

# Effects of Divalent Cation Incorporation on the Emission Characteristics of $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$ Phosphors

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## Abstract

*In this study, we have investigated the substitutional effects of In ions with divalent ones in the  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  phosphors and the relative change of the red and blue emissions. The substitutional Zn ions greatly intensified the blue emission band at 492 nm, but the red emission band at 608 nm was relatively less changed. On the other hand, Cd ions have no effect on the relative intensities. We explained the phenomena in connection with the distance of Pr-O, i.e., covalency experienced by a  $\text{Pr}^{3+}$  ion.*

## 1. Introduction

For field emission displays (FEDs) applications, intrinsically conducting materials were generally adopted as the host lattice to prevent the buildup of space charges at the surface of phosphors at low-voltage excitation. On the other hand, since the conventional sulfide phosphors are known to deteriorate metal emitters of FEDs by the sulfur desorption from the anode plate [1], the sulfide phosphors like ZnS with good brightness cannot be used. Therefore, it is necessary to investigate new oxide phosphors with good emission performance at low-voltage and sufficient intrinsic electrical conductivity for the practical uses.

Of various candidates,  $\text{ATiO}_3$  and  $\text{Aln}_2\text{O}_4$  ( $A = \text{Ca}, \text{Sr}, \text{Ba}$ ) are very promising ones, because of their intrinsic conductivity or semiconducting properties. It was reported that the Pr-activated  $\text{CaTiO}_3$ ,  $\text{CaIn}_2\text{O}_4$ , and  $\text{SrIn}_2\text{O}_4$  show very efficient luminescence [2-4]. On the other hand, although Pr-activated  $\text{SrTiO}_3$  and  $\text{BaTiO}_3$  rarely presented any visible emission, the codoping with trivalent ions greatly enhanced the red emission intensity.  $\text{SrIn}_2\text{O}_4$  is a promising candidate as a host lattice for FED phosphors, and Pr-activated

$\text{SrIn}_2\text{O}_4$  was an efficient red emitting phosphor and had good color purity [3].

The activator,  $\text{Pr}^{3+}$ , shows a number of different emission spectra depending on the host materials [5, 6]. One of the relative intense emission lines in the emission spectra is the transition (red) from the  $^1\text{D}_2$  level to the ground state of  $^3\text{H}_4$  and the other is the transition (blue) from the  $^3\text{P}_0$  level to  $^3\text{H}_4$ . The usual host material including  $\text{Pr}^{3+}$  shows either only red or only blue color, but there are host materials showing both of the colors. It has been found that the Pr-activated  $\text{CaTiO}_3$  phosphor shows intense red emission [2], but Pr-activated  $\text{SrIn}_2\text{O}_4$  phosphor does both of the emissions with rather intense blue emission [3]. Both of the blue and red emission was reported to greatly depend on the crystal structure of the host lattice, covalency of Pr-O bond, and additional codopants [7, 8]. The transition of  $^3\text{P}_0$  or  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  is a forbidden f-f dipole transition. However, when the rare earth ion occupies a non-inversion center, the odd crystal field terms mix the  $4f^n$  configuration with states of opposite parity, such as states of 5d configuration, and relax the parity selection rule [9]. Also, the relative position of the 4f5d level has an effect on the transition probabilities of the emissions. It is expected that other ions with the activators shift the 4f5d level and the relative intensity of the two emissions could be modified.

In this study, we have investigated the luminescence characteristics of Pr-activated  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  phosphors. First of all, we have investigated emission characteristics with various concentration of Pr and examined the quenching concentration of luminescence. With the optimized concentration of Pr, we investigated the substitutional effects of In ions with divalent ones such as Zn and Cd in the  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  phosphors and the relative change of the red and blue emissions.

## 2. Experimental

Powder  $\text{SrIn}_2\text{O}_4:x\text{Pr}^{3+}$  phosphors were prepared by the conventional solid state reactions. The starting materials for the host lattice were  $\text{SrCO}_3$  (Aldrich),  $\text{In}_2\text{O}_3$  (Aldrich). For the accurate control of the concentration of Pr, we used an atomic absorption standard solution of Pr (AccuStandard Inc.), which has a concentration of  $998\mu\text{g/ml}$ . The concentration of Pr was changed from 0.001% to 0.2%. The starting materials taken in stoichiometric proportions were thoroughly homogenized in an agate mortar for 90 minutes with ethanol and then transferred to alumina crucibles for heat treatment in air. The sintering temperature and time were  $1200^\circ\text{C}$  and 12 hours, respectively.

For the accurate incorporation of divalent ions such as Zn and Cd, we prepared and used solutions of zinc acetate or cadmium carbonate dissolved in diluted nitric acid. Divalent ions substituted In ions, so that the mixture with the stoichiometry such as  $\text{SrIn}_{2-y}\text{B}_y\text{O}_4:\text{Pr}^{3+}$  ( $\text{B}=\text{Zn}$  or  $\text{Cd}$ ) was sintered through the above procedure. The cathodoluminescence (CL) spectra were obtained using a demountable ultrahigh vacuum chamber equipped with in-house assembled CL spectrophotometer (ISS PC1). The adjustable electron beam (Kimball Physics, FRA-2X1-2/EGPS-2X1) is incident normal to the compacted powder specimen. The measurements were carried out with excitation voltage of 1 kV, and the beam current density of  $20\mu\text{A}/\text{cm}^2$ . The photoluminescence emission/excitation spectra were obtained using the ISS PC1 spectrophotometer.

## 3. Results and discussion

Figure 1 shows cathodoluminescence (CL) spectra of  $\text{SrIn}_2\text{O}_4:x\text{Pr}^{3+}$  with various concentrations of Pr. Contrary to usual lanthanide-activated phosphors, the quenching concentration was observed at a Pr concentration of 0.05 mole%, which is much lower than the usual value of 0.2 mole% [10]. Another example showing such a low quenching concentration is Pr-activated  $\text{CaTiO}_3$  phosphor, the concentration of which is 0.01 mole% [11]. It has been found that the degree of covalency experienced by the  $\text{Pr}^{3+}$  ions is the most important factor determining the quenching concentration of luminescence. The 4f and 5d orbitals of  $\text{Pr}^{3+}$  will be more delocalized in more covalent compound, thus leading to a larger wavefunction

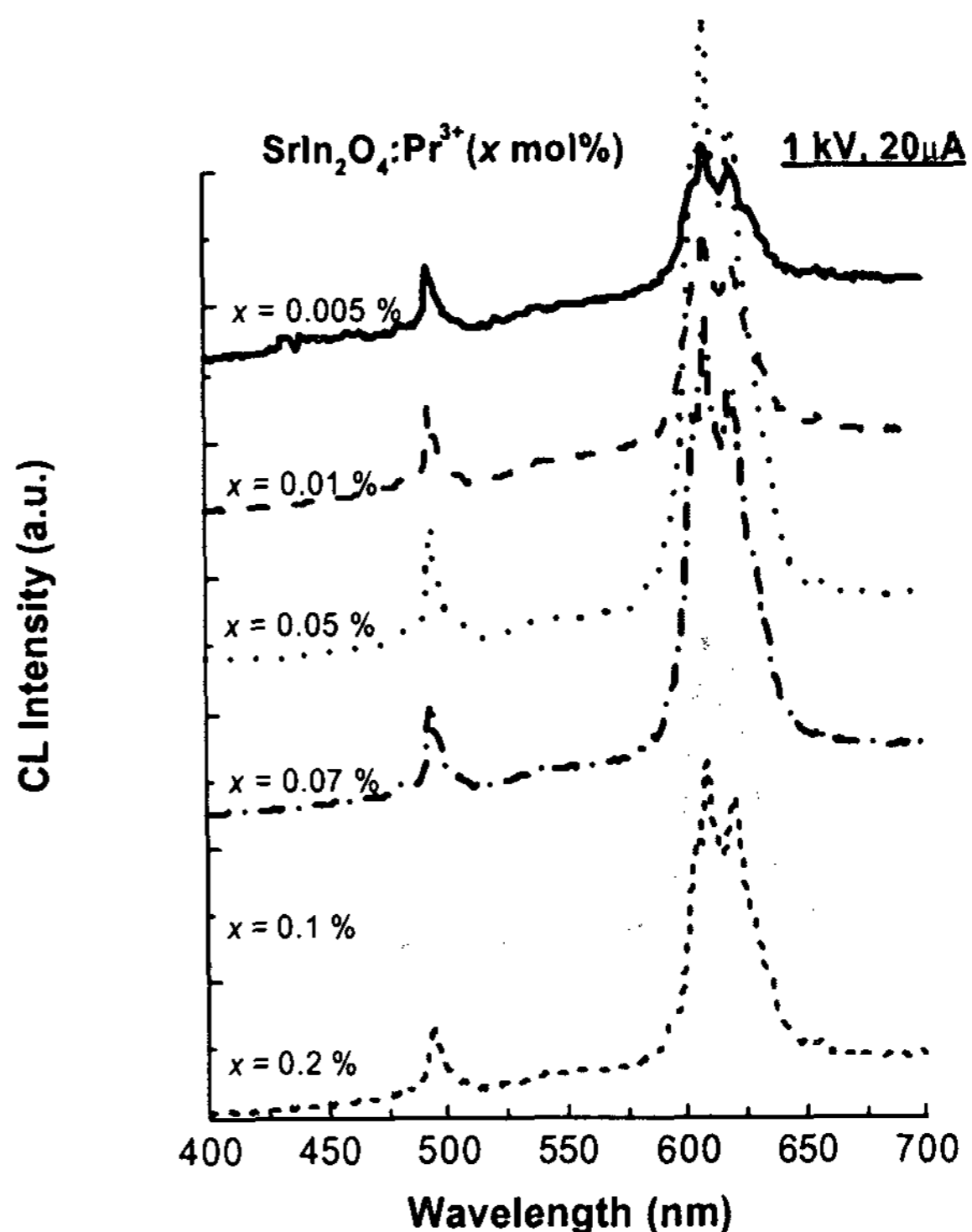
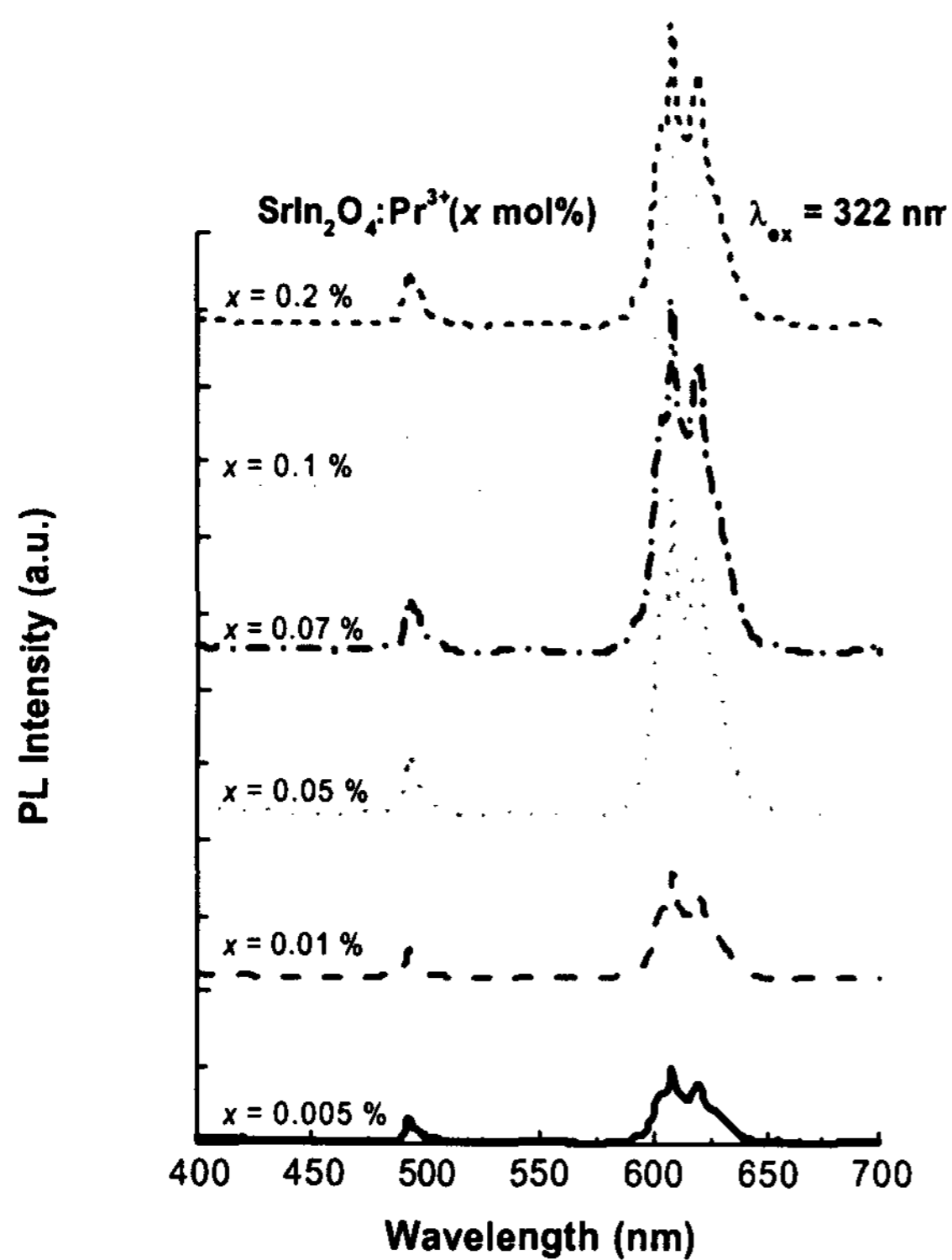


Figure 1. CL spectra of the  $\text{SrIn}_2\text{O}_4:x\text{Pr}^{3+}$  with various  $\text{Pr}^{3+}$  concentrations (extraction voltage and current = 1 kV,  $20\mu\text{A}$ ).

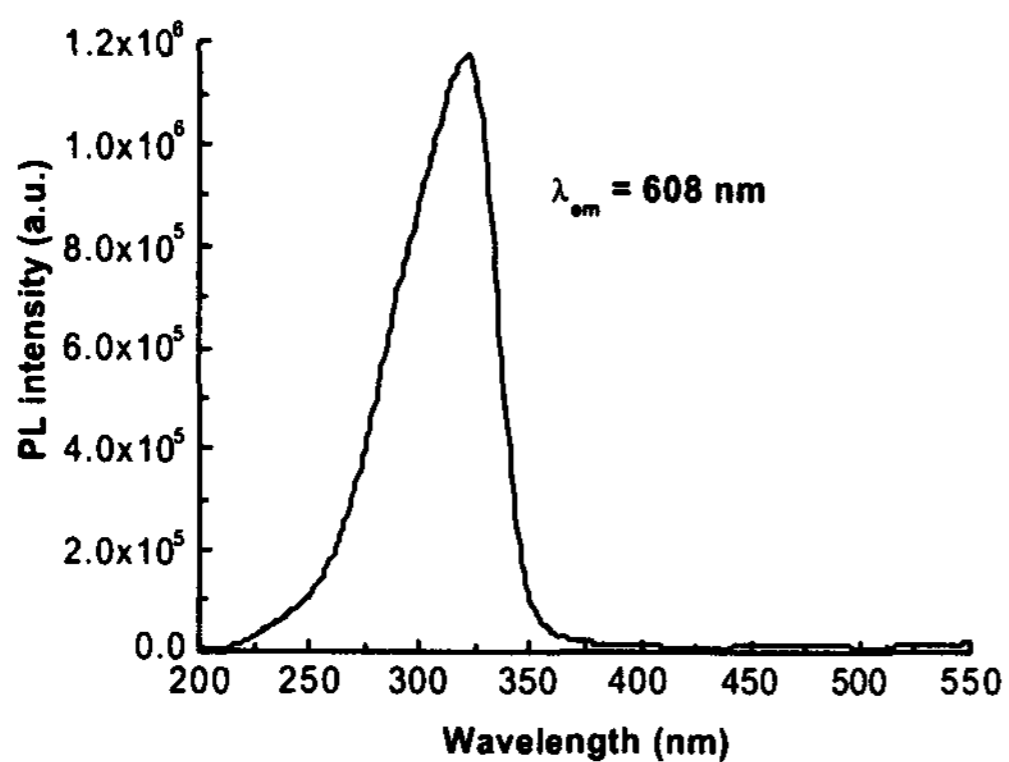
overlap and a more effective superexchange interaction between the  $\text{Pr}^{3+}$  ions [7]. The covalency of  $\text{Pr}^{3+}$  ions in each compound is uncertain and requires further investigations.

The CL spectra are the same for all concentrations and show the blue emission line at 492 nm from  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition. While the blue emission in  $\text{CaTiO}_3:\text{Pr}^{3+}$  phosphor was not observed,  $\text{SrIn}_2\text{O}_4:x\text{Pr}^{3+}$  shows relatively intense emission and behave like the red emission of 608 nm ( $^1\text{D}_2 \rightarrow ^3\text{H}_4$ ) with the concentrations.

Figure 2(a) shows photoluminescence (PL) emission spectra of  $\text{SrIn}_2\text{O}_4:x\text{Pr}^{3+}$  with various concentrations of Pr. Contrary to the CL spectra, the largest intensity was observed for the sample with a  $\text{Pr}^{3+}$  concentration of 0.07 mole%. Figure 2(b) illustrates excitation spectrum of  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  (0.07 mole%) with  $\lambda_{\text{em}} = 608$  nm. The broad band peaking at 322 nm was shown in Fig. 2(b). It was reported that the bandgap of the host lattice,  $\text{SrIn}_2\text{O}_4$ , is 3.6 eV [3, 12]. Therefore, the broad band corresponds to the



(a)



(b)

Figure 2. (a) PL emission spectra of the  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  with various  $\text{Pr}^{3+}$  concentrations ( $\lambda_{\text{ex}} = 322 \text{ nm}$ ), (b) PL excitation spectrum of  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  ( $\lambda_{\text{em}} = 608 \text{ nm}$ ).

interband transition of the host. Like the  $\text{CaTiO}_3:\text{Pr}^{3+}$  phosphor, the host material,  $\text{SrIn}_2\text{O}_4$ , absorbs the UV excitation energy and transfer the energy to the activator.

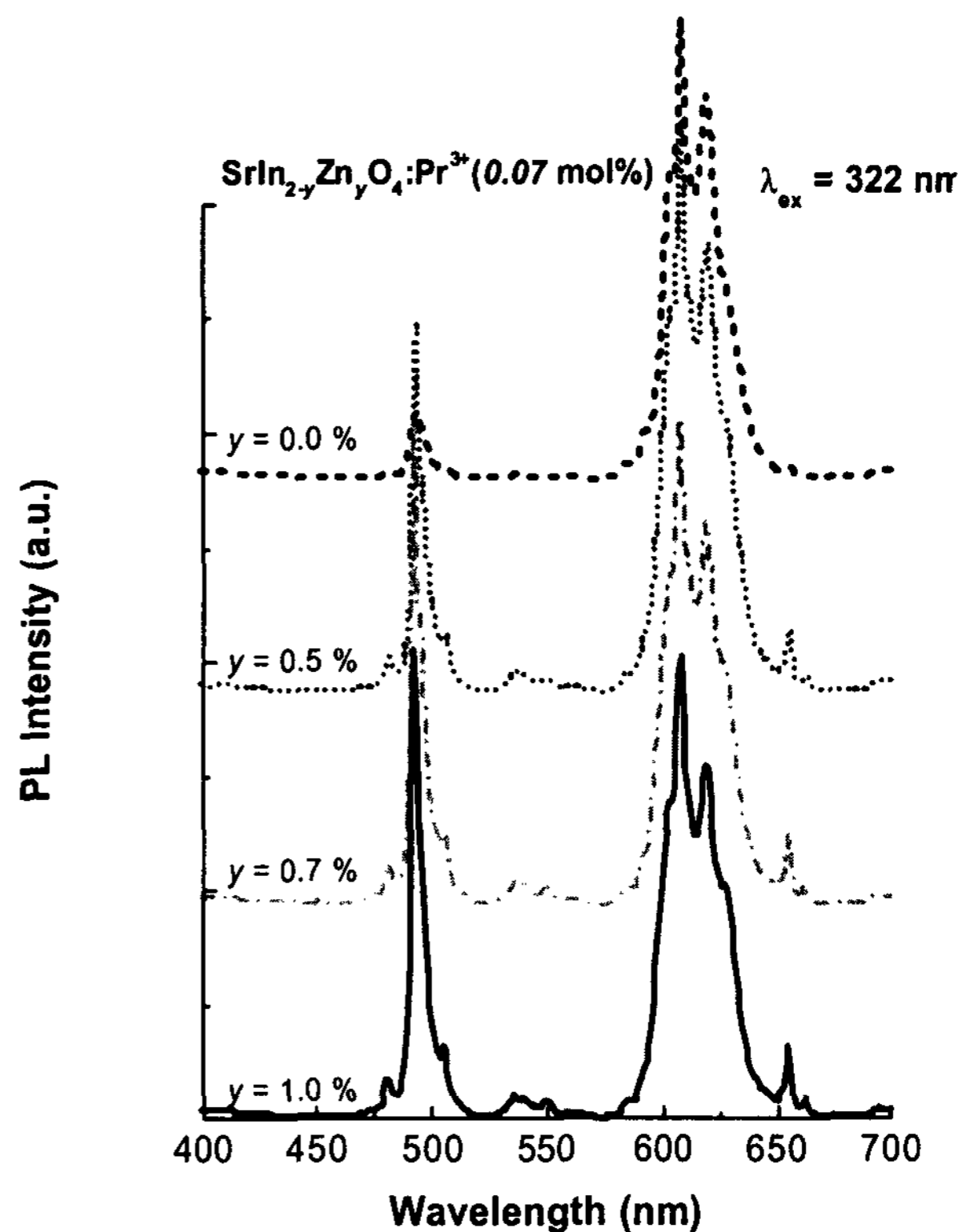


Figure 3. PL emission spectra of the  $\text{SrIn}_{2-y}\text{Zn}_y\text{O}_4:\text{Pr}^{3+}$  (0.07%) with various Zn concentrations ( $\lambda_{\text{ex}} = 322 \text{ nm}$ ).

We investigated the substitutional effects of In ions with divalent ones (Zn and Cd) in the  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  phosphors on the luminescence characteristics. The PL emission spectra of the phosphor with various concentrations of Zn are shown in Fig. 3. The dominant effect of the Zn substitution was the enhancement of the blue emission line at 492 nm. At the concentration of 0.7%, the peak intensities of 492 nm and 608 nm were the same and above the value, both of the intensities began to decrease. On the other hand, the substitution of Cd had rarely an effect on the relative intensities of 492 nm and 608 nm (Fig. 4). But, both of the intensities were decreased.

The ionic radii of In, Zn, and Cd in the octahedral site (coordination number = 6) are 94, 88, and 109 pm, respectively. And the radii of Sr and Pr with the coordination number = 8 are 140 and 126.6, respectively. Therefore, it is expected that the Zn or Cd ions should be substituted with In ion and the Pr ion with Sr ion.

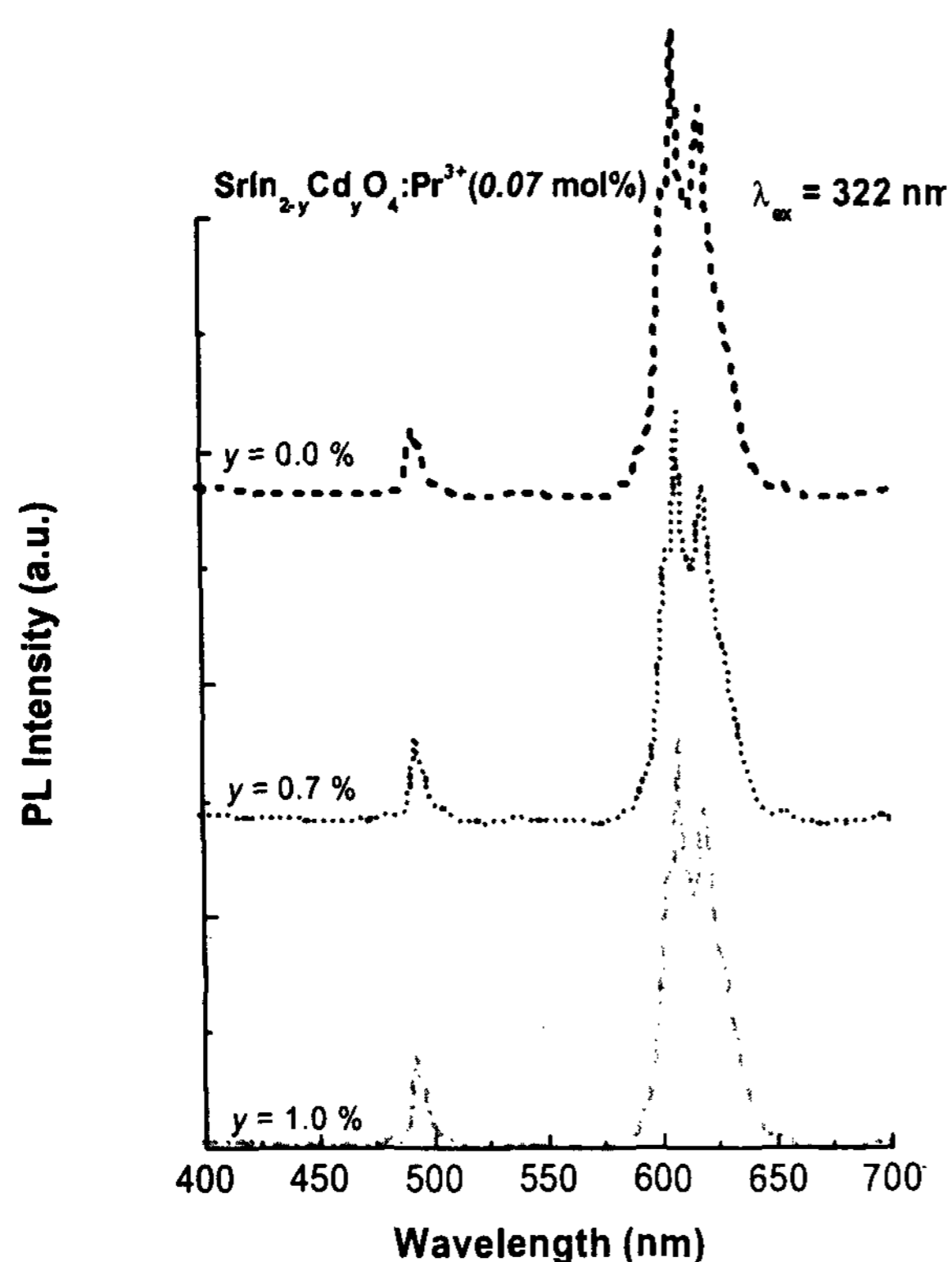


Figure 4. PL emission spectra of the  $\text{SrIn}_{2-y}\text{Cd}_y\text{O}_4:\text{Pr}^{3+}$  (0.07%) with various Zn concentrations ( $\lambda_{\text{ex}} = 322 \text{ nm}$ ).

It was found that the most important factor for determining the relative intensities of  $^3\text{P}_0$  and  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transitions is the distance of Pr-O [8]. If the distance of Pr-O is long, the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition is dominant. On the other hand, if the distance is short, the  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition is dominant.

If Zn ions with smaller radius substitute In ions, then the relative distance of Pr-O is expected to elongate. So, the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition will be dominant like in Fig. 3. On the other hand, if Cd ions with larger radius substitute In ions, the  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition will be dominant like in Fig. 4.

#### 4. Conclusion

In this study, we have investigated the luminescence characteristics of  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  phosphors with various concentrations of  $\text{Pr}^{3+}$  by cathodoluminescence and photoluminescence measurements. It was found that the quenching concentration for CL is 0.05 % and one

for PL is 0.07 %, which is very low compared with usual one. In addition, we have investigated the substitutional effects of In ions with divalent ones such as Zn and Cd in the  $\text{SrIn}_2\text{O}_4:\text{Pr}^{3+}$  phosphors and the relative change of the red and blue emissions. The Zn substitution leads to the enhancement of the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition, but the Cd one has no effect on the relative intensities of the  $^3\text{P}_0$  and  $^1\text{D}_2 \rightarrow ^3\text{H}_4$  transition. We explained that the variation of the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition should result from the relative change of the distance of Pr-O by the substitutional ions.

#### 5. Acknowledgements

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