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Enhanced luminescence of $\text{SrTiO}_3:\text{Pr}^{3+}$ by incorporation of Li^+ ion

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Abstract

Photoluminescence and low-voltage cathodoluminescence characteristics of the $[\text{xSrTiO}_3 + (1 - \text{x})\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ system have been investigated. The red luminescence intensity of this compound was enhanced remarkably by the incorporation of Li^+ ions as compared with that of lithium-free $\text{SrTiO}_3:\text{Pr}^{3+}$. The enhanced luminescence is conjectured to result mostly from the oxygen vacancy generated by Li^+ ion incorporation in the lattices. The oxygen vacancy in the lattice promotes the energy transfer from the excited carrier in lattices to the Pr^{3+} activator ion, leading to an increase in the luminescence efficiency.

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1. Introduction

Field emission displays (FEDs), one of the most promising flat panel displays, are based on cathodoluminescence (CL) and designed for operation at low voltages. However, most available phosphors do not have high enough luminescence efficiency with the cold electrons generated at low voltages [1–5]. The stability of oxide phosphors in high vacuum and the absence of corrosive gas emission from the oxide phosphors under electron bombardment offer advantages over commonly used sulfide phosphors [1–3]. FEDs operated at an anode voltage below 1 kV require phosphors that are sufficiently conductive to release electric charges generated on the phosphor particle surfaces by cold cathode electrons and that withstand the high-density electron irradiation. To satisfy these requirements, oxides with relatively narrow band-gaps have been investigated as host crystals [4–8]. Recently, oxides with perovskite structure were investigated

as the host matrices for red phosphors, such as $\text{CaTiO}_3:\text{Pr}^{3+}$ and $\text{SrTiO}_3:\text{Pr}^{3+}$ [6–8]. The band-gap of SrTiO_3 (3.3 eV) is comparable to that of CaTiO_3 (3.5 eV). Doping of a small number of carriers in SrTiO_3 by substituting La for Sr, Nb for Ti, or by introducing oxygen vacancies makes the system metallic and moreover, superconducting [9]. Particularly for display applications, the addition of Al^{3+} , Ga^{3+} , or In^{3+} to $\text{SrTiO}_3:\text{Pr}^{3+}$ phosphor highly increased the luminescence efficiency, which was explained by both charge compensation mechanism and by energy transfer from the carriers generated in SrTiO_3 lattices to the activator ions [4,7,8]. In this work, $[\text{xSrTiO}_3 + (1 - \text{x})\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ phosphors were investigated in order to enhance the luminescence of $\text{SrTiO}_3:\text{Pr}^{3+}$ by incorporating with Li^+ ions. Lithium ion and other monovalent ions have enhanced the blue luminescence of ZnGa_2O_4 by generating oxygen vacancies [10–12]. Monovalent ions substituted into the SrTiO_3 lattice can generate oxygen vacancies in the lattice for the charge neutrality in addition to compensate the extra positive charge generated by Pr^{3+} ion at Sr^{2+} sites. The effect of the addition of Li^+ ion in SrTiO_3 is discussed in the paper from the correlation of the XRD patterns and the luminescence characteristics.

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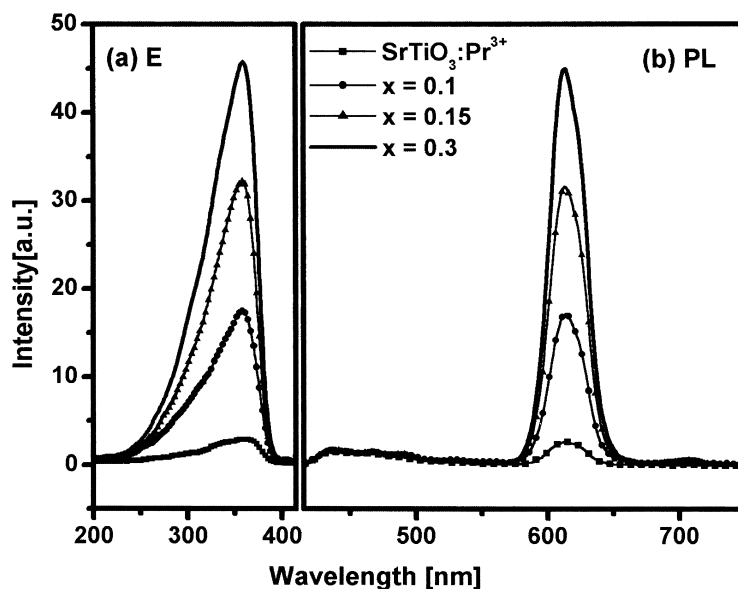


Fig. 1. Excitation (E) and photoluminescence (PL) spectra of $\text{SrTiO}_3:\text{Pr}^{3+}(1\%)$ (■) and $[(1-x)\text{SrTiO}_3 + x\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$ for $x = 0.1$ (●), 0.15 (▲), and 0.3 (—).

2. Experimental

The powder samples of Li^+ ion incorporated $\text{SrTiO}_3:\text{Pr}^{3+}$ with nominal compositions of $[x\text{SrTiO}_3 + (1-x)\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ and $[\text{SrTiO}_3 + y\text{Li}_2\text{O}]:\text{Pr}^{3+}$ ($x, y < 1$) were prepared by heating at 1180°C for 4 h the mixtures of appropriate amount of starting materials, such as SrCO_3 (Aldrich, 99.9%), Li_2CO_3 (Aldrich, 99.9%), TiO_2 (Aldrich, 99.99%) and Pr_6O_{11} (Aldrich, 99.9%). When Li_2CO_3 was added in the starting mixtures, Li_2CO_3 melted at temperatures above 723°C and it acted as a flux for the reaction to form SrTiO_3 co-doped with Pr^{3+} and Li^+ ions. The prepared powder samples were washed with HCl solution to get rid of the remained flux. The crystal structures of the phosphor powders were characterized by X-ray diffraction analysis using an X-ray diffractometer (XRD; Philips PWD 1840) with $\text{Cu K}\alpha$ radiation. The particle shapes and sizes of the products were observed with a scanning electron microscope (Leica, Stereoscan 440). A spectrofluorometer (Kontron, SFM25) with a 415 nm (Schott, WG415) cut-on filter was used for the photoluminescence (PL) measurement at room temperature. The spectrofluorometer is composed of a 150 W Xe arc lamp, two monochromators (f.l. = 100 mm, $D^{-1} = 8 \text{ nm/mm}$), and a photomultiplier tube (PMT, Hamamatsu R928). To measure the low-voltage CL, phosphors mixed with vehicle were silk-screened on ITO glass substrates and heated in air at 450°C for 1 h, 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. The CL

measurement were carried out with an acceleration voltage of 800 V and a source beam current of 1.50 A. The emission current at the cathode was about $110 \mu\text{A}$ during the CL measurement.

3. Results and discussion

The PL and low-voltage CL spectra of Pr^{3+} ion in perovskite structured SrTiO_3 incorporated with Li^+ ion as nominal compositions of $[x\text{SrTiO}_3 + (1-x)\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ are enhanced significantly, which are shown in Figs. 1 and 2. The luminescence spectra show red emission at 613 nm and very small green emission at 490 nm. The major luminescence at 613 nm originates from the $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition and at 490 nm, $^3\text{P}_0 \rightarrow ^3\text{H}_4$ [13]. $\text{SrTiO}_3:\text{Pr}^{3+}$ is barely luminescent without incorporation of Al^{3+} or Li^+ ions. The incorporation of Li^+ or Al^{3+} ions drastically intensifies the luminescence compared with that of $\text{SrTiO}_3:\text{Pr}^{3+}$. The CL spectrum of $[0.7\text{SrTiO}_3 + 0.3\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$ is compared with those of $\text{CaTiO}_3:\text{Pr}^{3+}(1\%)$ and $\text{SrTiO}_3:\text{Pr}^{3+}(1\%), \text{Al}(5\%)$ as shown in Fig. 2. The strongest emission is observed from $[0.7\text{SrTiO}_3 + 0.3\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$, although Pr^{3+} ion in CaTiO_3 shows a much higher luminescence than in SrTiO_3 with no addition of lithium ion nor aluminum ion. Luminescence color is a saturated red color with the color coordinate (0.664, 0.331). Were also prepared SrTiO_3 incorporated with Li^+ ion as nominal compositions of $[\text{SrTiO}_3 + y\text{Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$ in order to compare their luminescence characteristics with that of $[x\text{SrTiO}_3 + (1-x)\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$. The luminescence of Pr^{3+} in Li^+ co-doped SrTiO_3 as nominal

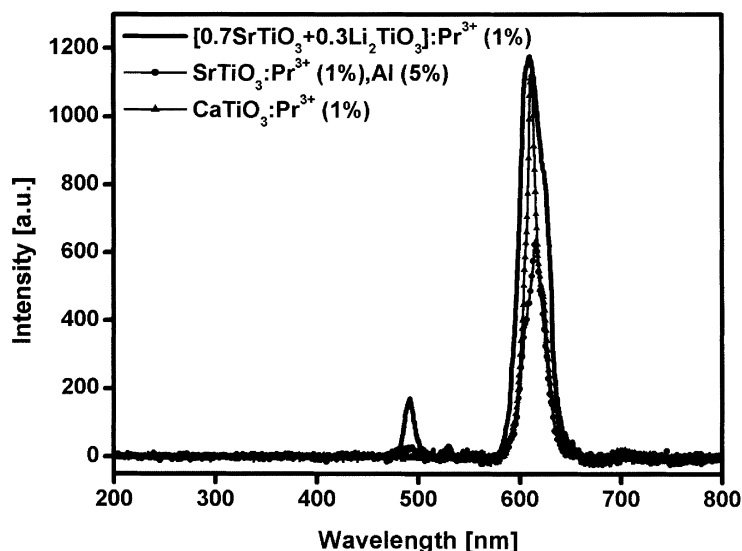


Fig. 2. Low-voltage CL spectra of $[0.7\text{SrTiO}_3 + 0.3\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$ (—), $\text{CaTiO}_3:\text{Pr}^{3+}(1\%)$ and $\text{SrTiO}_3:\text{Pr}^{3+}(1\%)$ (●) doped with Al (5%) (▲).

compositions of $[\text{SrTiO}_3 + y\text{Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$ is somewhat enhanced. However, the enhancement is insignificant and is still too weak. With 2.5% of Li_2CO_3 addition in the starting materials for $[\text{SrTiO}_3 + y\text{Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$ preparation, the resultant enhancement was only about two fold and the higher incorporation of lithium content enhanced the luminescence no more. Hence, excess amount of Li^+ ion incorporation into the SrTiO_3 lattices without corresponding excess Ti^{4+} ion for Li_2TiO_3 is not desirable for the luminescence enhancement. The resultant powder particles of both $[0.7\text{SrTiO}_3 + 0.3\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$ and $[\text{SrTiO}_3 + 0.3\text{Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$ were grown larger (ca 2–3 μm diameter) than that of Li^+ ion free $\text{SrTiO}_3:\text{Pr}^{3+}$ (ca 1 μm diameter), because the added Li_2CO_3 in the starting

mixtures acted as a flux for the reaction to promote the particle growth for SrTiO_3 co-doped with Pr^{3+} and Li^+ ions.

Praseodymium ion, Pr^{3+} , substitutes for the Sr^{2+} site in the SrTiO_3 lattices, which generates an extra positive charge to the lattices, $(\text{Pr}_{\text{Sr}})^\bullet$. The extra positive charge can be compensated by the defect site generated by the incorporation of aluminum ion into the titanium sites, $(\text{Al}_{\text{Ti}})'$ in $\text{SrTiO}_3:\text{Pr}^{3+}$, Al^{3+} sample [4,7,8]. Likewise, lithium ion in strontium site, $(\text{Li}_{\text{Sr}})'$, can compensate the extra positive charge generated by Pr^{3+} ion in the Sr^{2+} site, i.e. $(\text{Pr}_{\text{Sr}})^\bullet$ is neutralized with the negative charge $(\text{Li}_{\text{Sr}})'$ in $\text{SrTiO}_3:\text{Pr}^{3+}$, Li^+ sample. Lithium ion is small enough to fit any crystal site, such as $(\text{Li}_{\text{Sr}})'$ or $(\text{Li}_{\text{Ti}})'''$. However, Li^+ ion in the Ti^{4+} site is not likely because of the big charge difference between them. The possibility of Li^+ ion's occupying the interstitial sites cannot be excluded either, because of its small size. The dependence of the luminescence efficiency on the amount of Li^+ ion is shown in Fig. 3. With increasing the concentration of Li^+ , the luminescence intensity of the nominal composition $[(1-x)\text{SrTiO}_3 + x\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$ is enhanced until $x = 0.3$. When Li^+ ion is incorporated into $\text{SrTiO}_3:\text{Pr}^{3+}$, the efficiency of luminescence is increased up to a factor of ten times compared with that of lithium free $\text{SrTiO}_3:\text{Pr}^{3+}$. Only a small quantity of Li^+ ion can be used for the charge compensation of Pr^{3+} in the lattices, because the concentration of Pr^{3+} ion is only one percent. The excess amount of Li^+ ions occupying strontium sites, $(\text{Li}_{\text{Sr}})'$, in the lattices generate extra negative charges, which is speculated to generate oxygen vacancies, $\text{V}_{\text{O}}^\bullet$ for charge neutrality. The presence of the oxygen vacancies generated by the Li^+ ion incorporation is conjectured to promote the energy transfer from excited carriers in SrTiO_3 lattice to Pr^{3+} activator ions.

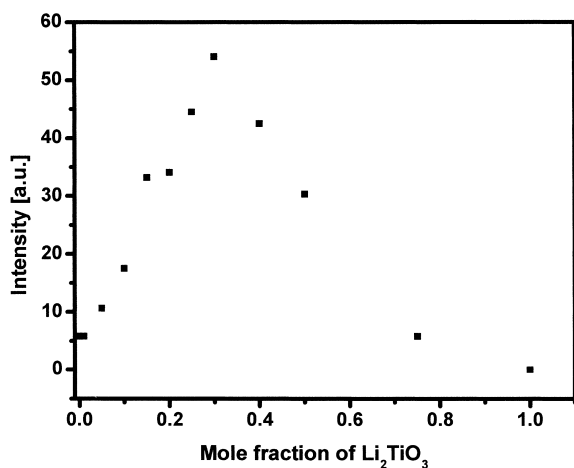


Fig. 3. Low-voltage CL intensities of $\text{Pr}^{3+}(1\%)$ at 613 nm as a function of lithium contents in $[(1-x)\text{SrTiO}_3 + x\text{Li}_2\text{TiO}_3]$.

In order to examine if there are any new minor phases or

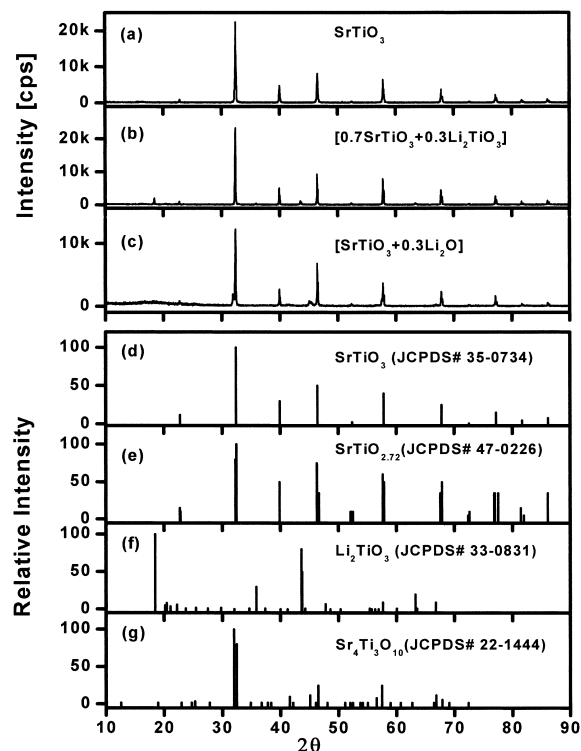


Fig. 4. XRD spectra for (a) $\text{SrTiO}_3:\text{Pr}^{3+}(1\%)$, (b) the nominal formula of $[\text{0.7SrTiO}_3 + \text{0.3Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$, (c) the nominal formula of $[\text{SrTiO}_3 + \text{0.3Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$, (d) SrTiO_3 (JCPDS# 35-0734), (e) $\text{SrTiO}_{2.72}$ (JCPDS# 47-0226), (f) Li_2TiO_3 (JCPDS# 33-0831), and (g) $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ (JCPDS# 22-1444).

any changes in the lattices, XRD spectra of $\text{SrTiO}_3:\text{Pr}^{3+}$ and nominal compositions $[(1-x)\text{SrTiO}_3 + x\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ and $[\text{SrTiO}_3 + y\text{Li}_2\text{O}]:\text{Pr}^{3+}$ are analyzed. Fig. 4 shows XRD patterns of $\text{SrTiO}_3:\text{Pr}^{3+}(1\%)$, $[\text{0.7SrTiO}_3 + \text{0.3Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$, and $[\text{SrTiO}_3 + \text{0.3Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$, along with JCPDS patterns of SrTiO_3 (JCPDS# 35-0734), $\text{SrTiO}_{2.72}$ (JCPDS# 47-0226), Li_2TiO_3 (JCPDS# 33-0831), and $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ (JCPDS# 22-1444). The diffraction peak positions and the relative intensities of the prepared samples (Figs. 4(a)–(c)) are well matched with those of cubic SrTiO_3 (Fig. 4(d)). However, the diffraction peaks of the prepared powder phosphor samples are doublets, which must result from the presence of $\text{SrTiO}_{2.72}$ phase (Fig. 4(e)). The powder samples prepared in this experiment contain some of $\text{SrTiO}_{2.72}$ in addition to SrTiO_3 phase. Hence, there must be oxygen vacancies in the lattice. This is a solid evidence for the importance of the oxygen vacancy in the luminescence characteristics of SrTiO_3 based phosphors. In addition to the major diffraction peaks corresponding to SrTiO_3 , there are additional weak diffraction peaks in the diffraction patterns (Figs. 4(b) and (c)). The minor peaks in the XRD spectrum (Fig. 4(b)) of the phosphor sample with the nominal composition of $[\text{0.7SrTiO}_3 + \text{0.3Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$ correspond to that of monoclinic Li_2TiO_3 phase

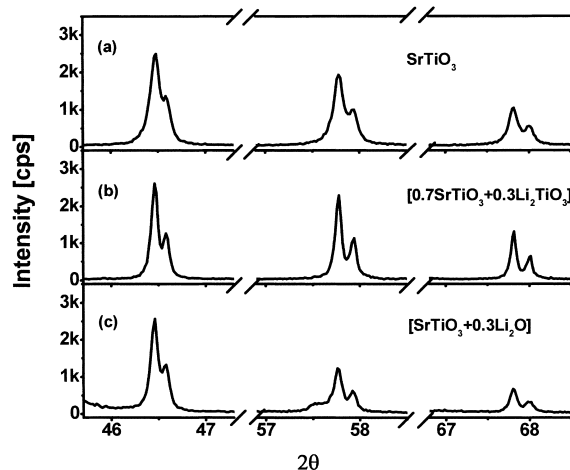


Fig. 5. Diffraction peaks at $2\theta = 46.5^\circ$, 57.8° , and 67.8° of (a) $\text{SrTiO}_3:\text{Pr}^{3+}(1\%)$, (b) the nominal formulae of $[\text{0.7SrTiO}_3 + \text{0.3Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$, and (c) $[\text{SrTiO}_3 + \text{0.3Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$.

(Fig. 4(f)). Consequently, some Li^+ ions are doped in the SrTiO_3 lattices and some are considered to segregate by forming another phase, Li_2TiO_3 . The minor peak at $2\theta = 32.1^\circ$ in the XRD spectrum (Fig. 4(c)) of the sample with nominal composition of $[\text{SrTiO}_3 + \text{0.3Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$ corresponds to the major peak of $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ phase (Fig. 4(g)). The excess Li^+ ions consume some Ti^{4+} ions to form Li_2TiO_3 phase, leading to the deficiency of Ti^{4+} ion, which results in the formation of $\text{Sr}_4\text{Ti}_3\text{O}_{10}$ phase. Hence, the incorporation of Li^+ ion into the SrTiO_3 lattice as Li_2TiO_3 is desirable in order to enhance the luminescence by generating oxygen vacancies.

No change in the lattice constant of cubic SrTiO_3 in the nominal $[\text{0.7SrTiO}_3 + \text{0.3Li}_2\text{TiO}_3]$ was detected with the addition of Li^+ ion. Diffraction peak positions (2θ) of SrTiO_3 are exactly the same. However, diffraction peak widths at half maximum are sharpened somewhat in the nominal $[\text{0.7SrTiO}_3 + \text{0.3Li}_2\text{TiO}_3]:\text{Pr}^{3+}(1\%)$ phase compared with those in $\text{SrTiO}_3:\text{Pr}^{3+}(1\%)$ and $[\text{SrTiO}_3 + \text{0.3Li}_2\text{O}]:\text{Pr}^{3+}(1\%)$ as shown in Fig. 5. Lithium ion incorporated into SrTiO_3 lattice as Li_2TiO_3 phase may help to relax the strain in the lattice by generating oxygen vacancies. The enhancement of luminescence and the lattice strain released by incorporating Li^+ ion into the lattice is thought to correlate with each other. The lattice strain relaxed by lithium ion incorporation into the lattice is correlated with the enhancement of the luminescence probably by presence of the oxygen vacancies. In other words, drastic increase in the luminescence intensity of $[(1-x)\text{SrTiO}_3 + x\text{Li}_2\text{TiO}_3]:\text{Pr}^{3+}$ with highly doping with Li^+ ion is considered to originate from efficient energy transfer through the oxygen vacancy, $V_{\text{O}}^{\bullet\bullet}$, in the lattice which also can relax the lattice strains. Hence, the activator Pr^{3+} ion is stabilized by incorporating large amount of Li^+ into SrTiO_3 lattice both by charge compensation ($(\text{Li}_{\text{Sr}})^+$ and $(\text{Pr}_{\text{Sr}})^{\bullet}$) and by

generating oxygen vacancies in the lattice ($2(\text{Li}_{\text{Sr}})' + \text{V}_{\text{O}}''$). In conclusion, the enhancement of red luminescence (${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$) of Pr^{3+} doped in the perovskite SrTiO_3 lattice in the nominal composition of $[\text{xSrTiO}_3 + (1 - \text{x})\text{Li}_2\text{TiO}_3]$ is conjectured to result from the efficient energy transfer from excited carrier in the lattice to Pr^{3+} ion through oxygen vacancies generated by Li^+ ion.

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