

2차원적 K_2NiF_4 형 구조의 $Sr_{2-2x}Eu_xK_xSnO_4$ 에서 Eu^{3+} 이온의 Luminescence

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(1997. 2. 12 접수)

Eu^{3+} Luminescence in Two-Dimensional $Sr_{2-2x}Eu_xK_xSnO_4$ with K_2NiF_4 Structure

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(Received February 12, 1997)

요 약. 2차원적 K_2NiF_4 형 구조를 갖는 $Sr_{2-2x}Eu_xK_xSnO_4$ 의 주격자 안에 존재하는 Eu^{3+} 이온의 luminescence에 대한 연구를 수행하였다. Eu^{3+} 이온의 ${}^5D_0 \rightarrow {}^7F_0$ 전이에 의한 방출선은 $J=0 \rightarrow J=0$ 전이로써 Eu^{3+} 이온의 4f 껍질에서 전기 이중극자 전이에 대한 Judd-Ofelt 선택규칙(selection rule)에 의하여 금지된 전이이다. 그러나 $Sr_{2-2x}Eu_xK_xSnO_4$ 의 Eu^{3+} 이온의 방출 스펙트럼에서는 ${}^5D_0 \rightarrow {}^7F_0$ 전이에 의한 방출선이 상당히 큰 세기로 나타난다. 이러한 ${}^5D_0 \rightarrow {}^7F_0$ 전이는 Eu^{3+} 주위 국부구조(local structure)의 뒤틀림에 의하여 허용된다.

ABSTRACT. Luminescence of Eu^{3+} has been studied in $Sr_{2-2x}Eu_xK_xSnO_4$ with two-dimensional K_2NiF_4 structure. The ${}^5D_0 \rightarrow {}^7F_0$ emission line of Eu^{3+} ion represents the $J=0 \rightarrow J=0$ transition which is forbidden by a Judd-Ofelt selection rule for electric dipole transition in 4f shell of Eu^{3+} ions. However, the emission line of ${}^5D_0 \rightarrow {}^7F_0$ transition gains remarkably high intensity in Eu^{3+} emission spectra of $Sr_{2-2x}Eu_xK_xSnO_4$. The transition of ${}^5D_0 \rightarrow {}^7F_0$ is allowed due to distortion of local structure around Eu^{3+} ions.

INTRODUCTION

The quasi-two dimensional oxide, A_2BO_4 of K_2NiF_4 structure, possessing ABO_3 layers in between rock-salt AO layers where in B-O-B interaction occurs only in the ab plane had been investigated in detail.¹ Electrical and magnetic properties of the A_2BO_4 oxides are distinctly different from those of the corresponding perovskites ABO_3 . Increasing the number of perovskite layer in $SrO(La_{1-x}Sr_xMnO_3)_n$ causes an increase in electrical conductivity as well as ferromagnetic interaction.²

The magnetization behavior of the $n=1$ oxide (K_2NiF_4 structure) is reported in the previous studies,¹

while the three dimensional $La_{1-x}Sr_xMnO_3$ ($x=0.3$) system is metallic. The two dimensional systems are all semi-conducting but the oxide becomes a highly conducting ferromagnet for $n \geq 2$.

Three dimensional perovskite, $La_{0.8}Sr_{0.2}MnO_{3+x}$, has a catalytic properties reported by Marti *et al.*³ A strict comparison of the magnetic, electrical, and other properties between the three-dimensional ABO_3 perovskites and the two-dimensional A_2BO_4 type oxides would be possible only when the same oxidation state of the transition metal(B) ion is maintained. Previous studies indicate fascinating differences between the two systems.^{2,4-6} Studies

of the quasi-two-dimensional oxides have been extensively developed but their optical studies are relatively fewer than those of the corresponding three dimensional oxide.

Luminescence properties are very sensitive for the local symmetry of luminophore. When rare earth ions are doped in two dimensional matrices,^{7,8} emission efficiency depends strongly on the crystallographic variety of energy migration in the excited state. Endo *et al.* indicate that $\text{Sr}_{n+1}\text{SnO}_{3n+1}$ ($n=1$ or 2) was available as host materials for doping Eu^{2+} ions and only $\text{Sr}_{2-x}\text{Eu}_x\text{SnO}_4$ showed an intense blue luminescence at about 470 nm corresponding to the transition from ${}^4\text{F}_7$ to ${}^4\text{F}_6$ and ${}^5\text{D}$.⁷ In the present work, the optical properties of Eu^{3+} ions in the same matrix have been studied in detail. The substitution of Eu^{3+} ion in the Sr^{2+} site with charge compensating ion is not so soft like Eu^{3+} and leads to excitation at high energy region. The phenomena will be discussed below.

EXPERIMENTAL

The starting materials are SrCO_3 , Eu_2O_3 , SnO_2 and K_2CO_3 , where the purity of all compounds is 99.99%, for the preparation of $\text{Sr}_{2-2x}\text{Eu}_x\text{K}_x\text{SnO}_4$ where $x=0.005$, 0.01 , and 0.03 . The components are weighed out to stoichiometric amount. The K_2CO_3 are added for charge compensation by solid state reaction. The starting materials are weighed in the desired proportions, then they are mixed and ground. The mixture is heated in the air at 1300°C for 4 hours.

The crystallographic structure of all compounds is confirmed using Philip diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation in the range $10^\circ \leq 2\theta \leq 80^\circ$. Photoluminescence experiments are carried out by using OPTON monochromator under excitation by nitrogen laser beam of $\lambda=337.1$ nm. The spectra are recorded by photomultiplier RCA 4832 and lock-in nanovoltmeter 232B. The excitation spectra were measured by using the monochromator Model 77250 and 77276 under excitation by xenon lamp XBO151. The spectra were recorded by photomultiplier tube Model 70680. The spectra of cathodoluminescence were obtained by exciting

the samples with anode voltage 15 kV.

RESULTS AND DISCUSSION

The X-ray diffraction assigns the crystallographic structure of the $\text{Sr}_{2-2x}\text{Eu}_x\text{K}_x\text{SnO}_4$ to the tetragonal system with a K_2NiF_4 type structure whose space group is $I4/mmm$. The XRD pattern of the sample is shown in Fig. 1 and its lattice parameters are $a=0.404$ nm and $c=1.259$ nm. The diagram of K_2NiF_4 type structure is presented in Fig. 2 where hatched circles and filled ones are Sr^{2+} and Sn^{4+} ions, respectively.

It is confirmed from the results of the XRD a-

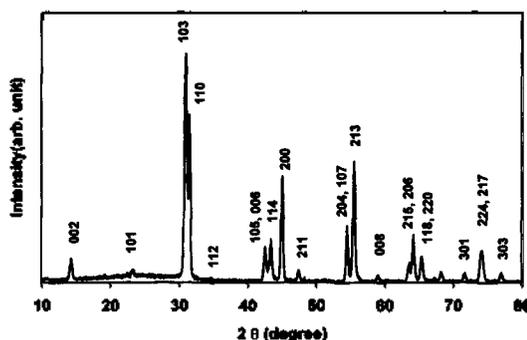


Fig. 1. The powder x-ray diffraction pattern for the compound of $\text{Sr}_{1.98}\text{Eu}_{0.01}\text{K}_{0.01}\text{SnO}_4$.

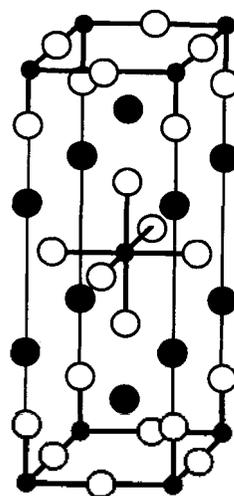


Fig. 2. Crystal structure Sr_2SnO_4 (K_2NiF_4 -type); filled circles, hatched circles, and open circles represent Sn^{4+} , Sr^{2+} , and O^{2-} , respectively.

analyses that the Sr²⁺ ions are replaced by Eu³⁺ ions in all the samples of Sr₂SnO₄·xEu³⁺ (x=0.005, 0.01, and 0.03) homogeneously. The same amount of K⁺ ions with Eu³⁺ ions is added in all compounds for charge compensation. The XRD patterns suggest that the structure of all the compositions is the same tetragonal as Sr₂SnO₄. The Eu³⁺ ions substituted for the Sr²⁺ ions are coordinated with 9 oxygen ions whose local symmetry is C_{4v} as shown in Fig. 2.

Excitation. The excitation spectra of Eu³⁺(4f⁶) ions in the Sr_{2-2x}Eu_xK_xSnO₄ where x=0.005, 0.01, and 0.03 are shown in Fig. 3. The excitation spectra show a charge transfer band from the 2p of oxygen ions to the 4f orbital of Eu³⁺ ions and the final state of the excitation is |4f⁷(Eu)-2p¹(O)>: two broad peaks at 259 nm and 312 nm for the compositions of x=0.005 and 0.01 respectively, but one peak at 312 nm for the composition x=0.03 under 619 nm radiation. The charge transfer from oxygen to Eu³⁺ is affected by the coordination geometry. In two-dimensional K₂NiF₄ type compounds, it has been generally suggested that the interplanar interactions along c-axis are very weak compared with the intraplannar interaction within *ab* planes. The ratio of *c/a* of Sr_{2-2x}Eu_xK_xSnO₄ is about 3.114 and the bond length of Eu-O along c-axis is longer than that of the other Eu-O. Therefore, the excitation spectra are depicted into two broad peaks due to in one hand, the different bond length of Eu-O and on the other hand, the ion radii of the charge compensating ion(K⁺) which are larger than

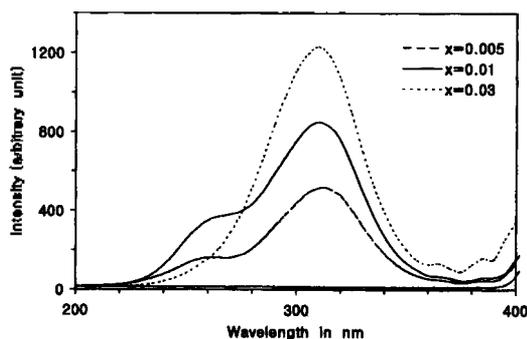


Fig. 3. The excitation spectra of Sr_{2-2x}Eu_xK_xSnO₄ for the compositions of x=0.005, 0.01, and 0.03. λ_{em} =619 nm.

those of the substitution ions (Eu³⁺ and Sr²⁺). This lead to create the deep center K⁺ ion at the Sr²⁺ site which need the excited energy higher than the charge transfer energy. It is displayed at about 259 nm region at low doped concentration compositions and disappeared at higher one. The ⁷F₀-⁵D_J transitions for J=0, 1, 2 of Sr_{2-2x}Eu_xK_xSnO₄ are depicted at about 366, 371 and 400 nm, respectively.

Emission. The spectra of luminescence of Sr_{2-2x}Eu_xK_xSnO₄ where (x=0.005, 0.01, and 0.03) have been measured at room temperature under the excitation of nitrogen laser (λ =337 nm) and that of Sr_{1.94}Eu_{0.03}K_{0.03}SnO₄ is shown in Fig. 4. Relative intensities of emission lines are listed in Table 1. The spectra consists of singlet of ⁵D₀→⁷F₀, triplet of ⁵D₀→⁷F₁, quartet ⁵D₀→⁷F₂, and singlet of ⁵D₀→⁷F₄.

In general, the J=0→J=0 transitions are forbidden by selection rule of Judd-Ofelt theory for the electric dipole transition of rare earth ion between 4fⁿ states.⁹ A theory based on the 4fⁿ wave functions which are improved by the effects of both spin-orbital interaction and odd-parity crystal field term with *L*≥3 accounts reasonably well for the absorption and emission intensities of those f-f transitions.¹⁰

The ⁵D₀→⁷F₀ transition with high intensity is detected at 580 nm in all the compositions of Sr_{2-2x}Eu_xK_xSnO₄ where x=0.005, 0.01, and 0.03 with K₂NiF₄ type structure as shown in Fig. 4. The ratio

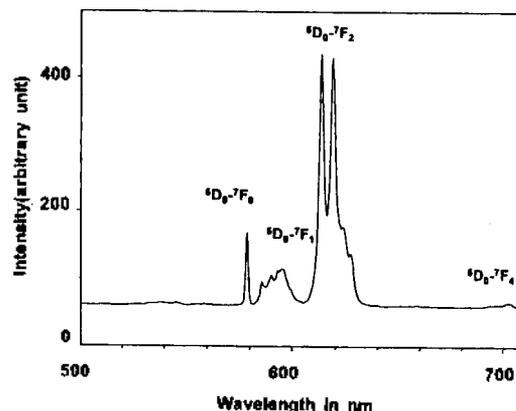
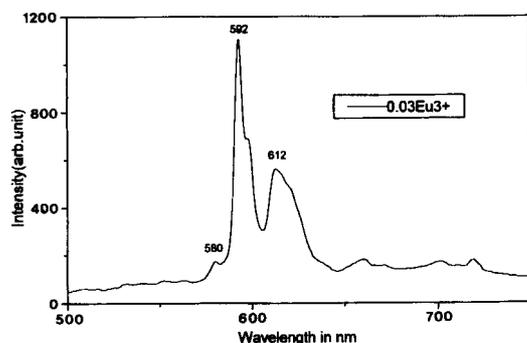


Fig. 4. The emission spectrum of Sr_{1.94}Eu_{0.03}K_{0.03}SnO₄ (λ_{ex} =337 nm).

Table 1. The data corresponding to the ${}^5D_0 \rightarrow {}^7F_j$ transitions of Eu^{3+} ions in $\text{Sr}_{1.94}\text{Eu}_{0.03}\text{K}_{0.03}\text{SnO}_4$

Peak ^a	${}^5D_0 \rightarrow {}^7F_0$		${}^5D_0 \rightarrow {}^7F_1$		${}^5D_0 \rightarrow {}^7F_2$		${}^5D_0 \rightarrow {}^7F_3$		${}^5D_0 \rightarrow {}^7F_4$	
	nm	I/I_0 ^b	nm	I/I_0	nm	I/I_0	nm	I/I_0	nm	I/I_0
1	580	2.2	585	61.5	612	723	-	-	702	15
2	-	-	589	86.4	617	877	-	-	-	-
3	-	-	594	100	622	285	-	-	-	-
4	-	-	-	-	625	192	-	-	-	-

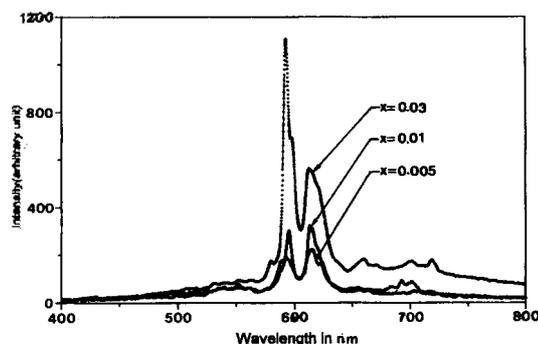
^aNumber of peaks introduced by hyperfine splitting at each ${}^5D_0 \rightarrow {}^7F_j$ transition. ^b I/I_0 is a relative intensity compared with the strongest peak of ${}^5D_0 \rightarrow {}^7F_1$ transition.

Fig. 5. The cathodoluminescent spectrum of $\text{Sr}_{1.94}\text{Eu}_{0.01}\text{K}_{0.01}\text{SnO}_4$.

of ${}^5D_0 \rightarrow {}^7F_0$ / ${}^5D_0 \rightarrow {}^7F_1$ is about 2.15. The relative intensity of Eu^{3+} ion increases with increase of the doping concentrations. The substituted Eu^{3+} ion is coordinated with 8 oxygen ions (4SnO_6) at one side and 1 oxygen ions (1SnO_6) at the other side as shown in Fig. 2. Therefore, the electric field around Eu^{3+} is not spherical and there is an electric field gradient in it.

It is obvious that the emission intensity of Ln^{3+} ion is sensitive to the nature of the site symmetry of the host and the nature of the excited energy. The energy gap between 7F_1 and 7F_0 of Eu^{3+} ion is so small that the character of 7F_1 may be mixed into 7F_0 level in the C_{4v} symmetry which is not centro-spherical.¹¹ The forbidden ${}^5D_0 \rightarrow {}^7F_0$ transition gains some intensity from the J states mixing by the coordination geometry around Eu^{3+} ion as C_{4v} .

The emission spectra of $\text{Sr}_{1.94}\text{Eu}_{0.03}\text{K}_{0.03}\text{SnO}_4$ excited by the electron beam is presented in Fig. 5. The peak intensity corresponding to ${}^5D_0 \rightarrow {}^7F_1$ transition is weaker than that of ${}^5D_0 \rightarrow {}^7F_2$ transition in

Fig. 6. The cathodoluminescent spectra of $\text{Sr}_{2-2x}\text{Eu}_x\text{K}_x\text{SnO}_4$ for the compositions of $x=0.005$, 0.01, and 0.03.

photoluminescence spectra as shown in Fig. 4. However, the spectra of cathodoluminescence shows that the peak intensity corresponding to ${}^5D_0 \rightarrow {}^7F_1$ is very stronger than that of ${}^5D_0 \rightarrow {}^7F_2$ transition. The spectra of cathodoluminescence of $\text{Sr}_{2-2x}\text{Eu}_x\text{K}_x\text{SnO}_4$ for $x=0.005$, 0.01, and 0.03 are presented in Fig. 6. The relative intensities of Eu^{3+} ion increased with increasing the dopant similar to the photoluminescence case. The excitation by the electron beam with higher energy leads to change the relative intensity ratio between magnetic dipole allowed ${}^7D_0 \rightarrow {}^7F_1$ and electric dipole ${}^5D_0 \rightarrow {}^7F_2$ transition as shown in Fig. 6. The peak intensity corresponding to ${}^5D_0 \rightarrow {}^7F_1$ and ${}^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ion depends on whether the transition is excited by the electron beam or the photon beam.

CONCLUSION

The compounds of $\text{Sr}_{2-2x}\text{Eu}_x\text{K}_x\text{SnO}_4$ for $x=0.00$, 0.005, 0.01, and 0.03 have two-dimensional K_2NiF_4 type structure. In the emission spectra of Eu^{3+} , the forbidden ${}^5D_0 \rightarrow {}^7F_0$ transition gains some intensity

by the coordination geometry around Eu³⁺ ion as C_{4v}. The strong intensity by the ⁵D₀ → ⁷F₀ transition of Eu³⁺ ions is explained by the linear crystal-field around Eu³⁺ ion. In the excitation spectra of Eu³⁺, the strong bands around 300 nm is given by charge transfer from O²⁻ to Eu³⁺. The excitation spectra are displayed into two broad peaks. One is due to different Eu-O bond length in two-dimensional K₂NiF₄ type structure and the order is due to the deep center of charge compensating ion in Sr²⁺ site which needs the excitation energy higher than the energy for charge transfer from oxygen to Eu³⁺ along the c-axis. The peak intensity corresponding to ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ transitions of Eu³⁺ ion in the Sr₂SnO₄ host lattice with two-dimensional K₂NiF₄ structure depends on whether the transition is excited by the electron beam or the photon beam.

Acknowledgments. The present study was supported by the Basic Science Research Institute Program, Ministry of Education of Korea, 1995, Project No. BSRI-95-3424. The authors would like to thank the Korea Science and Engineering Foundation for the financial support to a post-doctor. We are very grateful to Dr. C. H. Kim of Korea Institute of Science and Technology for the lu-

minescence measurements.

REFERENCES

1. Rao, C. N. R.; Gangly, P.; Sing, K. K.; Moan Ram, R. A. *J. Solid State Chem.* **1988**, *72*, 14-23.
2. Moan Ram, R. A.; Gangly, P.; Rae, C. N. R. *J. Solid State Chem.* **1987**, *70*, 82-87.
3. Mart, P. E.; Maciejewski, M.; Baiker, A. *Preparation of Catalyst VI.* **1995**, 617-626.
4. Dissmyake, I.; Kharas, K. C. C.; Lunsford, J. H.; Rosyneck, M. P. *J. Catal.* **1993**, *139*, 652.
5. Petit, C.; Kaidvri, K.; Libs, S.; Kiennemann, A.; Rehspringer, J. L.; Poix, P. *J. Catal.* **1993**, *140*, 328.
6. Kishan Kumar, V. S.; Acharyulu, B. S. V. S. R.; Sactry, S. B. S. *J. Mater. Sci.* **1991**, *26*, 1069.
7. Endo, T.; Masuda, T.; Takizawa, H.; Shimada, M. *J. of Materials Science Letter II.* **1992**, 1330-1332.
8. Schapter, H.; Gabowski, E.; Primet, M. *Appl. Catal.* **1991**, *75*, 119.
9. Kirby, A. F.; Foster, D.; Richardson, F. S. *Chem. Phys. Letters.* **1983**, *95*, 507.
10. Blasse, G.; Brill, A. *Philips Res. Repts.* **1966**, *21*, 368-378.
11. Blasse, G.; Brill, A. *Philips Technical Review.* **1970**, *31*, 10.