

Luminescence Enhancement by Ba in SrTiO₃:Pr, Al Red Phosphor for Field Emission Displays

Chang-Whan Won,*† Jong-Eun Lee,* Hyung-Il Won,* Kwang-Bok Kim,
Yoon-Ho Song, Seung-Youl Kang, and Kyoung-Wan Koo**

Electronics and Telecommunications Research Institute, Daejeon 305-350, Korea

**Department of Metallurgy, Chungnam National University, Daejeon 305-764, Korea*

***Faculty of Electronic Engineering, Youngdong University, Chungbuk 370-800, Korea*

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ABSTRACT

The luminescence properties of Sr_{1-x}Ba_xTiO₃:Pr, Al red phosphor for Field Emission Displays (FEDs) have been investigated in powders prepared through solid-state reactions. Sr_{1-x}Ba_xTiO₃:Pr, Al red phosphors indicate a higher luminescent intensity, and have been found to have potential for field emission displays. The addition of Ba increased the luminescence intensity at 617 nm by up to 30%. Ba ions are effective in producing the energy transfers from host-to-activator in 4f-5d transitions.

Key words : Cathodoluminescence, FED, Field emission display, Luminescence

1. Introduction

Until now, most Field Emission Displays (FEDs) employ conventional Cathode Ray Tube (CRT) phosphors due to the good efficiency of RGB.¹⁾ Compared with CRT phosphors, the phosphors of FEDs are required to generate light at a low voltage and high current density.²⁾ Sulfide phosphors, however, chemically degrade under electron-bombardment in ultra high vacuum devices and also require protective aluminum back layer.³⁾ In order to improve the stability of the FED emitter arrays, non-sulfide phosphors are desired in these applications. In the case of red phosphors, many researchers have investigated the luminescence efficiency of BaTiO₃:Sm³⁺, SrTiO₃:Eu³⁺, SrTiO₃:Pr³⁺, and SrTiO₃:Pr³⁺, Al³⁺ (or Ga³⁺) as perovskite-type oxides.^{4,7)}

In this paper, the experimental results and mechanisms of luminescence enhancement are discussed. The effect of Ba-addition is examined through the morphology, structure and spectrum of the Sr_{1-x}Ba_xTiO₃:Pr³⁺, Al³⁺ red phosphor.

2. Experimental Procedure

The red Sr_{1-x}Ba_xTiO₃:Pr³⁺, Al³⁺ phosphors were prepared using a conventional solid-state procedure. The stoichiometric amounts of SrCO₃, BaCO₃, Al(OH)₃, Pr₆O₁₁ and TiO₂ precursors were mixed uniformly with ethanol in an agate mortar and then dried for 24 h at 120°C. The dried samples were fired using an alumina crucible at 1250°C for 3 h

under air in a muffle furnace. The red phosphor samples were prepared with a variation of Al contents and a substitution of Ba elements. At this time, the concentration of Pr, an activator, was constant at 0.2 mole%. The X-ray diffraction data were measured in a scattering range of 2θ = 15~80° using Cu K_α radiation with a graphite monochromator. A field Emission Scanning Electron Microscopy (FE-SEM) was carried out using a HITACHI electron microscope operating at 30 kV. The photoluminescence (PL) excitation and emission spectra were measured using a Hg lamp at room temperature. The cathodoluminescence (CL) spectra were measured under cathode-ray excitation at 5, 10, and 20 kV. The spectral variation of PL and CL was obtained using a fiber-optic coupled spectrometer with a wavelength resolution of 1 nm.

3. Results and Discussion

The powder morphology and size of (a) Sr_{0.8}Ba_{0.2}TiO₃:Pr³⁺, Al³⁺ and (b) Sr_{0.2}Ba_{0.8}TiO₃:Pr³⁺, Al³⁺ phosphors after the solid-state reaction process are shown in Fig. 1.

These photographs show that the particles changed from a spherical type to a polyhedral type with an increasing addition of Ba. This result may be due to the change in the crystal structure from the cubic perovskite of the Sr-Ti-O phase to the tetragonal structure of the Sr_{1-x}Ba_xTi-O phase resulting from the addition of Ba.

Fig. 2 shows the XRD patterns with different (a) Al and (b) Ba contents. The intensity of the Sr_{1-x}Ba_xTiO₃:Pr, Al phosphors was constant with the increasing Al content. However, in the secondary phase, SrAl₁₂O₁₉, appeared at 30 mol% of the Al contents.⁸⁾ This result may be due to a large

†Corresponding author : Chang-Whan Won

E-mail : cwwon@cnu.ac.kr

Tel : +82-2-821-7081 Fax : +82-42-822-9401

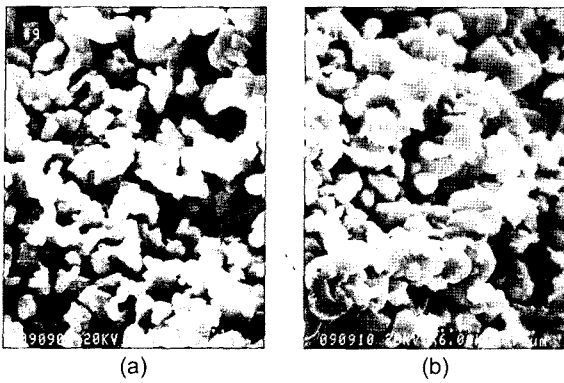


Fig. 1. Morphology of $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3\text{:Pr, Al}$ red phosphors: (a) $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{TiO}_3$ and (b) $\text{Sr}_{0.2}\text{Ba}_{0.8}\text{TiO}_3$.

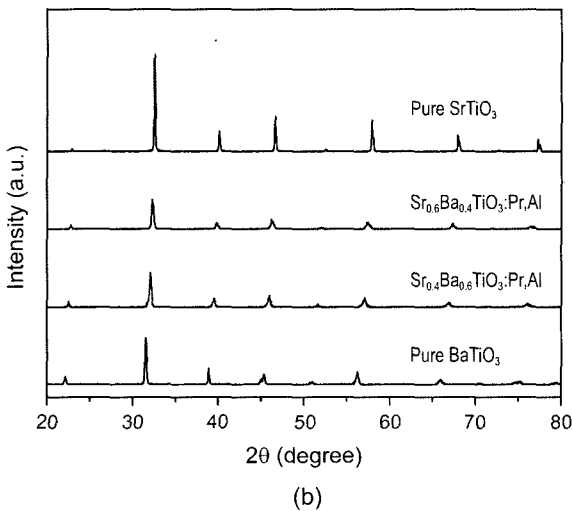
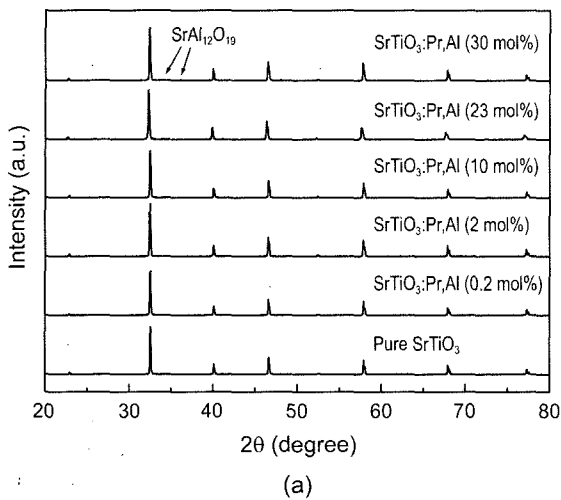


Fig. 2. X-ray diffraction patterns with the variation of (a) Al or (b) Ba contents, respectively.

amount of Al content creating a segregation of the alumina compound. The $\text{Sr}_{0.6}\text{-Ba}_{0.4}\text{-TiO}_3$ and $\text{Sr}_{0.4}\text{-Ba}_{0.6}\text{-TiO}_3$ phases were easily formed through solid-state reactions in Fig. 1 (b).

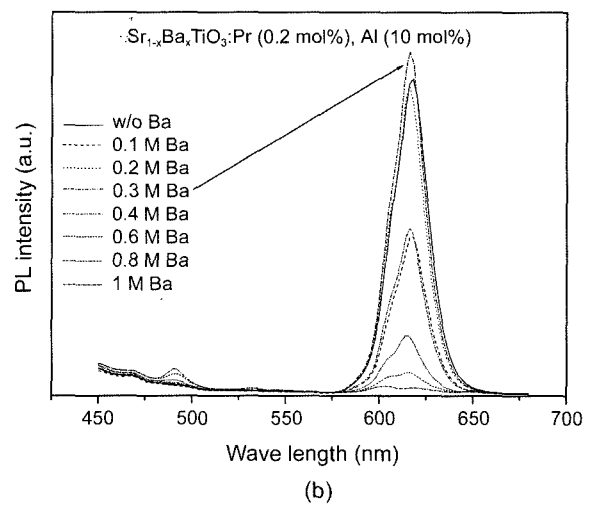
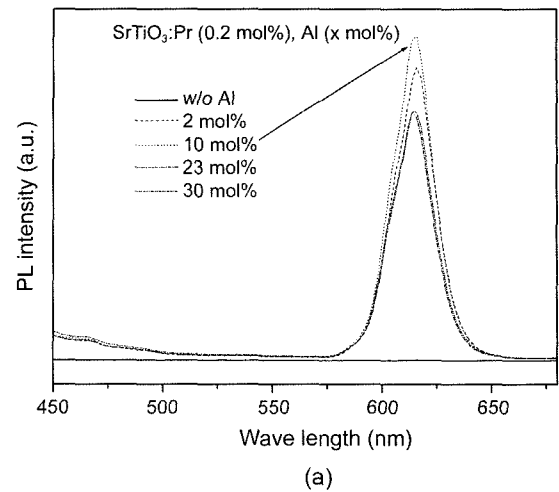


Fig. 3. Photoluminescence spectra with the variation of (a) Al or (b) Ba contents.

Fig. 3 shows the photoluminescence spectra with the variation of (a) Al or (b) Ba contents. The addition of Al created an emission peak at 617 nm.

The emission intensity increased until 10 mol% of Al, but it began to decrease after 10 mol%. These results do not agree with Yamamoto's reports⁹⁾ and show that the emission intensity does not only depend on the content of Al, but also the different firing conditions. This indicates that some Al ions penetrate into the SrTiO_3 lattice and become associated with Pr^{3+} , although most of the added Al ions are segregated from the SrTiO_3 by forming aluminates, as described in Fig. 2. According to Fig. 3(b), the maximum emission intensity was found at 0.3 mole% of Ba and the wavelength was shortened. These results indicate that an excess of Ba alone is not sufficient to intensify the light emissions efficiently.

Fig. 4 shows the CL spectra with a variation of Ba contents in $\text{Sr}_{1-x}\text{Ba}_x\text{TiO}_3\text{:Pr, Al}$ at 20 kV. When the Ba content is increased, the CL spectra show the same tendency of photoluminescence near 617 nm. The maximum emission intensity

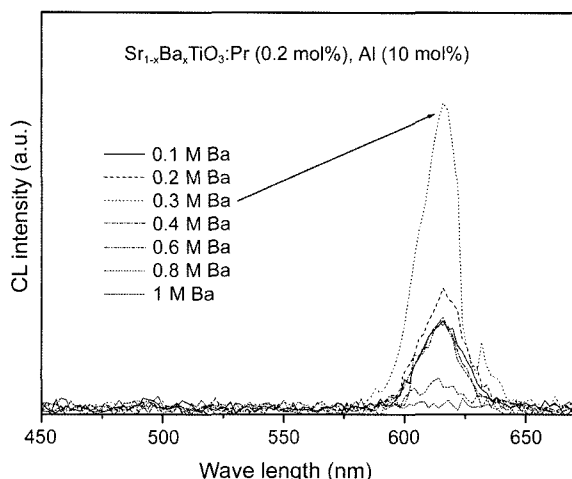


Fig. 4. Cathodoluminescence spectra with a variation of Ba contents in Sr_{1-x}Ba_xTiO₃:Pr, Al at 20 kV.

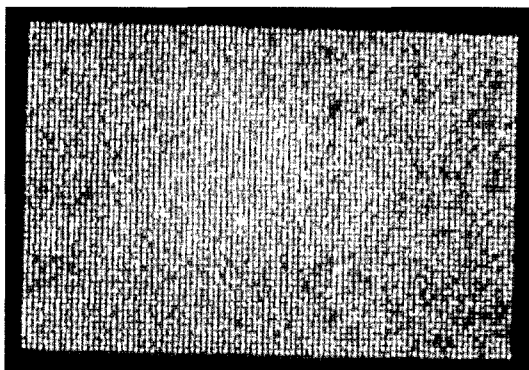


Fig. 5. Optical image of Sr_{0.7}Ba_{0.3}TiO₃:Pr, Al red phosphor in FED.

was found at the 0.3 mole ratio of Ba and this intensity is higher than the pure SrTiO₃:Pr, Al phosphors.¹⁰ Most phosphors have a low luminous efficiency at voltages below 5 kV due to the low electron penetration depth and the high non-radiative recombination rate at the surface. To adopt the FEDs, phosphors need to emit at a low electron voltage, under 5 kV. However, the tested results at low voltage are not shown due to the restrictions of the instrument resolution.

To generate a screen image, screen-printing technology was used by forming a paste with an organic binder on the transparent ITO electrodes of the anode front glass, as described elsewhere.¹¹ To fabricate a cathode emitter, the CNT pastes were mixed with organic vehicles, binders, surfactants and conductive materials. The mixed-CNT pastes were screen printed onto Ag/ITO coated glass through a metal mesh mask. In order to remove the organic binders, a firing treatment was performed in an annealing furnace. A proper surface treatment was then used to force the CNTs to protrude for efficient electron emissions. An additional firing process at a high temperature may remove the residual organic species. The direct emission image formed in a vacuum chamber is shown in Fig. 5. The panel size was 3-

inches diagonally with 96 × 64 pixels and fabricated using a diode structure with a 300 μm glass bead spacer. The final vacuum condition in the chamber was estimated to be under 10⁻⁵ Torr. The measured brightness was as high as 500 cd/m² at an anode voltage of 1000 V in a DC mode. The uniformity of the phosphor panel depended on the cathode emitters and the emission defect is due to the CNT emitters.

4. Conclusions

The luminescence properties of Sr_{1-x}Ba_xTiO₃:Pr, Al red phosphor for Field Emission Displays (FEDs) was investigated. It was found that the addition of Ba improved the PL and CL emission intensities. The optimal concentration of the co-activator, Al, and Ba was 10 mol% and 0.3 mole, respectively. Also this red phosphor showed a good image for FED anode plates.

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