New VUV Phosphor, $NaLnGeO_4:Eu^{3+}$ (Ln = Rare Earth)

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The synthesis and luminescence properties of Eu^{3+}-doped ordered olivine-type $NaLnGeO_4$ (Ln = rare earth) phosphors are reported. Under vacuum-UV (VUV) excitation, this phosphor showed intense red emission due to the $^5D_0$-$^7F_2$ transition. The $Na(Y_{0.3}Gd_{0.65}Eu_{0.05})GeO_4$ phosphor with optimum composition and synthetic condition under 147 nm excitation were higher than those of $(Y_{0.95}Eu_{0.05})_2O_3$.

In white fluorescent lamps, an ultraviolet (UV) irradiation from a mercury vapor is converted into visible light by various phosphors. Poisonous mercury causes serious damage to both human and the environment.[1] Xe-gas based discharge is promising candidates for excitation source of the mercury-free fluorescent lamp.[2,3] Since a main emission peak of this discharge is located at short wavelength (147 nm) than that of the conventional mercury discharge (254 nm), highly efficient VUV phosphors are required for the mercury-free fluorescent lamps and plasma display panels (PDP). Although current red phosphor, $(Y,Gd)BO_3:Eu^{3+}$, shows efficient red emission under the VUV excitation, a color purity of this material is poor.[4] The emitting color is red with a tint of orange. The color purity in the phosphors for the lamp and display is very important to make pure white color. In this study, we report luminescence characteristics of new VUV phosphor, $NaLnGeO_4:Eu^{3+}$ (Ln = rare earth), with a pure red color.

Polycrystalline samples of $NaLnGeO_4:Eu^{3+}$ (Ln = rare earth) were synthesized by conventional solid state reaction. The starting material was a stoichiometric mixture of Na_2CO_3 (Merck Japan Ltd., 99.9%), RE_2O_3 (Shin-etsu Chemical Co., Ltd., 99.99%) and GeO_2 (Kanto Kagaku, 99.99%). The material was ground, pelletized and then fired at 1223 K in an open alumina crucible for 24 h. After the reaction, the product was washed with distilled water. The formation of single phase was identified by X-ray powder diffraction patterns. The excitation and emission spectra in the UV range were measured on a powder sample using a JASCO FP-6500/6600 spectrofluorometer. The photoluminescence spectra in the VUV region were recorded under the VUV excitation (147 nm) by D_2 lamp. The relative luminance of the phosphors under the VUV excitation (lamp:UER20H-146VA USHIO INC.) was recorded by luminance colorimeter BM-7 (TOPCON CORPORATION).

$ALnBO_4$-type compounds (A = Li and Na; B = Si and Ge; Ln = rare earths) adopt five different structure types: olivine-type, β-K_2SO_4-type, hexagonal symmetry type, (pseudo) tetragonal symmetry type and an unknown type.[5] In the $NaLnGeO_4$ system, the compounds with RE = La - Nd are unknown, while the compounds with RE = Sm - Lu and Y are of olivine structure. Figure 1 shows the crystal structure of the $NaGdGeO_4$.[6] The Gd ions occupy a site (4c) with a C_s symmetry. An ordered olivine structure has a quasi-two dimensional rare earth sublattice. The excitation energy transfer would take place within the planes because of long separation among the emission centers under UV excitation.

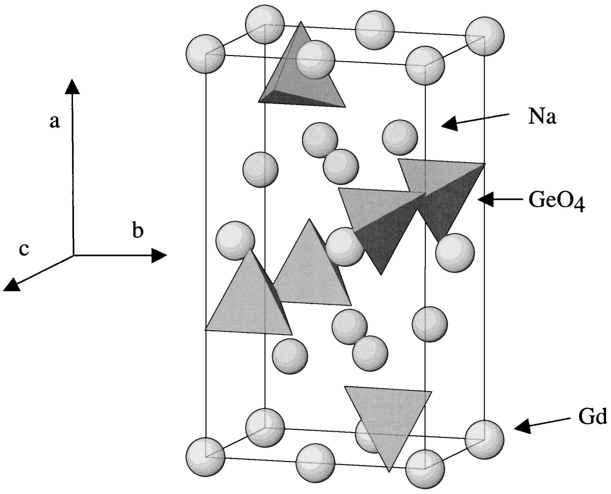

Figure 1. Crystal structure of $NaGdGeO_4$.

VUV emission spectra of the samples are shown in Figure 2. This compound shows several sharp peaks corresponding to 4f levels of the Eu^{3+} ions. The deep red emission of $^5D_0$-$^7F_2$ is

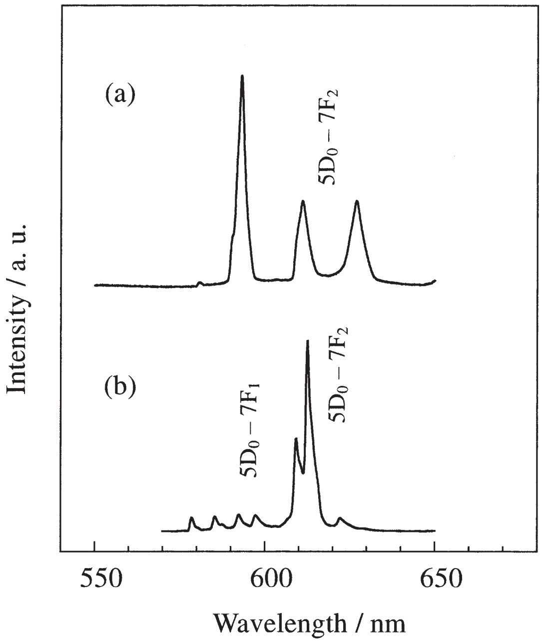

Figure 2. VUV emission spectra of (a) Commercial $(Y,Gd)BO_3:Eu^{3+}$ and (b) $NaGd_{0.95}Eu_{0.05}GeO_4$.

strongly influenced by the surroundings of the emission center. Since Eu^{3+} ions of $NaLnGeO_4:Eu^{3+}$ occupy the 4c positions without an inversion center, the $^5D_0$-$^7F_2$ emission is dominant for their electric dipole character. Concentration quenching of optimum composition $Na(Y_{0.3}Gd_{0.7-x}Eu_x)GeO_4$ under VUV excitation is shown in Figure 3. 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.[5] This result demonstrated that the energy transfer mechanism under VUV excitation is quite different from that under UV excitation. The low critical concentration may be due to high possibility of the energy transfer among the emission centers because of efficient excitation energy transfer between Gd^{3+} and Eu^{3+} 4f level.[7] According to simple concentration quenching model,[8] the critical distance of the energy transfer under VUV excitation was more than 2 times longer than that under UV excitation.

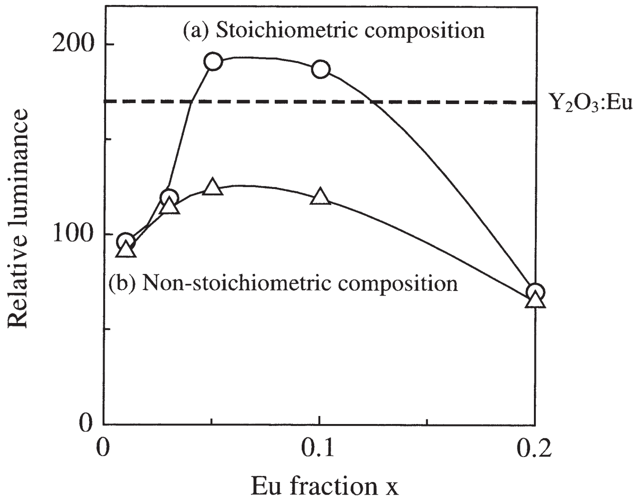

Figure 3. The Concentration quenching of $Na(Y_{0.3}Gd_{0.7-x}Eu_x)GeO_4$ with (a) stoichiometric and (b) non-stoichiometric composition under 146 nm excitation.

In addition, the effect of surface loss such as "dead layer" has also investigated. Excess amount of flux such as sodium carbonate (30 mol%)[6] or sodium fluoride[5] was added to accelerate the solid state reaction. As shown Figure 3, 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.[9] Therefore, the "dead layer" should be minimized in the synthesis of the VUV phosphors. Preliminary XPS study suggests that the "dead layer" consists of sodium germanate glass.

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