

A Fundamental Study of Structure-Property Relationships in Eu^{3+} Luminescence

Ki-Seog Chang

Department of Chemistry, Korea Air Force Academy, Chungbuk 363-849, Korea

Eu^{3+} 이온의 발광성에 대한 구조와 성질의 기본적인 연구

張 起 錫

공군사관학교 화학과

Abstract

The $\text{M}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ ($\text{M} = \text{Ca}$ and Sr) solid solution systems have been shown interstitial solid solutions and continuous substitutional solid solutions. The symmetry around the Eu site of $y\text{Eu}^{3+}:\text{M}_{1-x-y}\text{Na}_x\text{Al}_2\text{Mg}_y(\text{BO}_3)_2\text{O}$ ($\text{M} = \text{Ca}$ and Sr) changes the intensities and the chromaticities of transitions. The Eu^{3+} ion can be very bright and efficient and have the desired emission wavelength depending on the site symmetry of the Eu^{3+} ion site. As the amount of Na in the Eu^{3+} ion doped $\text{Ca}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ system increases, the Eu site symmetry is going to be a noncentrosymmetric site. With increasing x , the decreased intensity in the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (590 nm) transition relates to the low symmetry of the Eu^{3+} -doped $\text{Ca}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ system, because of the Ca -centered octahedron in the $\text{CaAl}_2(\text{BO}_3)_2\text{O}$ compound. The $\text{SrAl}_2(\text{BO}_3)_2\text{O}$ compound also provides an improved chromaticity due to the lower site symmetry of Eu^{3+} ion.

요 약

$\text{M}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ ($\text{M} = \text{Ca}$ and Sr) 고용체계는 치환형과 틸새형 고용체를 동시에 갖는다. 이상의 고용체계 물질에 첨가된 발광원자의 에너지 전이는 발광원자, Eu 주위의 대칭성에 깊은 관계가 있다. Eu^{3+} 이온의 경우, Eu^{3+} 이온의 주변 대칭성에 따라서 매우 밝고 효율적인 발광성 불순물이 될 수 있기 때문에 구조와 연계한 연구가 가능하다. $\text{Eu}^{3+}:\text{Ca}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ 고용체계의 Na 원자 양이 증가함에 따라 Eu^{3+} 이온의 대칭성이 낮아진다. $\text{CaAl}_2(\text{BO}_3)_2\text{O}$ 화합물은 Ca 원자 중심의 팔면체 구조를 갖기 때문에, 조성비 x 의 증가와 함께, 화합물의 낮은 대칭성에 의해서 $\text{Eu}^{3+}:\text{Ca}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ 고용체계의 $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (590 nm) 전이의 상대적인 세기가 감소한다. 그러한 또 다른 예는 비대칭성 물질인 $\text{Eu}^{3+}:\text{SrAl}_2(\text{BO}_3)_2\text{O}$ 화합물에서도 찾아 볼 수 있었다.

1. Introduction

Research involving optical and luminescent materials during the last 30 years has lead to the many development of their widely recognized uses. For example, laser applications encompass communications, image processing, computing, and medical surgery. Light emitting solid-state materials have also found far-reaching applications that include var-

ious types of display technology, e.g., television and fluorescent lamps. Clearly, the investigation of new materials issues forth a means of replacing older and less cost-effective devices with modern energy efficient ones, in addition to developing advanced technologies.

The red luminescence of the Eu^{3+} ion doped into inorganic solids has been extensively studied. The sharp emission feature near 612 nm has found

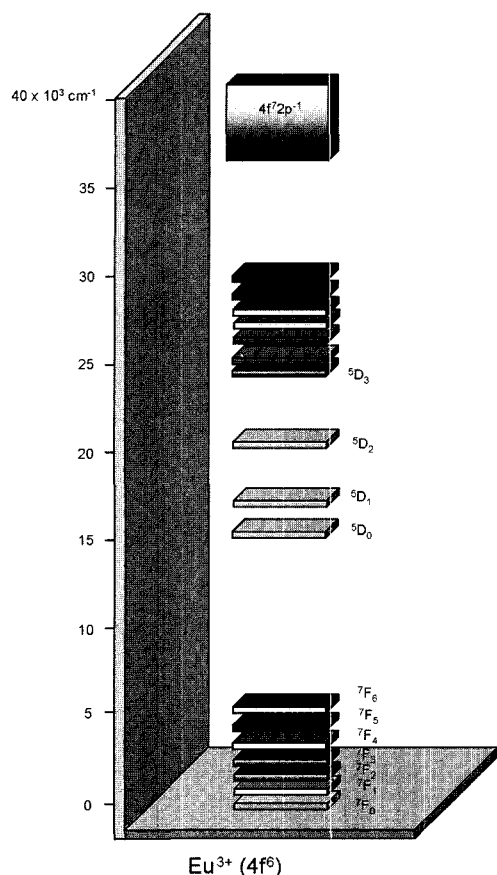


Fig. 1. Energy level diagram for Eu^{3+} ion.

important applications in fluorescent lighting and display technologies such as color television and plasma displays. The emission transition occurs from the excited $^5\text{D}_0$ level to the $^7\text{F}_J$ levels ($J = 0, 1, 2, 3, 4, 5, 6$) of the $4f^6$ configuration of the Eu^{3+} ion.^{1,2)} A Eu^{3+} energy level diagram is drawn in Fig. 1. Because $f \rightarrow f$ type transitions of the $4f$ orbitals are well shielded by the filled $5s^2$ and $5p^6$ levels, these transitions are only weakly influenced by the host lattice. Furthermore, since the transitions are not spin-allowed, long excited-state lifetime on the order of 10^{-3} are observed. For a luminescent center on a site of inversion, the most intense transition is $^5\text{D}_0 \rightarrow ^7\text{F}_1$, which occurs near 590 nm. The orange color of this line is inadequate for display and lighting purposes. However, once the symmetry constraint is lifted, the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition can dominate, thereby, generating a saturated red line near 612

nm. Some of the characteristics of this emission in the $\text{Eu}^{3+}:\text{M}_{1-x}\text{Na}_{2x}\text{Al}_2(\text{BO}_3)_2\text{O}$ ($\text{M} = \text{Ca}$ and Sr) systems are described in this work.

2. Experimental

2-1. Synthesis, Crystal Growth, and Solid Solution

Synthesis and Crystal Growth. A powdered sample of $\text{M}_{1-x}\text{Na}_{2x}\text{Al}_2(\text{BO}_3)_2\text{O}$ ($\text{M} = \text{Ca}$ and Sr) was prepared by heating a stoichiometric mixture of the reagents, MCO_3 ($\text{M} = \text{Ca}$, Sr , and Na_2) (Alfa, 99.99%), Al_2O_3 (Alfa, 99.999%), and B_2O_3 (Alfa, 99.98%). The mixture was heated at 893 K for 1 h, cooled and ground at room temperature, and again heated in a Pt crucible at 1173–1273 K for 12 h. An X-ray powder diffraction pattern of the product, obtained with a Philips diffractometer, matched with that the computer program LAZY-PULVERIX³⁾ generated on the basis of the results of the single-crystal study (*vide infra*). The compound $\text{M}_{1-x}\text{Na}_{2x}\text{Al}_2(\text{BO}_3)_2\text{O}$ ($\text{M} = \text{Ca}$ and Sr) melts congruently at 1283 K with flux, 30 mol% LiBO_2 . The melt was cooled at 0.07 K/min from 1333 to 900 K and then 5 K/min to room temperature. A clear, colorless crystal was physically separated from the matrix for X-ray measurements (Fig. 2).

Solid Solution. A powdered solid solution sample of $\text{M}_{1-x}\text{Na}_{2x}\text{Al}_2(\text{BO}_3)_2\text{O}$ ($\text{M} = \text{Ca}$ and Sr) system was prepared by heating a stoichiometric mixture of the reagents, MCO_3 ($\text{M} = \text{Ca}$, Sr , and Na_2), Al_2O_3 , and B_2O_3 . The mixture was heated at 893 K for 1 h, cooled and ground at room temperature, and again heated in a Pt crucible at 1173 K for 22 h. An X-ray powder diffraction pattern of the product, obtained with a Philips diffractometer, was collected. The peak positions were corrected by using an internal silicon powder standard. Peak positions and unit-cell constants were calculated by using the least squares with $\mu\text{-Vax-II}$ computer program, *POLSQ*.⁴⁾

2-2. Optical Measurement

Emission spectra were obtained by using a spectrofluorimeter equipped with Cary excitation and Oriel emission monochromators and an Oriel 350-W Xe lamp as the source (Fig. 3). Emission spectra

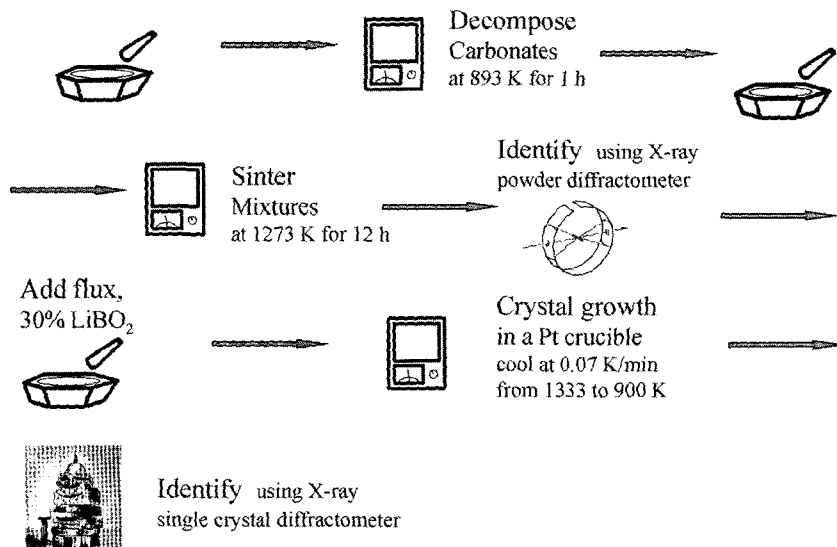


Fig. 2. Synthesis diagram of Eu³⁺ ion-doped aluminum borate materials.

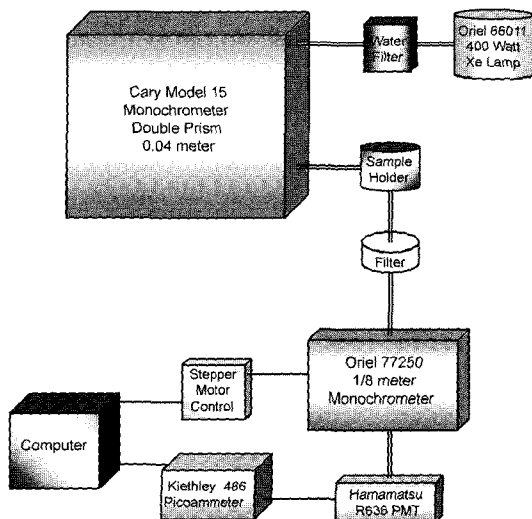


Fig. 3. Spectrometer diagram.

were corrected for variation in PMT response and the wavelength-dependent throughput of the monochromator.

3. Results and Discussion

3-1. Solid Solution

To identify the structures $M_xNa_{2-2x}Al_2(BO_3)_2O$ ($M = Ca$ and Sr), we examined the solid-solution

series $M_xNa_{2-2x}Al_2(BO_3)_2O$ over the range $0 < x < 1$; the results from powder X-ray diffraction measurements are summarized in Table 1.

The unit-cell parameters of $(Ca, Na_2)Al_2(BO_3)_2O$ solid solution systems were analyzed by a Rigaku AFC6R X-ray diffractometer [Fig. 5(a)]. Among the 2 series, the unit-cell parameters of $(Sr, Na_2)Al_2(BO_3)_2O$ solid-solution systems were determined by X-ray powder patterns [Fig. 4 and 5(b)] using a standard reference material 640b silicon powder⁸⁾ and the POLSQ software package⁴⁾ on a -Vax-II computer.

There are two types of solid solutions, substitutional and interstitial solid solutions. Interstitial solid solutions are formed by placing atoms between those which are already present, and substitutional solid solutions are formed by substituting one type of atom for another. The $Ca_xNa_{2-2x}Al_2(BO_3)_2O$ solid-solution systems have been shown as interstitial solid solutions and continuous substitutional solid solutions according to Vegard's law⁹⁾, and their crystal structures are shown in Fig. 5 and 6, in particular.

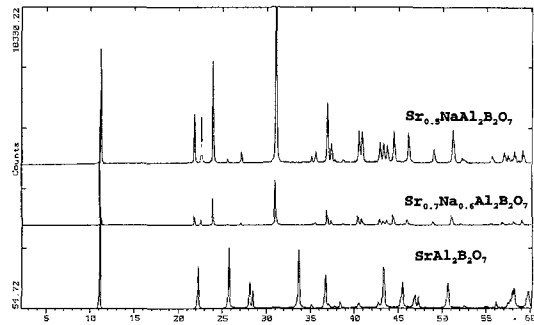
3-2. Luminescence

yEu^{3+} : $M_{1-x-y}Na_{2x}Al_{2-y}Mg_y(BO_3)_2O$ ($M \approx Sr$ and Ca) system has been studied for a red luminescence material, where Eu^{3+} ion is used at the M^{2+} ion site

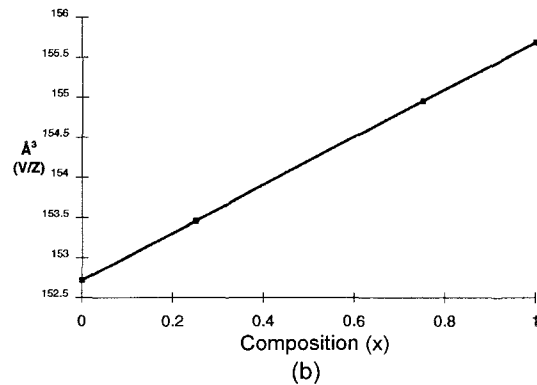
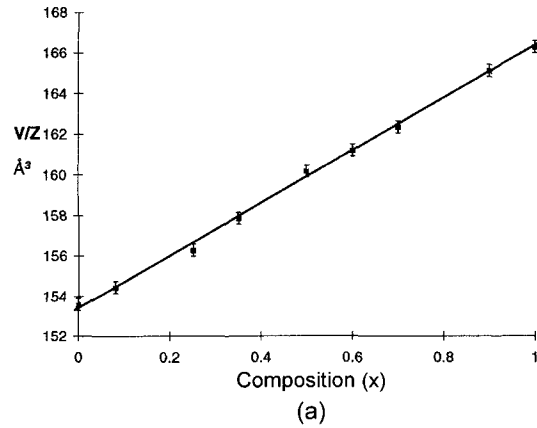
Table 1. Phase transition of $M_x\text{Na}_{2-2x}\text{Al}_2(\text{BO}_3)_2\text{O}$ ($M = \text{Ca}$ and Sr) systems

Composition	(x)	$\text{Ca}_x\text{Na}_{2-2x}\text{Al}_2(\text{BO}_3)_2\text{O}$	$\text{Sr}_x\text{Na}_{2-2x}\text{Al}_2(\text{BO}_3)_2\text{O}$
	0	NABO ⁵ (Space group $P31c$)	
	~0.2	NABO	SNABO
	~0.4	CNABO	SNABO
	~0.6	CNABO	SNABO
	~0.8	CNABO	SNABO
	1	CABO ⁶ ($R3c$)	SABO ⁷

NABO = $\text{Na}_2\text{Al}_2(\text{BO}_3)_2\text{O}$: $a = b = 4.8087(6)$ Å, $c = 15.273(4)$ Å, $V = 305.86(6)$ Å³, space group = $P31c$ (no. 159), $Z = 2$; CNABO($\text{Ca}_x\text{Na}_{2-2x}\text{Al}_2(\text{BO}_3)_2\text{O}$) $\text{Ca}_{0.74}\text{Na}_{0.52}\text{Al}_2(\text{BO}_3)_2\text{O}$: $a = b = 4.812(1)$ Å, $c = 15.453(1)$ Å, $V = 309.9(1)$ Å³, space group = $P6_322$ (no. 182), $Z = 2$; SNABO($\text{Sr}_x\text{Na}_{2-2x}\text{Al}_2(\text{BO}_3)_2\text{O}$) $\text{Sr}_{0.84}\text{Na}_{0.32}\text{Al}_2(\text{BO}_3)_2\text{O}$: $a = b = 4.870(3)$ Å, $c = 15.802(1)$ Å, $V = 325.63(5)$ Å³, space group = $P6_322$, $Z = 2$; CABO = $\text{Ca}_2\text{Al}_2(\text{BO}_3)_2\text{O}$: $a = b = 4.810(6)$ Å, $c = 46.633(5)$ Å, $V = 934(1)$ Å³, space group = $R3c(h)$ (no. 167), $Z = 6$; SABO = $\text{SrAl}_2(\text{BO}_3)_2\text{O}$: $a = b = 4.891(2)$ Å, $c = 23.923(4)$ Å, $V = 495.6(2)$ Å³, space group = $R32$ (no. 155), $Z = 3$.

Fig. 4. X-ray powder patterns in the $\text{Sr}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ system.

as an activator and Mg^{2+} ion is used at the Al^{3+} ion site for charge balance. The emission transition of the Eu^{3+} ion arises from the excited $^5\text{D}_0$ level to the $^7\text{F}_j$ levels ($j = 0, 1, 2, 3, 4, 5, 6$) of the $4f^6$ configuration. Changes in the spectrum of the Eu^{3+} ion are perhaps related to the symmetry of the Eu site. Sites with inversion symmetry, only allow magnetic-dipole transitions ($\Delta J = \pm 1$) corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition (≈ 590 nm), are usually too orange for most applications. However, if the site symmetry is noncentrosymmetric, the electric-dipole transition is allowed ($\Delta J = \pm 2$), which is the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition (≈ 620 nm), to generate the perfect red.^{1,2)} As the symmetry around the Eu site changes, the intensities and the chromaticities of all transitions change. The Eu^{3+} ion can be very bright and efficient and has the desired emission wavelength depending on the site symmetry of the Eu^{3+} ion site. It also has unique properties based on the environment around

Fig. 5. Graph of the continuous substitutional solid solutions of the $\text{M}_{1-x}\text{Na}_x\text{Al}_2(\text{BO}_3)_2\text{O}$ system: (a) Powder crystal cell parameters in $M = \text{Sr}$; (b) Single crystal cell parameters in $M = \text{Ca}$.

it, which can lead to structural information. The high intensity of the $^5\text{D}_{00} \rightarrow ^7\text{F}_4$ transition near 700 nm may be an unacceptable loss, but this intensity

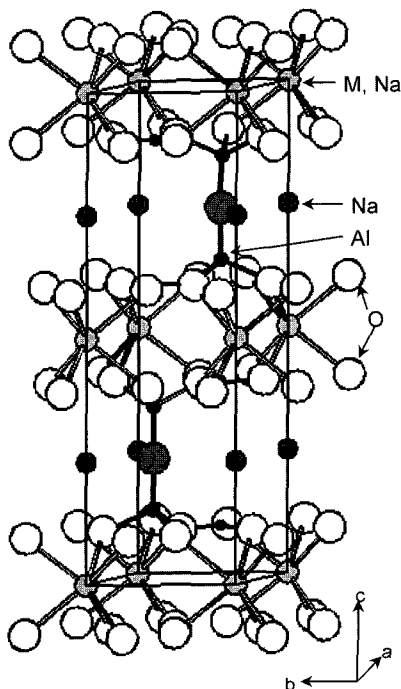


Fig. 6. Drawing of the unit cell of $M_{1-x}Na_{2x}Al_2(BO_3)_2O$ system ($M = Ca$ and Sr).

should be monitored as a function of Na substitution. Because of a strong and efficient saturated red emission at 612 nm, $Eu^{3+}:Y_2O_3$ is generally considered to set the standard for the comparison with other red-emitting photoluminescent materials. The red-emitting phosphor is currently used in the device of Eu^{3+} -doped Y_2O_3 ,¹⁰⁾ which has the chromaticity of $X = 0.652$ and $Y = 0.348$. The emission spectrum would be chromatically variable. Such a transition typically occurs in distorted octahedra since the activator site will deviate from the inversion symmetry to yield a hypersensitive forced electric-dipole transition.^{1,2)} As the amount of Na in the Eu^{3+} ion-doped $Ca_{1-x}Na_{2x}Al_2(BO_3)_2O$ system increases,

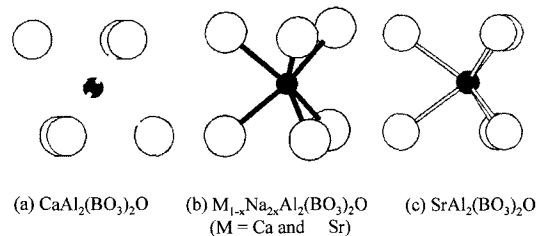


Fig. 7. MO_6 structures of aluminum borates ($M = Na, Ca$ and Sr).

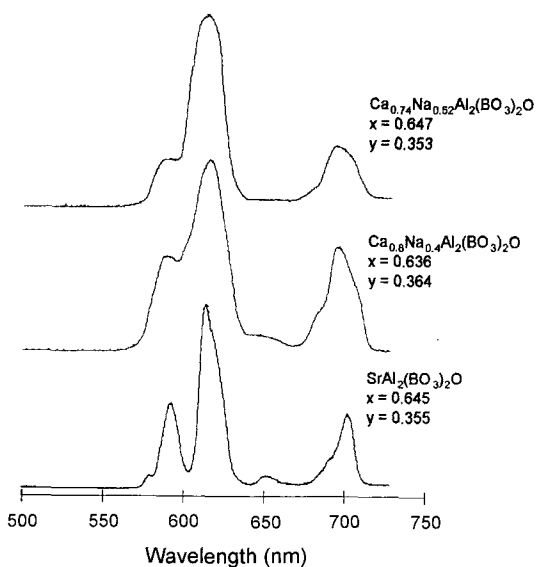


Fig. 8. Emission spectra and chromaticity of $yEu^{3+}: M_{1-x-y}Na_{2x}Al_{2-y}Mg_y(BO_3)_2O$ ($M = Ca$ and Sr).

the Eu site-symmetry becomes a noncentrosymmetric site. Therefore, the intensity in the $^5D_{00} \rightarrow ^7F_1$ (≈ 590 nm) transition relative to that of the Eu^{3+} -doped $Ca_{1-x}Na_{2x}Al_2(BO_3)_2O$ system decreases, because the compound $CaAl_2(BO_3)_2O$ has a Ca-centered octahedron due to a Eu-doping site symmetry (Table 2 and Fig. 7). The $SrAl_2(BO_3)_2O$ compound also provides an improved chromaticity due to the lower site

Table 2. Site symmetry and geometry of MO_6 ($M = Na, Ca$ and Sr) structures in $M_xNa_{2-2x}Al_2(BO_3)_2O$ ($M = Ca$ and Sr) systems

Compound	Space group	Site symmetry	Site geometry
$CaAl_2(BO_3)_2O$	$R\bar{3}c(h)$	S_6	Trigonal antiprism
$SrAl_2(BO_3)_2O$	$R32$	D_3	~Trigonal prism
$Na_2Al_2(BO_3)_2O$	$P31c$	D_3	Distorted trigonal prism
$M_xNa_{2-2x}Al_2(BO_3)_2O$	$P6_322$	C_3	Distorted trigonal antiprism

symmetry of the Eu^{3+} ion. The emission spectra and chromaticity of the Eu^{3+} -doped $\text{Ca}_{1-x}\text{Na}_{2x}\text{Al}_2(\text{BO}_3)_2\text{O}$ ($x = 0.2$ and 0.26) and $\text{SrAl}_2(\text{BO}_3)_2\text{O}$ compounds are shown in Fig. 8.

Acknowledgment

This work was supported by the Aerospace Research Institute at the Korea Air Force Academy. KSC would like to thank Professor Douglas A. Keszler of Oregon State University for the use of the emission spectrometer and the single-crystal diffractometer.

References

- 1) Judd, B. R., *Phys. Rev.*, **127**, 750 (1966).
- 2) Ofelt, G. S., *J. Chem. Phys.*, **37**, 511 (1966).
- 3) Yvon, K., Jeitschko, W. and Parthe, E., *J. Appl. Cryst.*, **10**, 73 (1977).
- 4) POLSQ: Least Squares Unit Cell Refinement, David Cahen (1973).
- 5) Chang, K. S., *Ph.D. Thesis*, Oregon State University in USA, Chap. 6 (1998).
- 6) Chang, K. S. and Keszler, D. A., *Mat. Res. Bull.*, **33**, 299 (1998).
- 7) Chang, K. S., *Ph.D. Thesis*, Oregon State University in USA, Chap. 3 (1998).
- 8) This Standard Reference Material (SRM) was prepared for use as either an external or internal $2\theta/d$ -spacing calibration standard for powder diffractometry by U.S. Department of Commerce Malcolm Baldrige.
- 9) Athony, R. W., *Solid State Chemistry and Its Applications*, Chap. 10, 358 (1985).
- 10) Welker, T., *J. of Luminescence*, **48-49**, 49 (1991).