

Enhanced Luminescence of SrTiO₃:Pr³⁺ by Incorporating with Li⁺ or Na⁺ Ion

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▪Abstract

Photoluminescence (PL) and low-voltage cathodoluminescence (CL) characteristics of [xSrTiO₃+(1-x)Li₂TiO₃]:Pr³⁺ and [xSrTiO₃+(1-x)Na₂TiO₃]:Pr³⁺ systems were investigated. The red luminescence intensities of these compounds are enhanced remarkably by the incorporation of Li⁺ or Na⁺ ion as compared to that of SrTiO₃:Pr³⁺. The enhanced luminescence is speculated to result from both the charge compensation of Pr³⁺ site and oxygen vacancies generated in the lattices by Li⁺ or Na⁺ ion.

1. Introduction

Field emission displays (FEDs), like CRTs are based on cathodoluminescence, where the emission of light is a result of excitation by electrons [1-3]. Many FEDs are being designed for operation in 5-10 kV range, operation in the 1-5 kV range or lower is desirable. However, most available phosphors do not have high enough efficiencies at low voltage, and due to the degradation problems with sulfides, oxide phosphors are beginning to receive more attention [2,3]. Some of the phosphors include (Zn,Mg)O:Zn (blue), ZnGa₂O₄:Mn²⁺ (green), and CaTiO₃:Pr³⁺ (red). FEDs operated at an anode voltage below 1 kV require phosphors that are sufficiently conductive to release electric charges stored on the phosphor particle surface and also resistant to high-density electron irradiation. To satisfy the requirements, oxides with relatively narrow band-gaps have been investigated as host crystals. Recently, many oxides with perovskite structure were investigated as the host matrices for red phosphors, such as CaTiO₃:Pr³⁺, CaZrO₃:Pr³⁺, SrTiO₃:Pr³⁺ [4,5]. Particularly addition of Al³⁺ and Ga³⁺ to SrTiO₃:Pr³⁺ phosphor highly increased the luminous efficiency [6,7], since the band-gap of SrTiO₃ (3.2 eV) [8] is narrow compared with CaTiO₃ (3.5 eV) [9]. In this work, [xSrTiO₃ + (1-x)

Li₂TiO₃]:Pr³⁺ and [xSrTiO₃+(1-x)Na₂TiO₃]:Pr³⁺ phosphors were investigated. The luminescence of SrTiO₃:Pr³⁺ was enhanced remarkably by incorporating with Li⁺ or Na⁺ ions.

2. Experimental

The compounds [xSrTiO₃+(1-x)Li₂TiO₃]:Pr³⁺ were prepared by typical solid state reaction. The ground stoichiometric mixtures of SrCO₃, Li₂CO₃, TiO₂ and Pr₆O₁₁ were heated at 1180°C for 4 hrs. And the compounds [xSrTiO₃+(1-x)Na₂TiO₃]:Pr³⁺ were also prepared by similar solid state reactions by firing at 1250°C for 2 hrs.

The crystal structures of the phosphors were characterized by X-ray diffraction analysis using a Philips PWD 1840 X-ray diffractometer (XRD) with Cu K α radiation. A spectrofluorometer (Kontron, SFM25) with a 415 nm (Schott, WG415) cut-on filter was used for the photoluminescence measurement at room temperature. The spectrofluorometer is composed of a 150 W Xe high pressure tube arc lamp, monochromators (f.l. = 100 mm, D⁻¹ = 8 nm/mm), and a photomultiplier tube (PMT, Hamamatsu R928). To measure the low-voltage cathodoluminescence, phosphors mixed with vehicle silkscreened on ITO glass substrates and heated in air at 450°C for 1 hr and then placed in a high vacuum chamber ($\leq 9.0 \times 10^{-6}$ Torr). The vacuum chamber is equipped with an electron gun (Kimball Physics FRA-2X1-2) with a power supply (Kimball Physics Inc. EGPS-2X1-2) and a diode array detector (ORIEL, 77400 MultiSpec™ Spectrograph) system.

3. Results and discussion

The photoluminescence and low-voltage CL spectra of [xSrTiO₃+(1-x)Li₂TiO₃]:Pr³⁺ are shown

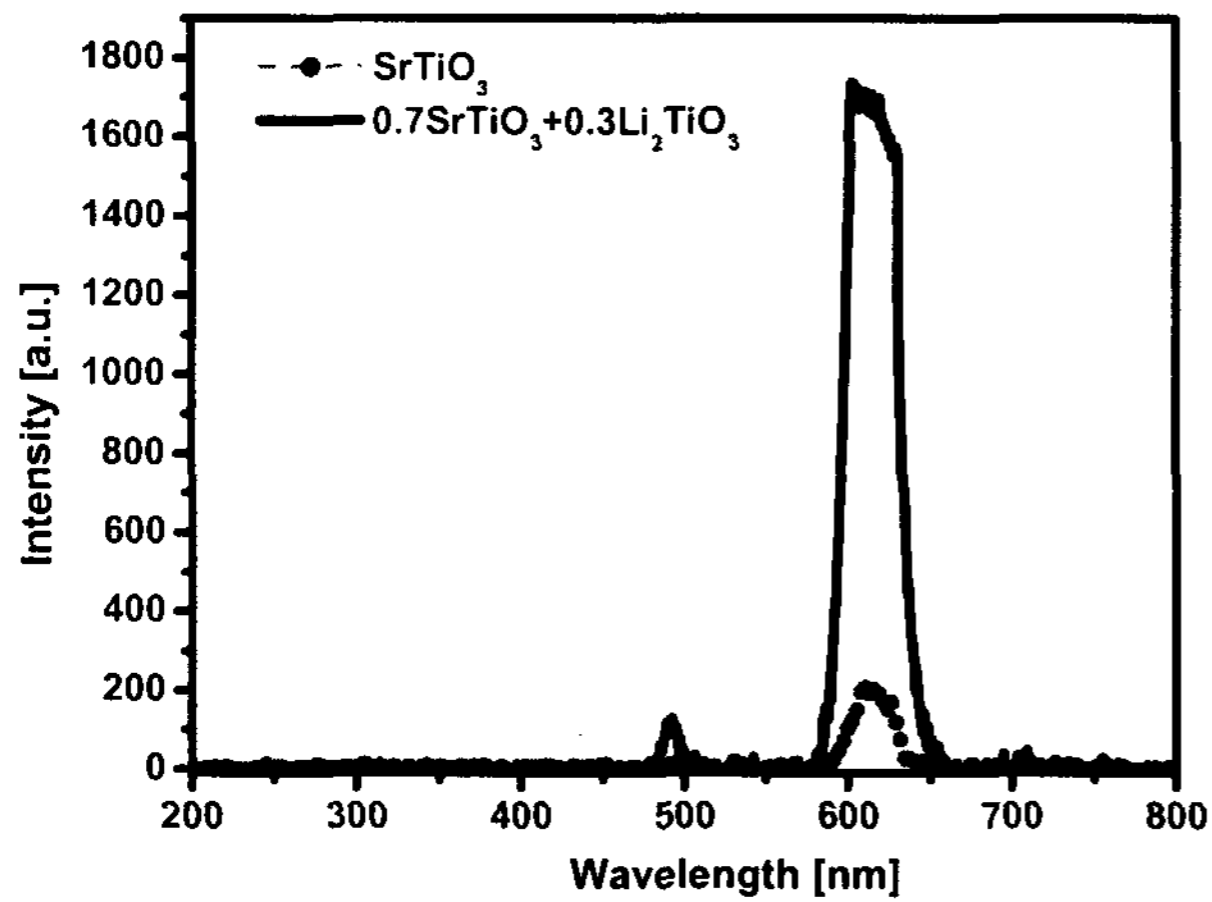


Fig. 1. Low-voltage CL spectra of $\text{SrTiO}_3:\text{Pr}^{3+}$ and $[\text{0.7SrTiO}_3+\text{0.3Li}_2\text{TiO}_3]:\text{Pr}^{3+}$. The CL measurements were carried out with an acceleration voltage of 800 V and a source beam current of 1.5 A.

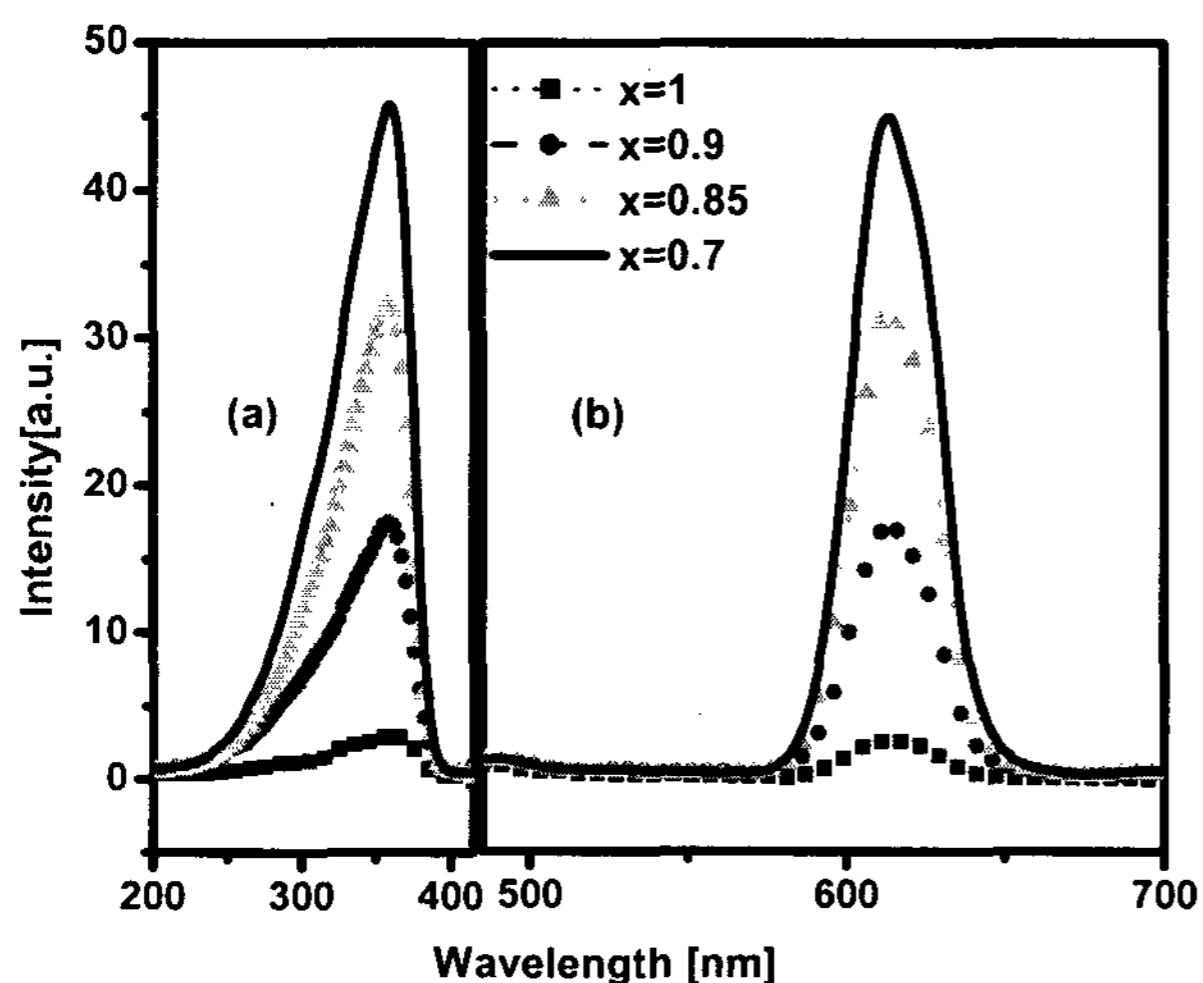


Fig. 2. (a) Excitation spectra of $[\text{xSrTiO}_3+(1-\text{x})\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ monitoring at 613 nm and (b) Photoluminescence spectra of $[\text{xSrTiO}_3+(1-\text{x})\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ ($\text{x} = 1, \text{x} = 0.90, \text{x} = 0.85, \text{x} = 0.70$) with the exciting wavelength at 362 nm.

in Fig.1 and Fig. 2. The activator ion Pr^{3+} shows a number of different emission spectra depending on the host matrix, infrared (${}^3\text{P}_0 \rightarrow {}^3\text{F}_4$), red (${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$, ${}^3\text{P}_0 \rightarrow {}^3\text{F}_2$), green (${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$), blue (${}^1\text{S}_0 \rightarrow {}^1\text{I}_6$) and ultraviolet ($5\text{d} \rightarrow 4\text{f}$) [10]. In $\text{SrTiO}_3:\text{Pr}^{3+}$, the emission spectra show red emission at 613 nm and very small green emission at 490 nm. When Li^+ ions are incorporated into $\text{SrTiO}_3:\text{Pr}^{3+}$, the efficiency of

luminescence is increased by a factor of ten times compared with that of $\text{SrTiO}_3:\text{Pr}^{3+}$. With increasing the concentration of Li^+ , the luminous intensity of $[\text{xSrTiO}_3+(1-\text{x})\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ is enhanced until $\text{x} = 0.7$. The dominative emission peak at 613 nm is increased highly. And the luminous intensity of $[\text{xSrTiO}_3+(1-\text{x})\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ changed with the concentration of Pr^{3+} as shown in Fig. 3.

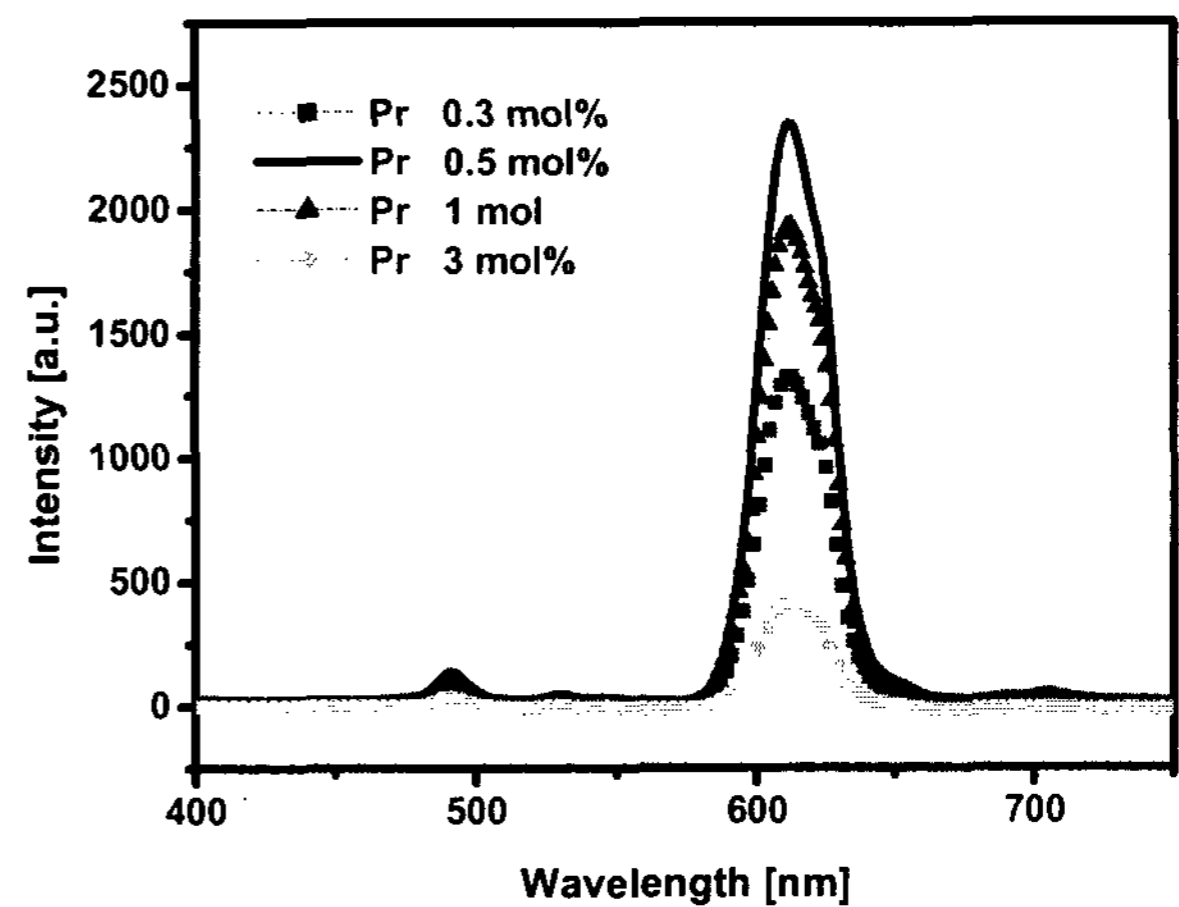


Fig. 3. Low-voltage CL spectra of $[\text{0.7SrTiO}_3+\text{0.3Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ compared with different concentration of Pr^{3+} . The CL measurements were carried out with an acceleration voltage of 800 V and a source beam current of 1.5 A.

When Na^+ ion is incorporated in $\text{SrTiO}_3:\text{Pr}^{3+}$, the luminescence intensities are also enhanced as shown in Fig. 4. The incorporation of these monovalent ions intensifies drastically the red luminescence compared with that of $\text{SrTiO}_3:\text{Pr}^{3+}$.

The increase in the Pr^{3+} luminescence by incorporating large amount of Li^+ into SrTiO_3 lattice can be speculated as the stabilization of Pr^{3+} ion in the lattice both by charge compensation ($(\text{Li}_{\text{Sr}})'$ + $(\text{Pr}_{\text{Sr}})^\bullet$) and by oxygen vacancies generated in the lattice ($(\text{Li}_{\text{Sr}})'$ + $(\text{V}_{\text{O}})^{\bullet\bullet}$).

4. Conclusion

Perovskite structured oxide phosphors $[\text{xSrTiO}_3+(1-\text{x})\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ and $[\text{xSrTiO}_3+(1-\text{x})\text{Na}_2\text{TiO}_3]:\text{Pr}^{3+}$ have high red luminous efficiency. Enhancement of red luminescence of Pr^{3+}

($^1D_2 \rightarrow ^3H_4$) in the perovskite $SrTiO_3$ lattices is conjectured to result both from charge compensation by Li^+ ion and from the oxygen vacancies generated by Li^+ ion.

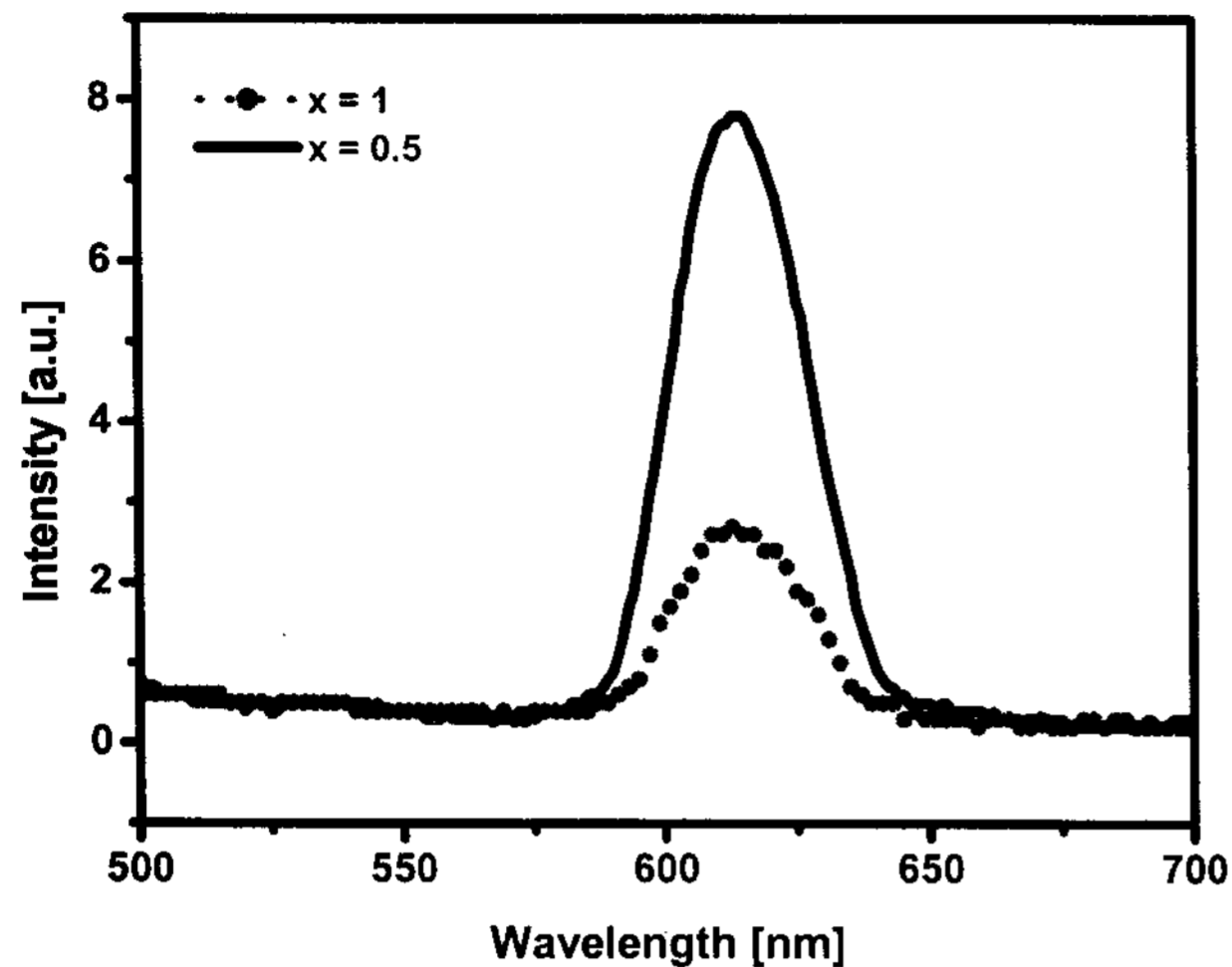


Fig. 4. Photoluminescence spectra of $[xSrTiO_3+(1-x)Na_2TiO_3]:Pr^{3+}$ ($x = 1$ and $x = 0.5$) with the exciting wavelength at 362 nm.

5. References

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