{3+}-activated $SrIn_2O_4$ phases were collected by using a MAC Science MXP-3 automatic diffractometer with a graphite-monochromatized and Ni-filtered Cu$K\alpha$ radiation. Special caution was taken to make sure that no starting material or any other allotropic form is present in the XRD profiles. The ambient temperature photoluminescence (PL) spectra in the spectral region of 350–800 nm and excitation spectra were measured by using a Spex Fluorolog-3 spectrofluorometer equipped with a 450-W xenon lamp. An UV-35 cut-off filter was used to eliminate the second-order emission from the source. The cathodoluminescence (CL) spectra of polycrystalline $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ ($x = 6.25 \times 10^{-4}$) powder were measured with a Topcon ABT-150s type scanning electron microscope equipped with a Jobin Yvon H20UV monochromator, with the operation voltage ranging from 5 to 20 kV.

The measurements of decay lifetimes for Pr^{3+}-activated $SrIn_2O_4$ phases were carried out by exciting the samples using a Lamda Physik LPX150T excimer laser with a wavelength of 248 nm and a pulse duration of 0.1 sec, and the detector was equipped with a Hamamatsu R928 type photomultiplier. The absolute brightness of $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ was recorded by using a Topcon BM-7 luminance colorimeter.

3. RESULTS AND DISCUSSION

The XRD profiles for $SrIn_2O_4{:}x\mathrm{Pr}$ ($x = 6.25 \times 10^{-4}$, 0.5%, 2%, and 4%) phases were found to be exactly the same as that of $SrIn_2O_4$ reported in the JCPDS card no. 33-1336. The XRD data indicate that the as-prepared samples are essentially single-phased regardless the amount of Pr^{3+} doped. However, the presence of a second phase in the proportion of a few percents cannot be ruled out for the samples with the highest Pr^{3+} concentrations. Furthermore, no systematic shifting in XRD profiles was observed as x was increased and this observation indicated that the lattice dimension is insensitive to the variation of dopant content for $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ phases.

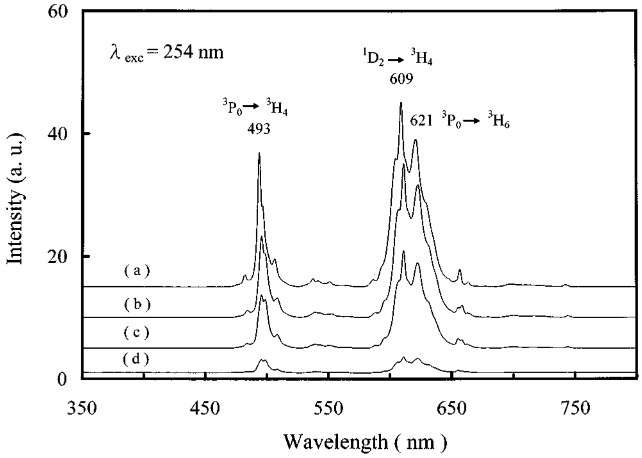

FIG. 1. PL emission spectra for the $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ phases with $x =$ (a) 6.25×10^{-4}, (b) 0.5%, (c) 2%, and (d) 4%.

The activator concentration-dependent PL spectra of $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ phosphors were measured under ultraviolet excitation with λ_{exc} of 254 nm at ambient temperature and the results are shown in Fig. 1. Although the excitation energy does not coincide with any energy difference between any two $4f$ levels of Pr^{3+}, it might correspond to a transition coupling the valence to the conduction band. However, typical Pr^{3+} emissions presumably induced by the excitation through the host were clearly observed. The emission spectra for as-prepared $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ phases exhibited the typically narrow line features of rare earth ions and consisted of two major groups in the blue and red spectral regions. The emission maxima peaking at 493 nm, 609 nm, and 621 nm were attributed to the transitions $^3P_0 \rightarrow {}^3H_4$, $^1D_2 \rightarrow {}^3\mathrm{H}_4$, and $^3P_0 \rightarrow {}^3H_6$ of Pr^{3+}, respectively (7).

For simplicity, only the excitation spectrum for $SrIn_2O_4{:}x\mathrm{Pr}^{3+}$ ($x = 6.25 \times 10^{-4}$) exhibiting the optimal luminescence intensity is represented in Fig. 2. The spectrum reveals the luminescence output with λ_{em} of 615 nm as a function of the exciting wavelength (λ_{exc}). The excitation spectrum for Pr^{3+}-activated $SrIn_2O_4$ consists of five groups of emission peaks corresponding to transitions from the fundamental multiplet $^3H_4$ level to $^1D_2$ ($\lambda = 583$ nm), $^3P_0$ ($\lambda = 492$ nm), $^3P_1$ ($\lambda = 480$ nm), $^1I_6$ ($\lambda = 473$ nm) and $^3P_2$ ($\lambda = 452$ nm), respectively.

To investigate the concentration quenching effect on the PL emission intensity and the lumen intensity attributed to activator concentration, we have doped different levels of Pr^{3+} with composition ranging from 6.25×10^{-4} to 4% into the $SrIn_2O_4$ host. The excitation wavelength and band slit of the spectrofluorometer were maintained consistent dur-

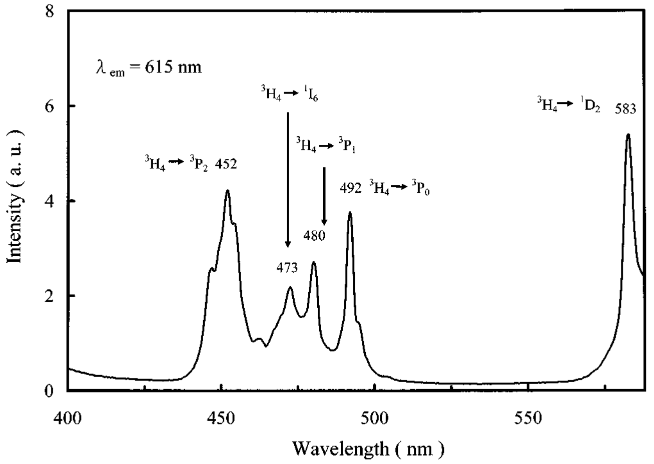

FIG. 2. PL excitation spectra for the $SrIn_2O_4$:xPr^{3+} ($x = 6.25 \times 10^{-4}$) phase with λ_{em} = 615 nm.

TABLE 1
Decay Lifetime (τ_R) for $SrIn_2O_4$:xPr Phases

x (atom %)	τ_R (μsec)
0.0625	49
0.5	63
2	42
4	23

ing measurements for accurate comparison of intensity. A drastic decrease of more than 1 order of magnitude in the PL emission intensity was observed while the Pr^{3+} content was increased from 6.25×10^{-4} to 4%, as indicated by the data shown in Fig. 3. For the composition range investigated, the maximal PL emission intensity was observed for the sample with $x = 6.25 \times 10^{-4}$. On the other hand, the absolute brightness for $SrIn_2O_4$:xPr^{3+} phases under ultraviolet excitation (λ_{exc} = 365 nm) is measured with the power of excitation source of 2.3 mW and is also represented in Fig. 3. The absolute brightness was found to be 0.305, 0.153, 0.115 and 0.001 cd/m^2 for $SrIn_2O_4$:xPr^{3+} phases with $x = 6.25 \times 10^{-4}$, 0.5%, 2%, and 4%, respectively. The strongest brightness was observed for the sample with a Pr^{3+} concentration of 6.25×10^{-4}, which is considered to be the optimum activator concentration. Therefore, it is concluded that for $SrIn_2O_4$:xPr^{3+} phases the luminescence quenching due to Pr^{3+} occurs at a relatively low concentration (i.e., below 6.25×10^{-4}), much lower than that observed by Diallo *et al.* in $CaTiO_3$:Pr^{3+} (6). This observation indicates that the concentration quenching due to Pr^{3+} is very sensitive to the type of host into which Pr^{3+} is doped. With such a low quenching concentration a technique to disperse Pr^{3+} ions effectively in the host lattice of $SrIn_2O_4$ may have to be developed to gain some emission efficiency.

The observed apparent luminescence decay lifetimes τ_R (8) for $SrIn_2O_4$:xPr^{3+} phases are summarized in Table 1. The experimental decay lifetimes for Pr^{3+} in $SrIn_2O_4$: xPr^{3+} phases with different activator contents were found to be of the same order of magnitude but significantly shorter than that (i.e., 132 μsec) observed in $CaTiO_3$:Pr^{3+} (6). The observed τ_R was also found to meet the application requirement for CRT color televisions. As a matter of fact, not only fluorescence but also phosphorescent afterglow lasting for few seconds were observed by the naked eye under ultraviolet excitation for the $SrIn_2O_4$:xPr^{3+} ($x = 6.25 \times 10^{-4}$) phase. Investigations of the phosphorescent properties of $SrIn_2O_4$:xPr^{3+} phases are currently in progress.

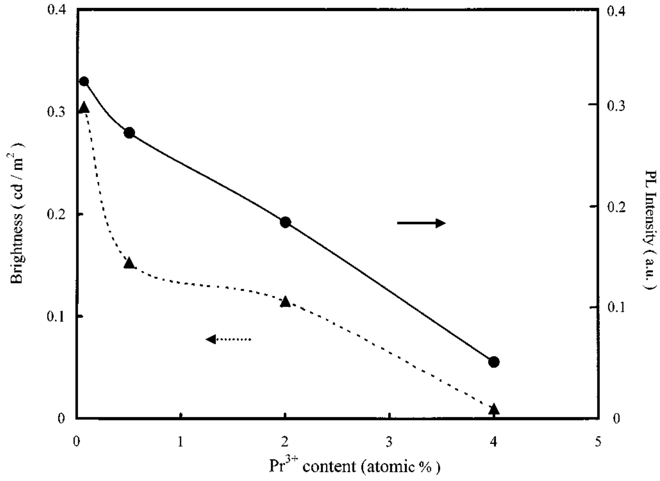

FIG. 3. Integrated PL intensity and absolute brightness as functions of Pr^{3+} content (x) for the $SrIn_2O_4$:xPr^{3+} phases. The solid and dashed lines are guides only.

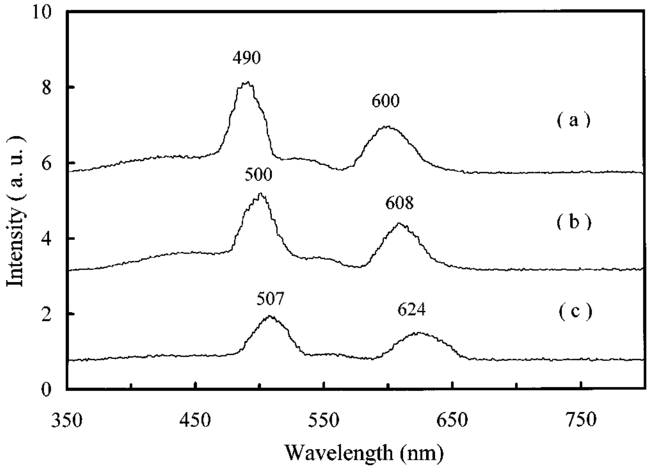

FIG. 4. CL spectra for the $SrIn_2O_4$:xPr^{3+} ($x = 6.25 \times 10^{-4}$) phase with excitation voltage of (a) 5 kV, (b) 10 kV, and (c) 20 kV.

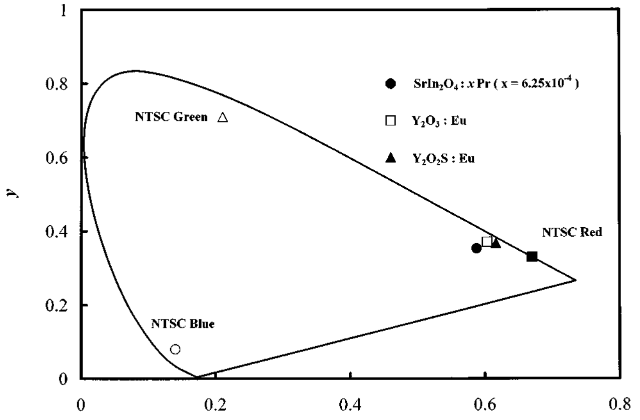

FIG. 5. Chromaticity diagram indicating the difference of hues for red-emitting phosphors of $SrIn_2O_4{:}xPr^{3+}$, $Y_2O_3{:}Eu^{3+}$, and $Y_2O_2S{:}Eu^{3+}$. NTSC represents National Television Standard Committee.

To investigate the potential of Pr^{3+}-activated indates as a cathodoluminescent material, we have also studied the CL spectra of $SrIn_2O_4{:}xPr^{3+}$ ($x = 6.25 \times 10^{-4}$). The luminescence intensity as a function of excitation voltage (from 5 to 20 kV) was measured and is represented in Fig. 4. An analysis of the CL spectra for $SrIn_2O_4{:}xPr^{3+}$ indicated that the Pr^{3+} emission tends to be broadened, as compared to that observed in the PL spectra. Due to the thermal effect that originates from heating induced by electron beam bombardment, the full width at half-maximum (FWHM) of the emission bands was found to be much wider than that of the PL spectra for $SrIn_2O_4{:}xPr^{3+}$ phases. We have also observed an apparent red shift in the emission wavelength for $SrIn_2O_4{:}xPr^{3+}$ as the excitation voltage increases, as indicated by the CL spectra shown in Fig. 4. The rationalization for this observation is uncertain and requires further investigations.

On the other hand, the Commission Internationale de l'Eclairage (CIE) chromaticity coordinates of $SrIn_2O_4{:}xPr^{3+}$ ($x = 6.25 \times 10^{-4}$) were calculated from the corresponding PL spectrum represented in Fig. 1a and found to be (0.587, 0.354) with an accuracy of ± 0.001 in (x, y). The chromaticity coordinates for $SrIn_2O_4{:}xPr^{3+}$ ($x = 6.25 \times 10^{-4}$) were then compared with those of two well-known red phosphors, $Y_2O_3{:}Eu^{3+}$ with (0.666, 0.332) and $Y_2O_2S{:}Eu^{3+}$ with (0.630, 0.365), respectively (9), and the results are summarized in the CIE chromaticity diagram shown in Fig. 5.

We found that the hue of $SrIn_2O_4{:}xPr^{3+}$ ($x = 6.25 \times 10^{-4}$) is apparently more orange than that of $Y_2O_3{:}Eu^{3+}$ or $Y_2O_2S{:}Eu^{3+}$. This observed hue may be attributed to the contribution from the blue emission band centered at λ_{em} of 493 nm of $SrIn_2O_4{:}xPr^{3+}$ ($x = 6.25 \times 10^{-4}$). Furthermore, the observed brightness decrease in green and red in $SrIn_2O_4{:}xPr^{3+}$ is also worthy of investigation. The purity of as-prepared samples and/or whether they are free of Pr^{4+} (since samples of $SrIn_2O_4{:}xPr^{3+}$ were sintered in the air at 1200°C) may be the key factor responsible for the above observations. Special techniques capable of detecting these impurities may have to be adopted.

4. CONCLUSIONS

We have synthesized a series of new red-emitting $SrIn_2O_4{:}xPr^{3+}$ phases and investigated their luminescent properties. The PL emission spectra of $SrIn_2O_4{:}xPr^{3+}$ phases exhibited two groups of emission with λ_{em} peaking at 493 nm, 609 nm, and 621 nm which are attributed to the transitions of $^3P_0 \rightarrow {}^3H_4$, $^1D_2 \rightarrow {}^3H_4$, and $^3P_0 \rightarrow {}^3H_6$ for Pr^{3+}, respectively. The optimal Pr^{3+} content was determined to be 6.25×10^{-4} for $SrIn_2O_4{:}xPr^{3+}$ phases, as indicated by studies on the quenching effect of activator concentration. On the other hand, the Pr^{3+} emission tends to be broadened and to shift to a slightly longer wavelength, as indicated by the CL spectra. Analysis of the chromaticity diagram indicated that the emitting hue was orange-red for $SrIn_2O_4{:}xPr^{3+}$ phases, as compared to a purely red-emitting $Y_2S_2O{:}Eu^{3+}$ phosphor.

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