

Research and Characterization of the Phosphor for Mercury-free Fluorescent Lamps

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The synthesis and luminescence properties of Eu^{3+} -doped ordered olivine-type NaLnGeO_4 ($\text{Ln} = \text{rare earth}$) phosphors are reported. Under vacuum-UV (VUV) excitation, this phosphor shows intense red emission due to the ${}^5\text{D}_0$ - ${}^7\text{F}_2$ transition. The $\text{Na}(\text{Y}_{0.3}\text{Gd}_{0.65}\text{Eu}_{0.05})\text{GeO}_4$ phosphor with optimum composition and synthetic condition under 147 nm excitation are higher than those of red phosphor $(\text{Y}_{0.95}\text{Eu}_{0.05})_2\text{O}_3$.

Keywords: Germanate, Olivine, VUV, Luminescence, Europium

1. INTRODUCTION

Modern human society requires advanced phosphor materials with a high efficiency for various excitation sources. In white fluorescent lamps, an invisible ultraviolet (UV) light from a mercury vapor is converted into visible light by Red – Green - Blue phosphors. The mercury is a poison and causes serious damage to both humans and the environment.¹ Millennium project (Environment, No. 12317; Research and development of phosphors for mercury-free fluorescent lamp) in Japan focuses on the development of new phosphors for a mercury-free fluorescent lamp. A discharge of Xe-gas is promising candidate for excitation source of the mercury-free white fluorescent lamp.^{2,3} Since a main emission peak of the Xe discharge is located at short wavelength (147 nm) than that of the conventional mercury discharge (254 nm), efficient vacuum-UV (VUV) phosphors are required for the mercury-free fluorescent lamps and plasma display panels (PDP). Typical VUV phosphors are shown in Table I. Although current red phosphor, $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$, shows efficient red emission under the VUV excitation, a color purity of

this material is very poor.⁴ The color purity of the phosphors is very important to make pure white color for the lamps and displays. In this study, we report the luminescence characteristics of new olivine-type VUV phosphor, $\text{NaLnGeO}_4:\text{Eu}^{3+}$ ($\text{Ln} = \text{rare earth}$), with a pure red color.

2. EXPERIMENTAL

Powder samples of $\text{NaLnGeO}_4:\text{Eu}^{3+}$ ($\text{Ln} = \text{rare earth}$) were synthesized by a conventional solid state reaction. The starting material was a stoichiometric mixture of Na_2CO_3 (Merck Japan Ltd., 99.9 %), Ln_2O_3 (Shin-etsu Chemical Co., Ltd., 99.99 %) and GeO_2 (Kanto Kagaku, 99.99 %). The material was ground and then fired at 1223 K in an open alumina crucible for 24 h.

The crystal structure of NaLnGeO_4 was analyzed by powder X-ray diffraction patterns, which were recorded on a Rigaku RAD-rA diffractometer equipped with a curved crystal graphite monochromator using $\text{CuK}\alpha$ radiation. The data were collected by a step-scanning mode in the 2θ range of $10 - 110^\circ$ with a step width of 0.02° and a step time of 4 s. Indexing of the powder XRD

Table I. Lumimnescence properties of commercial VUV Phosphors

Composition	Color	1/10 Decay time (ms)	Against baking	
$(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$	Orange-red	3-9	Weak	Poor chromaticity
$(\text{Y,Gd})_2\text{O}_3:\text{Eu}^{3+}$	Red	3	Strong	Low efficiency
$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$	Green	8-16	Weak	Long afterglow
$\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$	Blue	< 1	Weak	Degradation

patterns was performed with the aid of the computer program of CELL.⁵ Data analysis was carried out by the Rietveld method, using the RIETAN2000 profile refinement program.⁶

The excitation and emission spectra in the UV range were measured on a powder sample using a JASCO FP-6500/6600 spectrofluorometer. Photoluminescence spectra under the VUV excitation (147 nm) were recorded using D₂ lamp. The relative brightness of the phosphors under the VUV excitation was recorded with a vacuum monochromator combined with a deuterium lamp using sodium salicylate, HOC₆H₄COONa, as a reference.

3. RESULTS AND DISCUSSION

In the Na-Ln-Ge-O system, the compounds with Ln = La - Nd are unknown, while the compounds with Ln = Sm - Lu and Y are of olivine structure.⁷ The space group of NaGdGeO₄ was determined to be Pnma based on the systematic absences of powder XRD patterns and packing considerations. The Rietveld refinement of the structure carried out on NaGdGeO₄. The crystallographic data finally obtained by the Rietveld refinement are given in Table II. Figure 1 shows the crystal structure of an ordered-olivine NaGdGeO₄.⁸ The rare earth ions occupy a site (4c) with a C_s symmetry. The ordered olivine structure has a quasi - two dimensional rare earth sublattice. Under UV excitation, the excitation energy transfer would take place within the planes because of long separation among the emission centers.

VUV emission spectra of the samples are shown in Figure 2. This compound shows several sharp peaks corresponding to 4f levels of the Eu³⁺ ions. The deep red emission of ⁵D₀-⁷F₂ is strongly influenced by the surroundings of the emission center. Since Eu³⁺ ions of NaLnGeO₄:Eu³⁺ occupy the 4c positions without an inversion center, the ⁵D₀-⁷F₂ emission is dominant for their electric dipole character.

Figure 3 shows a plot of the concentration dependence of Eu³⁺ for the luminescence intensity for the ⁵D₀-⁷F₂ transitions in the NaGd_{1-x}Eu_xGeO₄. The luminescence intensity of the NaGd_{0.25}Eu_{0.75}GeO₄ is comparable to that

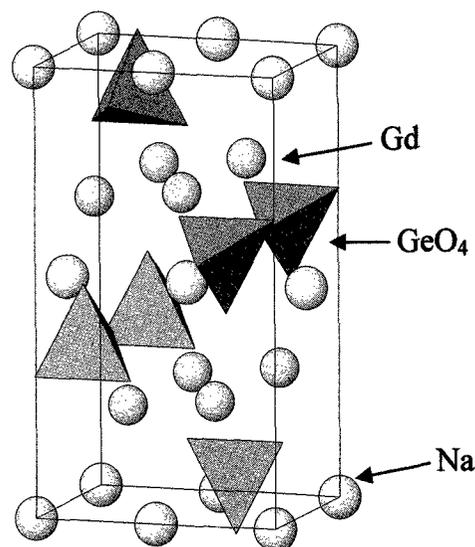


Fig. 1 Crystal structure of NaGdGeO₄.

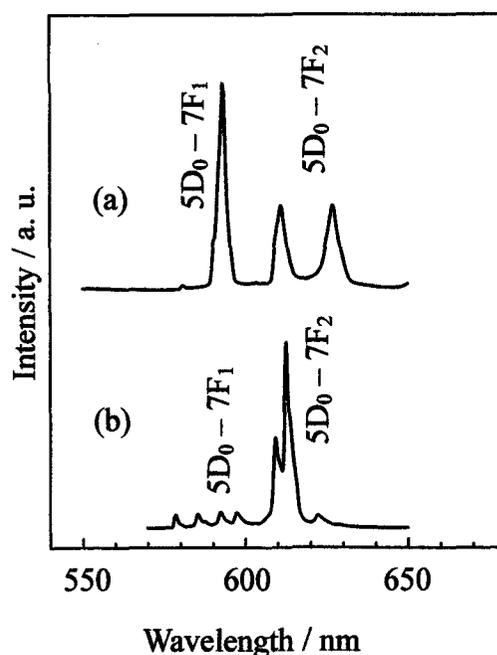


Fig. 2 VUV emission spectra of (a) YBO₃:Eu³⁺ and (b) NaGd_{0.95}Eu_{0.05}GeO₄.

Table II. Crystallographic data of ordered olivine-type NaGdGeO₄.

	Site	g	x	y	z	B×10 ⁻² / nm ²
Na	4a	1.0	0.0	0.0	0.0	1.16(1)
Gd	4c	1.0	0.27832(8)	0.25	-0.0007(2)	0.65(2)
Ge	4c	1.0	0.0955(1)	0.25	0.5599(3)	0.69(5)
O(1)	4c	1.0	0.1045(7)	0.25	0.249(1)	0.1(1)
O(2)	4c	1.0	0.4608(8)	0.25	0.824(1)	0.1(1)
O(3)	8d	1.0	0.1642(5)	0.0451(9)	0.702(1)	0.1(1)
Pnma (No. 62), a = 1.15486(2) nm, b = 0.65334(1) nm, c = 0.53000(1) nm						
R _{wp} = 8.84 %, R _p = 6.66 %, R _F = 2.74 %, R _G = 5.96 %, R _T = 5.15 %						

of a commercial high brightness red phosphor, $Y_2O_3:Eu^{3+}$. A concentration quenching behavior was observed in the ordered-olivine compound, where a critical concentration was found to be $x_{cr} = 0.75$. This value is about one order of magnitude higher than those of conventional inorganic phosphors. Such high luminescent efficiency is attributed to the long separation of the emission centers from each other, which prevents from the excursion of excited energy.

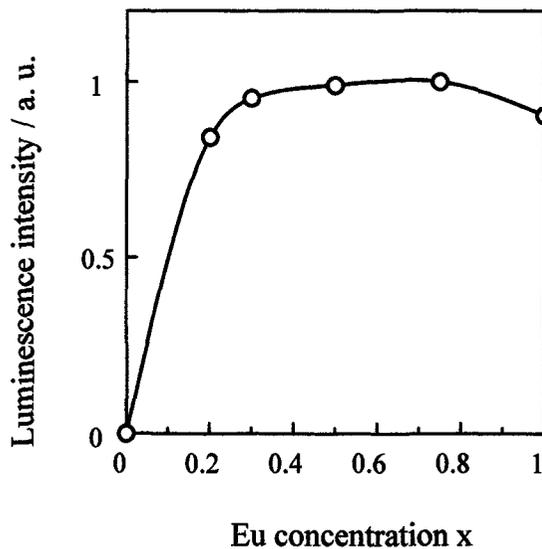


Fig. 3 The concentration dependence of the luminescence intensity for the ${}^5D_0-{}^7F_2$ transitions of Eu^{3+} in the $NaGd_{1-x}Eu_xGeO_4$ under UV excitation

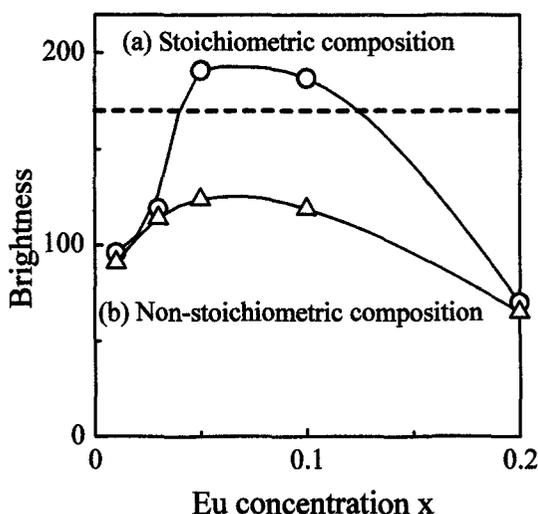


Fig. 4 The Concentration quenching of $Na(Y_{0.3}Gd_{0.7-x}Eu_x)GeO_4$ with (a) stoichiometric and (b) non-stoichiometric composition under 147 nm excitation. (----- : $Y_2O_3:Eu(5 \text{ mol}\%)$)

Concentration quenching of optimum composition $Na(Y_{0.3}Gd_{0.7-x}Eu_x)GeO_4$ under VUV excitation is shown in Figure 4. The brightness of conventional VUV phosphor, $(Y_{0.95}Eu_{0.05})_2O_3$, is also shown by dotted line as a reference. The critical concentration ($x = 0.05$) under VUV excitation is much lower than that ($x = 0.75$) obtained under UV excitation.⁸ This result demonstrates that the energy transfer mechanism under the VUV excitation is quite different from that under the UV excitation. The low critical concentration may be due to high possibility of the energy transfer among the emission centers because of large excitation energy under VUV excitation. According to simple concentration quenching model⁹, the critical distance of the energy transfer under VUV excitation was more than 2 times longer than that under UV excitation. Therefore, the phosphor matrix with the low-dimensional arrangement of the emission center should be favorable in the designing of VUV phosphors.

In addition, the effect of surface loss such as "dead layer" has also investigated. In general, excess amount of flux such as sodium carbonate (30 mol%)⁸ or sodium fluoride⁹ was added to accelerate the solid state reaction of the phosphors. As shown Figure 4, the stoichiometric compound exhibited higher emission intensity than the non-stoichiometric product synthesized by the self-flux method using 30 mol% excess sodium carbonate. The penetration depth in phosphors of VUV radiation is estimated to be about 100 nm.¹⁰ Therefore, the "dead layer" should be minimized in the synthesis of the VUV phosphors.

4. CONCLUSIONS

Pure red-emitting VUV phosphor, $NaLnGeO_4:Eu^{3+}$ ($Ln = \text{rare earth}$), was prepared by the conventional solid state reaction. The composition, $Na(Y_{0.3}Gd_{0.65}Eu_{0.05})GeO_4$, shows the highest brightness under VUV excitation (147 nm), which is higher than that of red phosphor $(Y_{0.95}Eu_{0.05})_2O_3$.

ACKNOWLEDGMENT

This research was supported by a Science and Technology Agent for the Millennium Projects (No. 12317) and a Grant-in-Aid for Encouragement of Young Scientists (No. 13750773) from the Ministry of Education, Science, Sports and Culture of Japan.

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(Received December 20, 2002; Accepted January 31, 2003)