

## STRUCTURAL ORDERING EFFECT ON PHOTOLUMINESCENCE PROPERTIES OF $\text{Eu}^{3+}$ DOPED PEROVSKITE TUNGSTATE $\text{A}_2\text{BWO}_6$ SYSTEM

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**Abstract** – The optical spectroscopic properties of the ordered perovskite structure  $\text{A}_2\text{BWO}_6$  doped with  $\text{Eu}^{3+}$  have been studied. The experimental result about  $\text{Eu}^{3+}$  ordering in the system of  $\text{A}_2\text{BWO}_6$  indicate the different structural conditions. Some influence of  $\text{Eu}^{3+}$  substitution on the different types of cation site have been investigated.

### INTRODUCTION

Recently, a number of studies have been performed on the optical properties of rare earth ions in perovskites.<sup>1-4</sup> Among the host compositions of perovskite materials, the molecular systems of  $\text{A}_2\text{BWO}_6$  and  $\text{A}_2\text{BUO}_6$  have been known as good systems for the model compounds in the investigation of nonradiative transitions.<sup>5-9</sup>

The  $\text{B}^{2+}$  and  $\text{W}^{6+}$  ions are crystallographically ordered in a way and placed at octahedral sites coordinated with 6 oxygen ions. A cation which is usually larger than B cation is placed in a cavity which is structured by corner shared octahedron, which is shown in Fig. 1. In fact, this crystal structure allows an extended cation substitution at the A and B sites.

To investigate the quenching dynamics depending on the structure,<sup>2,3,5,10,11</sup> we assigned  $\text{Eu}^{3+}$  ion as a rare earth ion substitute in different A and B sites in the ordered perovskite structure  $\text{A}_2\text{BWO}_6$ . This study reveals more detailed picture about the structures of the compounds and the corresponding energy quenching dynamics. In order to determine the roles of A and B sites we chose barium as the A ion and the other alkaline earth ions of  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$  as B ions. Selected compounds for the detailed studies are  $\text{Ba}_{2.75-x}\text{Eu}_x\text{Sr}_{0.25}\text{WO}_6$ ,  $\text{Ba}_2\text{Sr}_{1-x}\text{Eu}_x\text{WO}_6$ ,  $\text{Ba}_{2-x}\text{Eu}_x\text{Sr}\text{WO}_6$ , and  $\text{Ba}_2\text{Ca}_{1-x}\text{Eu}_x\text{WO}_6$ .

### MATERIALS AND METHODS

The series of  $\text{A}_2\text{BWO}_6$  compounds were prepared by solid state reaction methods. The starting materials were  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Eu}_2\text{O}_3$ ,  $\text{WO}_3$ , and  $\text{Na}_2\text{CO}_3$  (all the purities  $\geq 99.99\%$ ). The concentration of  $\text{Eu}^{3+}$  ions was varied from 0.01 to 0.05 mol%. The components were weighed by stoichiometric amount, and then the compensated ions of  $\text{Na}_2\text{CO}_3$  were

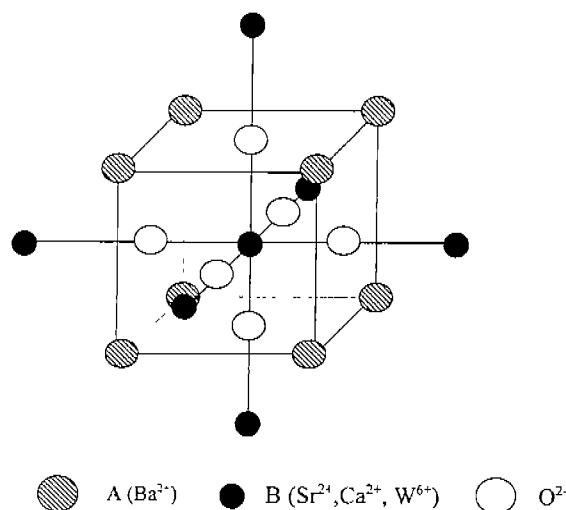


Figure 1. The ordered perovskite structure of  $\text{A}_2\text{BWO}_6$ .

added. The reaction conditions corresponding to the compounds are the followings :

1. For the compounds of  $\text{Ba}_{2.75-x}\text{Eu}_x\text{Sr}_{0.25}\text{WO}_6$ ,  $\text{Ba}_2\text{Sr}_{1-x}\text{Eu}_x\text{WO}_6$ , and  $\text{Ba}_{2-x}\text{Eu}_x\text{Sr}\text{WO}_6$ , the samples after weighing and mixing were placed in the ceramic board and heat treated at  $700\text{ }^\circ\text{C}$  for 1 h and then at  $1200\text{ }^\circ\text{C}$  for 1.5 h.

2. For the  $\text{Ba}_2\text{Ca}\text{WO}_6\text{-Eu}^{3+}$  compounds, after the preparation of calcium tungstate by heating at  $700\text{ }^\circ\text{C}$  for 2 hours in air,  $\text{Ba}_2\text{CO}_3$ ,  $\text{Eu}_2\text{O}_3$ , and  $\text{Na}_2\text{CO}_3$  were added to the calcium tungstate and, after mixing and grinding, the mixtures were heated at  $1200\text{ }^\circ\text{C}$  for 1.5 h.

The mono-phases of all samples were confirmed using Philips X-ray diffractometer 1710 with Ni-filtered  $\text{CuK}\alpha$  ( $\lambda=1.5418\text{ \AA}$ ) radiation in the range of  $10 \leq 2\theta \leq 80^\circ$ . The lattice parameters and crystal structures of the prepared samples have been determined. Photoluminescence experiments were carried out by nitrogen laser beam of  $\lambda=337\text{ nm}$ . The luminescence spectra were recorded by photomultiplier (RCA 4832) and lock-in nanovoltmeter (232B). The excitation spectra were measured under excitation by

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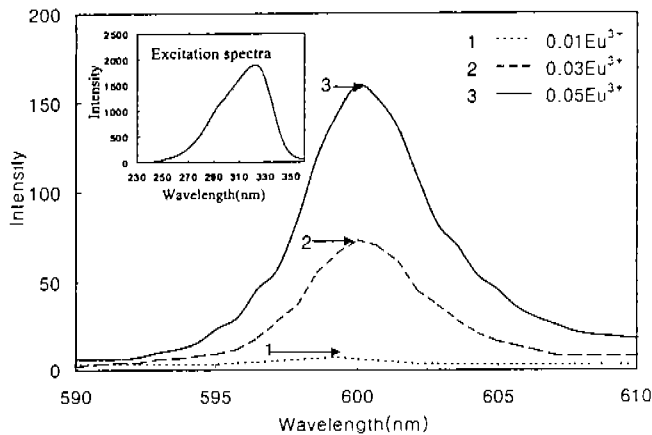


Figure 2. The luminescence spectra for the  $\text{Ba}_2\text{Sr}_{1-x}\text{Eu}_x\text{WO}_6$  of  $x=0.01$ ,  $x=0.03$ , and  $x=0.05$ .

Xe lamp(Oriel XBO151). All the luminescence experiments were carried out in a same condition.

## RESULTS AND DISCUSSION

### X-ray

The X-ray analysis showed that the samples were good solid solutions. The cell parameters are calculated by using least-square method. The samples of  $\text{Ba}_{2.75-x}\text{Eu}_x\text{Sr}_{0.25}\text{WO}_6$  and  $\text{Ba}_2\text{Ca}_{1-x}\text{Eu}_x\text{WO}_6$  have cubic structures with the lattice parameters of  $a=16.78 \text{ \AA}$  and  $8.32 \text{ \AA}$ , respectively. The samples of  $\text{Ba}_2\text{SrWO}_6$  show some distortions from cubic system and go lower symmetry. It is known that the series of the samples can be assigned to the monoclinic structure due to the dipoles which are induced by the distortion of the cells. A cubic system with larger lattice parameter of  $a=50.1 \text{ \AA}$  is determined for  $\text{Ba}_2\text{SrWO}_6$ .

In the ordered perovskite structure of  $\text{A}_2\text{BWO}_6$  system, the  $\text{Eu}^{3+}$  ions substitute into A sites of  $\text{Ba}_{2.75-x}\text{Eu}_x\text{Sr}_{0.25}\text{WO}_6$  and  $\text{Ba}_{2-x}\text{Eu}_x\text{SrWO}_6$  systems and into B sites of  $\text{Ba}_2\text{Sr}_{1-x}\text{Eu}_x\text{WO}_6$  and  $\text{Ba}_2\text{Ca}_{1-x}\text{Eu}_x\text{WO}_6$  systems.

### Emission

The excitation spectra were obtained for the four samples, at the emission wavelength of 600 nm corresponding to the emission band of  $\text{Eu}^{3+}$ .<sup>10-11</sup> The excitation spectra show asymmetric shape, which implies inhomogeneous broadening due to the mixed energy states of  $\text{Eu}^{3+}$  caused by the different surrounding ions. The emission spectra were measured by the excitation of  $\text{Eu}^{3+}$  absorption band at 337 nm and the spectra were shown in Figure 2 and 3. These emission bands are known to be originated from the transition of  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  of  $\text{Eu}^{3+}$  ion.<sup>3, 10</sup> In the  $\text{Ba}_{2-x}\text{Eu}_x\text{SrWO}_6$  systems of  $x=0.01$ ,  $x=0.03$  and  $x=0.05$ , the strongest intensity of the emission appears at the system of  $x=0.03$

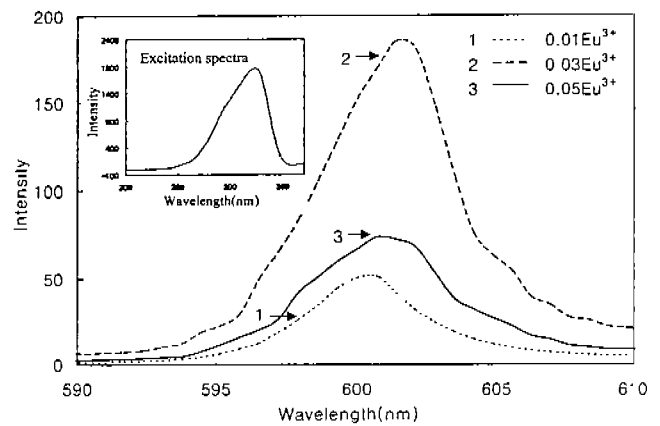


Figure 3. The luminescence spectra for the  $\text{Ba}_2\text{Sr}_{1-x}\text{Eu}_x\text{WO}_6$  of  $x=0.01$ ,  $x=0.03$ , and  $x=0.05$ .

On the other hand, for the systems of B site substitution, the emission intensity increases as the  $x$  concentration increases. Thus, in the system of B substitution, there is no significant fluorescence quenching state depending on the  $\text{Eu}^{3+}$  concentrations. It indicates that the  $\text{Eu}^{3+}$  locates in a energetically far distance which creates no quenching states among  $\text{Eu}^{3+}$  ions. However the system of A site substitution shows a similar trend to the B site substitution case until the  $\text{Eu}^{3+}$  concentration increases up to 0.03 mol%, but then the emission intensity decreases at the  $\text{Eu}^{3+}$  concentration of 0.05 mol%, indicating the change in the structural order around  $\text{Eu}^{3+}$  at the concentration of 0.05 mol%. Namely, at the  $\text{Eu}^{3+}$  concentration of 0.05 mol%,  $\text{Eu}^{3+}$  ions no longer keep the energetically isolated states. Instead, it seems that they tend to locate in the nearby positions enough to couple each other, resulting multiple energy bands among  $\text{Eu}^{3+}$  ions. Such multiplicity of energy states should induce more probability of curve crossing between the ground and the excited electronic states, which enhances the nonradiative relaxational cross section. Therefore the enhanced nonradiative relaxational cross section appears as the decrease of the fluorescence intensity in the A substitution system at  $\text{Eu}^{3+}$  concentration of 0.05 mol%. The  $\text{Eu}^{3+}$  ion structural ordering can be effected by the radii of surround atom, but the substitution site reveals more important factor for  $\text{Eu}^{3+}$  ion ordering, it is can be conformed by the observed emission spectra. Only A site substituted samples reveal concentration quenching effect in the samples.

Conclusively it is interesting to note that, in the B site substituted  $\text{Ba}_2\text{Sr}_{1-x}\text{Eu}_x\text{WO}_6$  system, the dopants of  $\text{Eu}^{3+}$  ions do not affect the energy quenching states of each other in the concentration range of 0 - 0.05 mol%. On the other hand the A site substituted  $\text{Ba}_{2-x}\text{Eu}_x\text{SrWO}_6$  systems show the concentration quenching at the  $\text{Eu}^{3+}$  concentration of 0.05 mol%, implying that the dopants of  $\text{Eu}^{3+}$  ions are closely located enough to interact each other for the formation of the nonradiative quenching states at the  $\text{Eu}^{3+}$  concentration of 0.05 mol% in the A substituted systems.

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## REFERENCES

1. Blasse, G. and B. C. Grabmaier (1994) *Luminescent Materials*, Springer, Berlin, Heidelberg, New York, p. 1.
2. Struct, C. W. and W. H. Fonger (1991) *Understanding Luminescence Spectra and Efficiency using Wp and Related Function*, Springer, New York, p. 1.
3. Blasse, G. (1993) *Properties and Applications of Perovskite type Oxide*, Marcel Dekker Inc., New York, p. 1.
4. Fu, W. T., C. Fouassier and P. Hagenmuller (1987) Influence of energy migration on the luminescence of  $\text{Li}_6\text{Eu}(\text{BO}_3)_3$ ; A material with predominant one-dimensional interactions. *J. Phys. Chem. Solids* **48**, 245-248.
5. Blasse, G. (1990) The influence of the ligands on the luminescence of metal ions. *Photochem. and Photobiol.* **52**(2), 417-422.
6. Brixner, L. H. (1987) New X-ray phosphors. *Mater. Chem. Phys.* **16**, 253-281.
7. Verwey, J. W. M., G. J. Dirksen and G. Blasse (1988) A study of the  $\text{Eu}^{3+}$  charge transfer state in lanthanide-borate glasses. *J. Non. Cryst. Solids* **107**, 49-54.
8. Blasse, G., J. P. M. Van Vliet, J. W. M. Verwey, R. Hoogedam and M. Weigel (1989) Luminescence of  $\text{Pr}^{3+}$  in scandium borate ( $\text{ScBO}_3$ ) and the host lattice dependence of the stokes shift. *J. Phys. Chem. Solids* **50**, 583-585.
9. Blasse, G. and L. H. Brixner (1990) The intensity of vibronic transitions in the spectra of the trivalent europium ion. *Inorg. Chim. Acta* **167**, 33-37.
10. Van Vliet, J. P. M., D. Van der Woort and G. Blasse (1989) Luminescence and energy migration in  $\text{Eu}^{3+}$  containing scheelites with different anions. *J. Luminescence* **42**, 305-316.
11. Blasse, G. (1990) Luminescence of inorganic solids. *Prog. Solid State Chem.* **35**, 319.