

# Emitting Level Change and Enhancement of Red Emission from SrTiO<sub>3</sub>:Pr<sup>3+</sup> by Y<sup>3+</sup> Addition

Hee-Kyung An, Kyung-Soo Suh\*, Jin-Ho Lee\*, Kyoung-Ik Cho\* and Shin-Hoo Kang

Dept. of inorganic material science and engineering, Seoul National University, Seoul, 151-742

\*Micro-Electronics Technology Lab., ETRI, Yusong, P.O. Box 106, Taejeon , 305-600

## Abstract

The effect of Y<sup>3+</sup> addition to SrTiO<sub>3</sub>:Pr<sup>3+</sup> on the photoluminescence and cathodoluminescence was studied. We discovered that light emitting levels of Pr<sup>3+</sup> vary by addition of Y<sup>3+</sup>. In (Sr<sub>1-x</sub>Y<sub>x</sub>)TiO<sub>3</sub>:Pr<sup>3+</sup>, both the green and red emission are discovered while the red emission prevails in Sr(Ti<sub>1-x</sub>Y<sub>x</sub>)O<sub>3</sub>:Pr<sup>3+</sup>. Sr(Ti<sub>1-x</sub>Y<sub>x</sub>)O<sub>3</sub>:Pr<sup>3+</sup> shows enhancement of red emission by two kinds of enhancement process.

## INTRODUCTION

Field emission display (FED) is promising flat panel display for next generation. But, one of the most serious problems to be solved is to find proper phosphors. Although cathode ray phosphors have been optimized to work at high voltages and relatively low current densities, the requirements for FED are totally different. So new phosphors are required for FED and various kinds of phosphor are being researched.

SrTiO<sub>3</sub>:Pr<sup>3+</sup> is known as the red phosphor under low-energy electron or uv light excitation and its intensity is enhanced by addition of Al<sup>3+</sup>, Ga<sup>3+</sup><sup>1)</sup>. In this work, we discovered the light emitting level change and red emission enhancement by Y<sup>3+</sup> addition.

## EXPERIMENT

Polycrystalline compounds with nominal compositions (Sr<sub>1-x</sub>A<sub>x</sub>)TiO<sub>3</sub>:Pr<sup>3+</sup> and Sr(Ti<sub>1-x</sub>A<sub>x</sub>)O<sub>3</sub>:Pr<sup>3+</sup> were prepared. The appropriate amounts of SrCO<sub>3</sub>, TiO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and PrCl<sub>3</sub>·7H<sub>2</sub>O were mixed together under ethanol in agate mortar for 4hrs, then fired under air at 1200°C for 6 hours.

XRD pattern was obtained using Rigaku, D/Mac-RC. The PL excitation and emission spectra were obtained with a Aminco Bowman Luminescence spectrometer. The CL was measured at room temperature using a demountable ultrahigh vacuum chamber equipped with in-house assembled CL spectrophotometer. The CL measurements were carried out with an accelerating voltage of 700V. The fluorescence were measured by pulsed radiation PL Perkin Elmer spectrometer.

## RESULTS AND DISCUSSIONS

XRD patterns in Figure 1 reveal that a small amount of Y<sup>3+</sup> can be incorporated in SrTiO<sub>3</sub>:Pr<sup>3+</sup>.

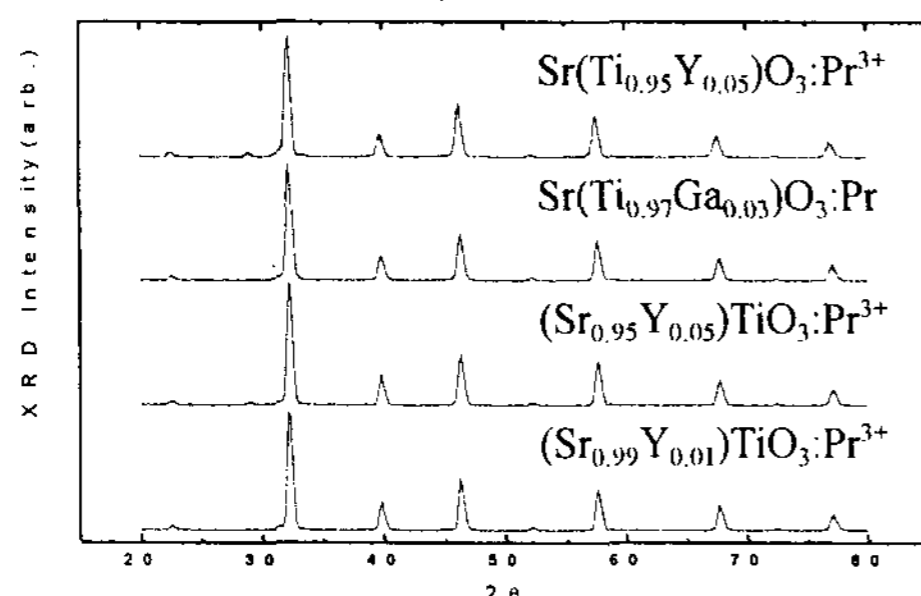


Fig.1. XRD patterns of Sr(Ti<sub>1-x</sub>Y<sub>x</sub>)O<sub>3</sub>:Pr<sup>3+</sup> and (Sr<sub>1-x</sub>Y<sub>x</sub>)TiO<sub>3</sub>:Pr<sup>3+</sup> doped with different amount of Y<sup>3+</sup>.

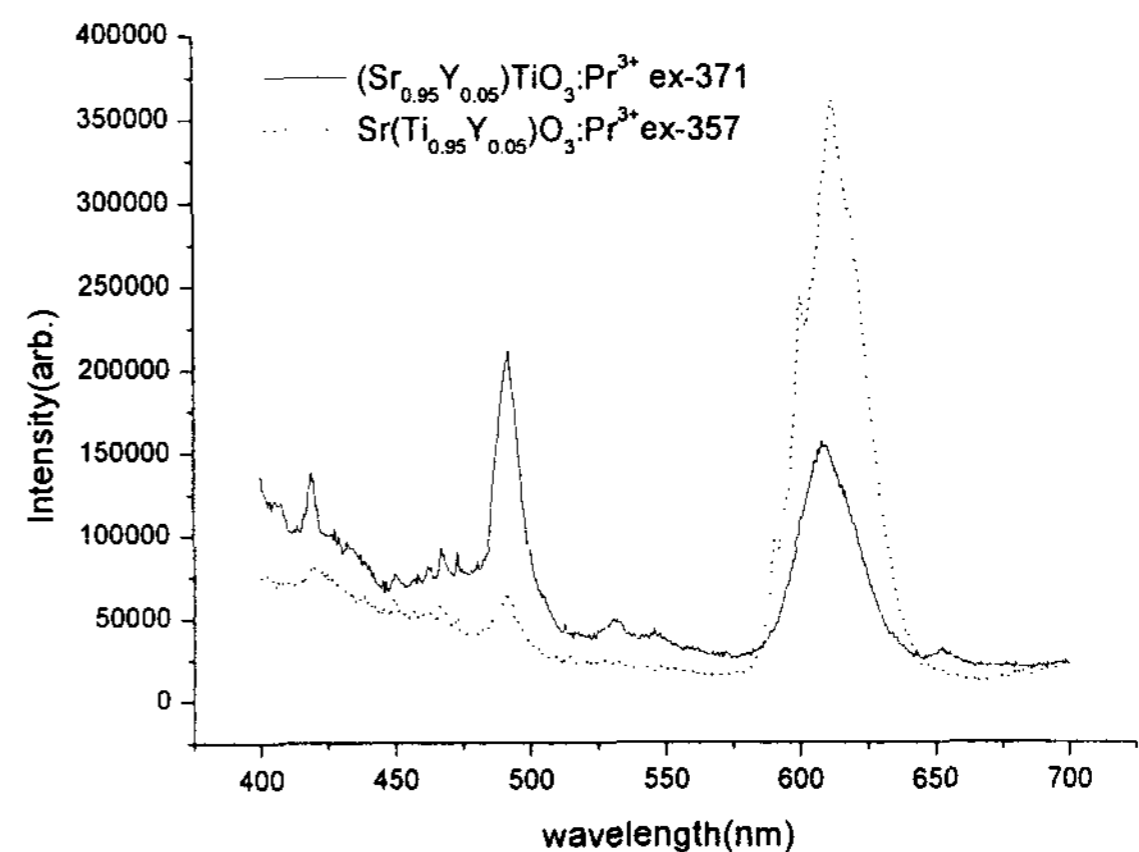


Fig.2. PL emission spectra of Sr(Ti<sub>0.95</sub>Y<sub>0.05</sub>)O<sub>3</sub>:Pr<sup>3+</sup> and (Sr<sub>0.95</sub>Y<sub>0.05</sub>)TiO<sub>3</sub>:Pr<sup>3+</sup> at highest peak of excitation band.

Figure 2 shows the PL emission spectra of 5 mol% of Y<sup>3+</sup> doped SrTiO<sub>3</sub>:Pr<sup>3+</sup> with different molar ratio of Sr and Ti. As shown in the figure, the green emission band is due to the transition from <sup>3</sup>P<sub>0</sub> to <sup>3</sup>H<sub>4</sub> at 493 nm and red emission band due to the transition from <sup>1</sup>D<sub>2</sub> to <sup>3</sup>H<sub>4</sub> at 614 nm. The red emission band is very weak in SrTiO<sub>3</sub>:Pr<sup>3+</sup> without Y<sup>3+</sup><sup>1)</sup>. There is severe influence of excitation and emission bands depending on the molar ratio of Sr and Ti for SrTiO<sub>3</sub>:Pr<sup>3+</sup>. The addition of Y<sup>3+</sup> to Ti-deficient SrTiO<sub>3</sub>:Pr<sup>3+</sup> ( Sr(Ti<sub>1-x</sub>Y<sub>x</sub>)O<sub>3</sub>:Pr<sup>3+</sup>: a-type) reveals that the red emission band increases, but the green emission at 493nm is very weak. Intensity of the red emission decreases while the green emission increases by the addition of Y<sup>3+</sup> to Sr-deficient SrTiO<sub>3</sub>:Pr<sup>3+</sup> ( (Sr<sub>1-x</sub>Y<sub>x</sub>)TiO<sub>3</sub>:Pr<sup>3+</sup>: b-type). This green emission of Pr<sup>3+</sup> is discovered in other host lattices<sup>2),3)</sup>, but not in SrTiO<sub>3</sub>:Pr<sup>3+</sup> at room temperature.

Figure 3 shows the PL excitation spectra for 5 mol% of Y<sup>3+</sup> doped SrTiO<sub>3</sub>:Pr<sup>3+</sup> with different molar ratio of Sr and Ti. The excitation spectrum consists of broad band below 380 nm and sharp band in the region 440 ~ 490 nm. The sharp band consists of three bands peaked at 450, 470 and 486 nm, it is assigned to optical transition of <sup>3</sup>H<sub>4</sub>→<sup>3</sup>P<sub>J</sub> (J=0,1,2) in Pr<sup>3+</sup>, respectively. The broad band below 380 nm is different between a-type and b-type. In the case of a-type, there is intense broad band below 380nm at emission due to <sup>1</sup>D<sub>2</sub>→<sup>3</sup>H<sub>4</sub>(614nm) but not at emission due to <sup>3</sup>P<sub>0</sub>→<sup>3</sup>H<sub>4</sub>(493 nm).

In the case of b-type, the intensity of excitation band below 380 nm at emission due to  $^3P_0 \rightarrow ^3H_4$  (493 nm) is greater than at emission due to  $^1D_2 \rightarrow ^3H_4$  (614 nm). This process can be explained by  $^3P_0 \rightarrow ^1D_2$  non-radiative relaxation. After absorbing the energy in UV region, the population of the  $^3P_0$  state occurs. We confirmed this by measuring fluorescence. After exciting both of them at 360 nm by pulsed radiation, we discovered the very intense peak at 493 nm in both emission spectra. Through  $^3P_0 \rightarrow ^1D_2$  non-radiative relaxation, it results in the population of the  $^1D_2$  state. In a-type,  $^3P_0 \rightarrow ^1D_2$  non-radiative relaxation is too fast for to emit 493 nm emission originating from  $^3P_0$ , so only 614 nm emission originating from  $^1D_2$  is dominant. But, in b-type  $^3P_0 \rightarrow ^1D_2$  non-radiative relaxation is not so fast that 493 nm emission originating from  $^3P_0$  can occur quite well.

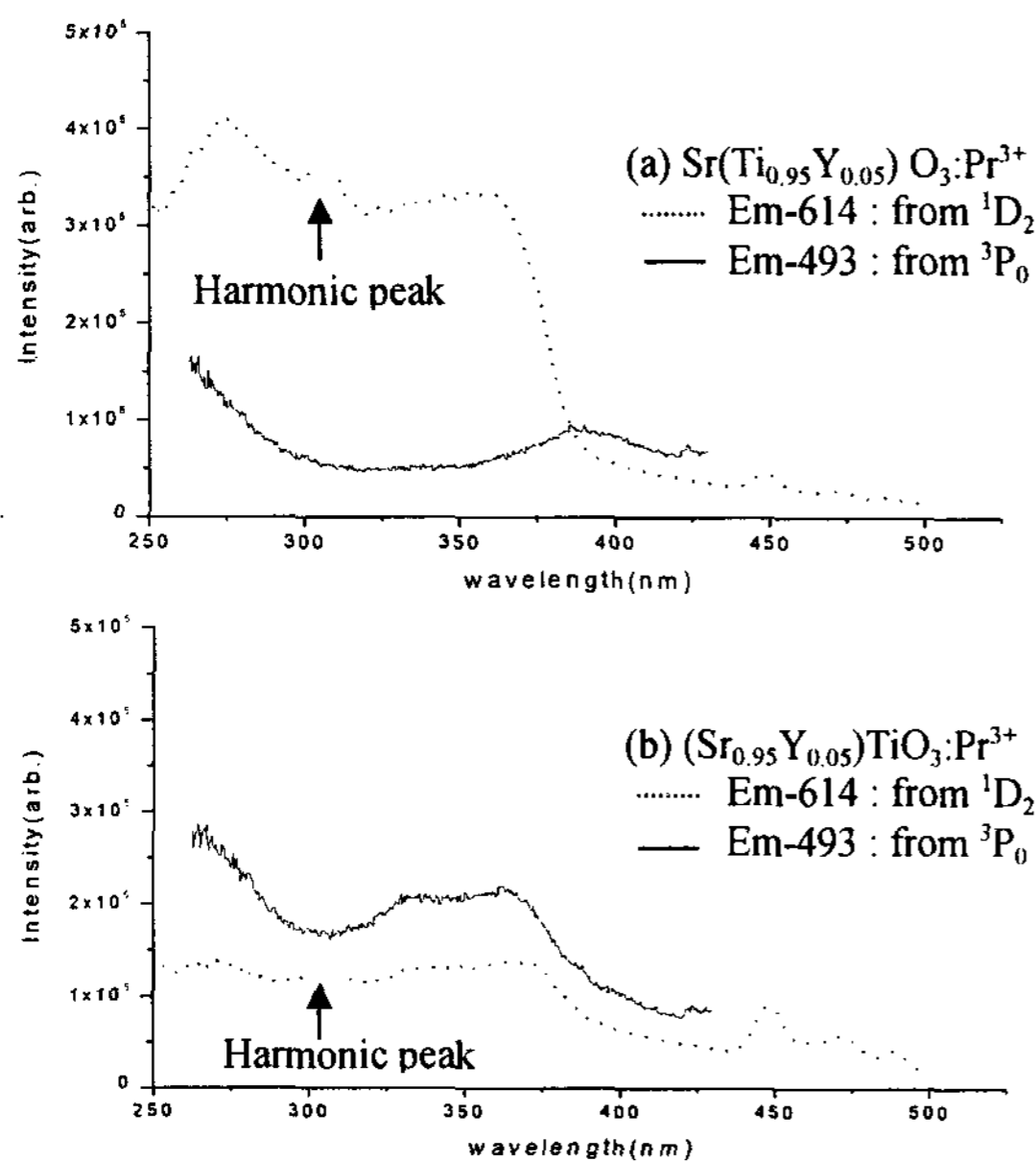


Fig. 3. PL excitation spectra of (a)  $\text{Sr}(\text{Ti}_{0.95}\text{Y}_{0.05})\text{O}_3:\text{Pr}^{3+}$  and (b)  $(\text{Sr}_{0.95}\text{Y}_{0.05})\text{TiO}_3:\text{Pr}^{3+}$

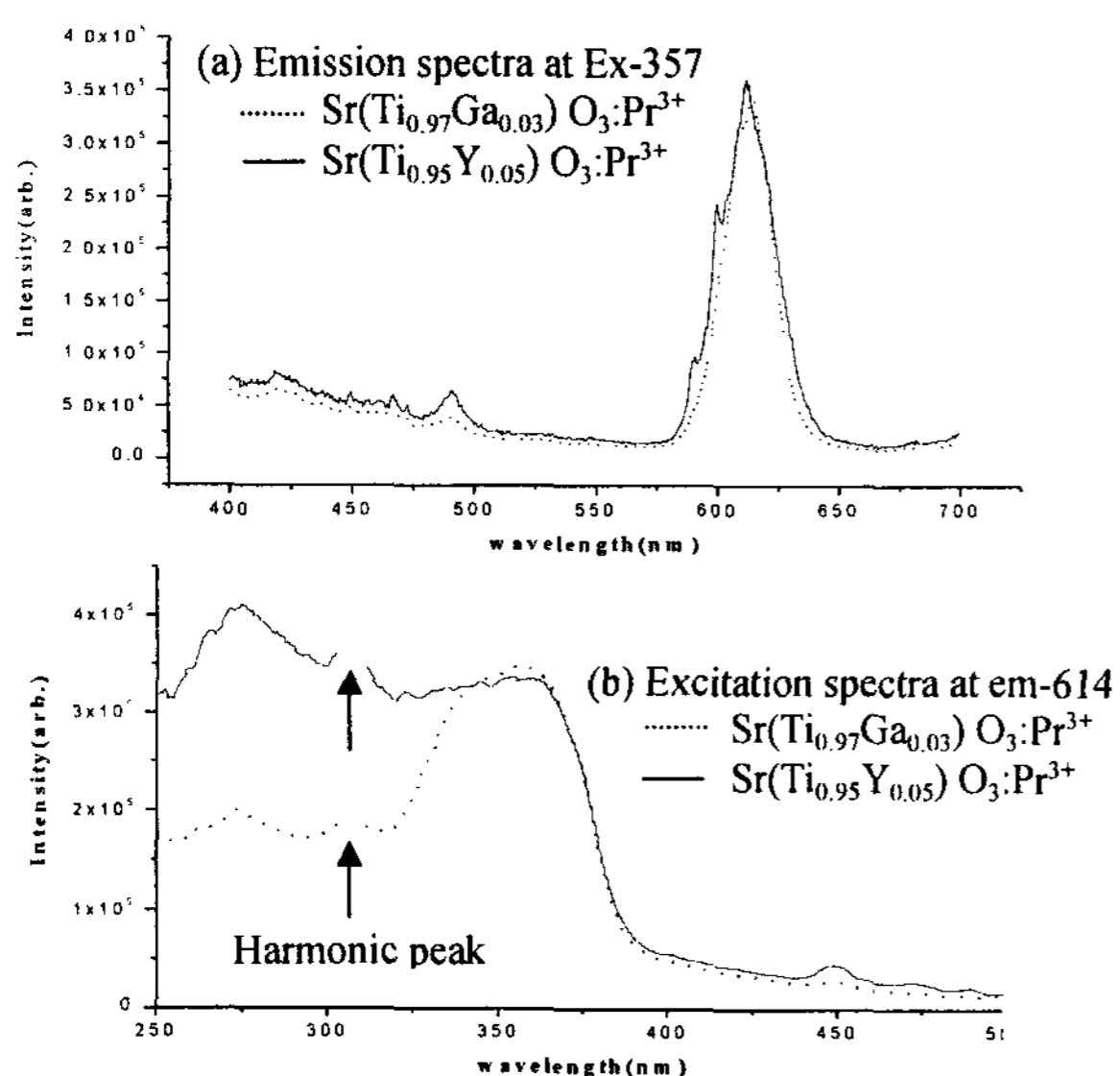


Fig. 4. PL (a) emission and (b) excitation spectra of  $\text{Sr}(\text{Ti}_{0.95}\text{Y}_{0.05})\text{O}_3:\text{Pr}^{3+}$  and  $\text{Sr}(\text{Ti}_{0.97}\text{Ga}_{0.03})\text{O}_3:\text{Pr}^{3+}$

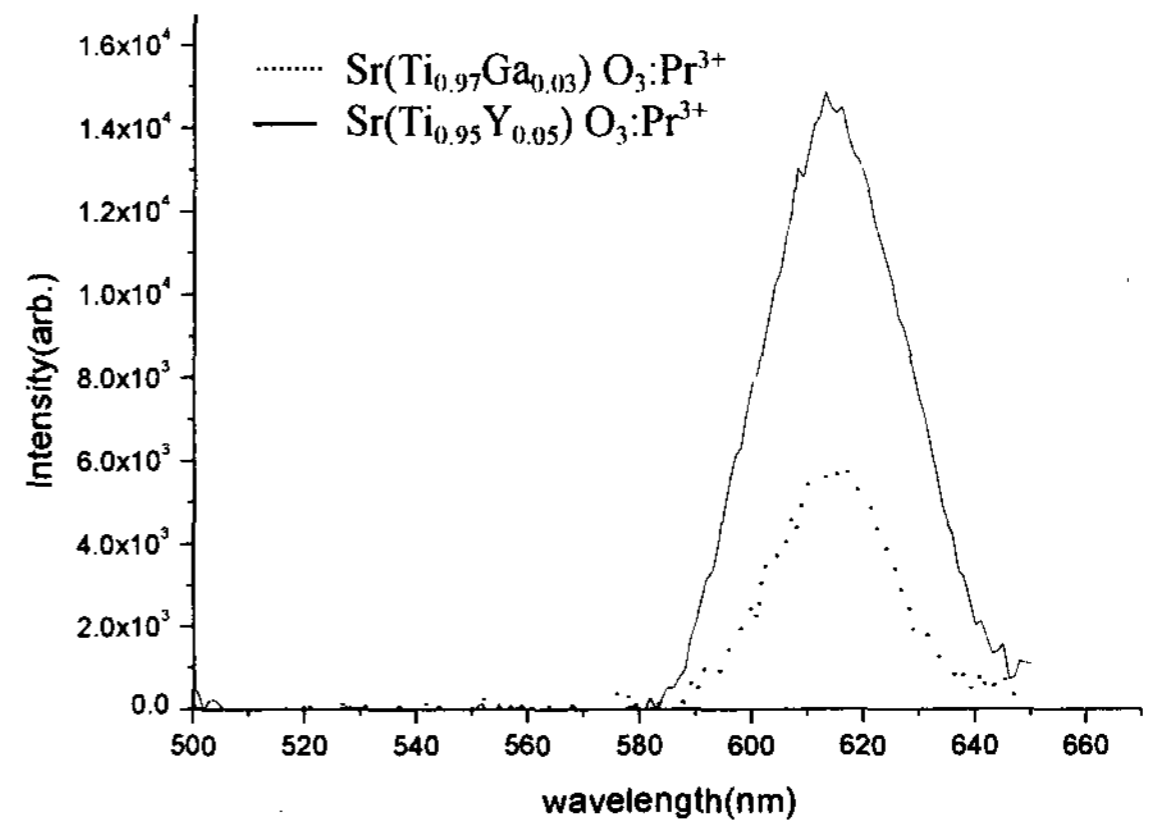


Fig.5. CL spectra of  $\text{Sr}(\text{Ti}_{0.95}\text{Y}_{0.05})\text{O}_3:\text{Pr}^{3+}$  and  $\text{Sr}(\text{Ti}_{0.97}\text{Ga}_{0.03})\text{O}_3:\text{Pr}^{3+}$  (acceleration voltage: 700 V).

Figure 4 shows PL excitation and emission spectra of  $\text{Ga}^{3+}$  doped a-type and  $\text{Y}^{3+}$  doped a-type. Their emission spectra are similar, but excitation spectra is absolutely different. The intensity of excitation band around 360 nm is nearly same, but the intensity of excitation band around 270 nm is different. The intensity of excitation for  $\text{Y}^{3+}$  doped a-type is two times higher than  $\text{Ga}^{3+}$  doped a-type. This result coincides with CL result that the CL intensity of  $\text{Y}^{3+}$  doped a-type will be higher than that of  $\text{Ga}^{3+}$  doped a-type as shown in Fig. 5. And emission at 493 nm is higher in  $\text{Y}^{3+}$  doped a-type than in  $\text{Ga}^{3+}$  doped a-type so we think that excitation band around 270 nm is related with green emission.

Recently, it was reported that the broad excitation band around 360 nm is due to host lattice excitation at emission by self-trapped excitations (500 nm) in  $\text{SrTiO}_3$ .<sup>1,4,5)</sup> But, the broad excitation band around 270 nm is not explained yet. We think this band is related with absorption of  $\text{Pr}^{3+}$  itself and affected by the distance between  $\text{Pr}^{3+}$  and O ligand, which can be varied by the size of co-activator. We also suppose that the location of this band is related with emitting level change discussed before.

## CONCLUSION

We have observed the change of emission band of green and red emission for  $\text{SrTiO}_3:\text{Pr}^{3+}$  by  $\text{Y}^{3+}$  and  $\text{Ga}^{3+}$  addition. The addition of  $\text{Y}^{3+}$  to Sr-deficient  $\text{SrTiO}_3:\text{Pr}^{3+}$  reveals the enhancement of green emission at 493 nm. But the addition of  $\text{Y}^{3+}$  to Ti-deficient  $\text{SrTiO}_3:\text{Pr}^{3+}$  reveals the enhancement of red. The mechanism of enhancement<sup>1)</sup> was suggested for Al-doped  $\text{SrTiO}_3:\text{Pr}^{3+}$ , there will be another mechanism which is not explained yet. Further investigation is necessary to find it out.

## REFERENCES

- 1) Shinji Okamoto, Hiroshi Kobayashi, Hajime Yamamoto, J. of Appl. Phys., Vol. 86, No. 10, 5594 (1999).
- 2) H.E. Hoefdraad and G. Blasse, Phys. Stat. Sol., (a) 89, K95, (1975).
- 3) M. Arai, N. Matsuda and M. Tamatani, J. Alloys Compounds, 192, 45, (1993).
- 4) T. Feng, Phys. Rev. B 25, 627 (1982).
- 5) R. Leonelli and J. L. Brebner, Phys. Rev. B 33, 8649 (1986).