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Recent research and development of VUV phosphors for a mercury-free lamp

Kenji Toda [*]

Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-nocho,
Niigata 950-2181, Japan

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Abstract

This study specifically addresses development of new inorganic oxide phosphors for a Xe-discharge mercury-free lamp. We describe the relationship between the luminescence property under vacuum ultraviolet (VUV) excitation and the crystal structure of new VUV phosphors.

Keywords: Vacuum ultraviolet; Mercury-free lamp; Phosphor; Rare earth; Borophosphate

1. Introduction

1.1. Why a mercury-free fluorescent lamp?

"Cold" light such as that emitted by a fluorescent lamp, surrounds us and aids our comfortable life. Nevertheless, a shadow of extinction has been cast over present fluorescent lamps. Waste electrical and electric equipment (WEEE) and restriction of the use of certain hazardous substances in electrical and electric equipment (RoHS) directives restrict the use of hazardous substances (lead, mercury, cadmium and hexavalent chromium, etc.) in the manufacture of electrical and electronic equipment. After July 2006, electrical and electronic equipment containing such harmful chemicals can not be introduced to the European market. Although fluorescent lamps, which are based on a mercury-discharge, were not the object of the present restrictions, their use of mercury will be prohibited in the near future. In addition, backlight of liquid crystal displays [1] and black-lights (UV lamp) [2] also incorporate mercury-based fluorescent lamps. Consequently, demand for new materials for modern illuminating engineering have therefore increased recently.

What is the new lighting system of the near future? White LEDs and organic ELs are possible candidates. However, both technologies are faced with knotty problems for lighting applications. The present white LED is a pseudo-white light that consists of yellow photoluminescence of a cerium-doped yttrium aluminum garnet (YAG) phosphor and blue emission of a blue LED. This light color is not true white and its light directivity is too high for interior lighting and backlighting. In contrast, the organic EL is a flat panel lighting that is suitable for interior lighting. Notwithstanding, the organic EL has a limited life span for practical application. Therefore, the importance of mercury-free fluorescent lamps as flat panel lighting is increasing [3].

1.2. Mechanism of the mercury-free fluorescent lamp

The mercury-free fluorescent lamp is fundamentally a Xe-discharge lamp with a phosphor layer inside the flat glass [3]. This emission mechanism, based on Xe-gas discharge, has already been utilized in plasma display panels (PDPs). The phosphors of the mercury-free fluorescent lamp and PDP are almost identical compounds. A difference between the present mercury-based fluorescent lamp and the mercury-free fluorescent lamp is the radiation wavelength of the gas discharge. The mercury-free fluorescent lamp contains a

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[*] Tel.: +81 25 262 6771; fax: +81 25 262 6771.
E-mail address: ktoda@eng.niigata-u.ac.jp.

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mixture of Xe and Ne gases. The generated internal radiation is mostly 147 nm (8.4 eV), which is the resonance wavelength of the Xe-discharge. The other (molecular Xe state) is distributed in 173 nm (7.2 eV). The molecular state becomes important as the gas pressure increases. In the PDP and the mercury-free fluorescent lamp, the resonance line (147 nm) provides the main radiation. Vacuum ultraviolet (VUV) irradiation from the Xe gas is converted into visible light by various VUV phosphors. Highly efficient VUV phosphors are required for mercury-free fluorescent lamps because the main emission peak of this discharge is located at a shorter wavelength (147 nm) than that of the conventional mercury discharges (254 nm).

2. Research and development of new VUV phosphors

2.1. Requirements for VUV phosphors in a mercury-free fluorescent lamp

For VUV phosphors, the oxide host is utilized from high chemical stability in the high-energy plasma. Rare-earth-ion doped compounds have received attention for their high luminescence efficiency [4,5]. However, many problems remain, including deterioration of phosphors, surface damage and poor excitation efficiency because of their high-energy VUV excitation. Especially, a commercial blue VUV phosphor, $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM), poses a serious problem for PDP application. Although the BAM blue phosphor shows efficient blue emission under VUV excitation, it has strong thermal degradation, rendering it vulnerable to heat processes of PDP production [6,7]. In addition, BAM is vulnerable to continuous VUV irradiation. A typical indoor lighting system must function for long periods. Therefore, a mercury-free fluorescent lamp requires a new material that offers durability at low cost.

2.2. Design concept of the mercury-free lamp phosphor

Conventional phosphors in the mercury discharge based fluorescent lamp are emitted by direct excitation, including a charge-transfer transition. On the other hand, high-VUV energy (8.4 eV) is transferred from the host matrix to the luminescence center for the VUV phosphor. Oxide phosphors have a high absorption coefficient in the VUV region. Therefore, the typical penetration depth of the exciting photons is of the order of a few tens of nanometers [8]. The standard phosphor grain has a diameter of 2–4 μm. Therefore, all VUV photons of the plasma discharge are absorbed in the phosphor surface. The host matrix with a transparent (short wavelength) fundamental absorption band should be selected. In addition, excitation phenomena of the phosphors by high-energy photons were considered to result from interaction between the excitation energy (exciton) and an impurity (localized luminescence center) in the oxide semiconductor. Therefore, better knowledge of semiconductor theory along with elucidation and design of the band structure and high synthetic technology realizing good surface crystallinity are all necessary to design the new VUV phosphors. The millennium project (environment, no. 12317; research and development of phosphors for a mercury-free lamp) in Japan focuses on the development of new inorganic oxide phosphors for a Xe-discharge mercury-free lamp. Partial results of that research effort are reported in this paper.

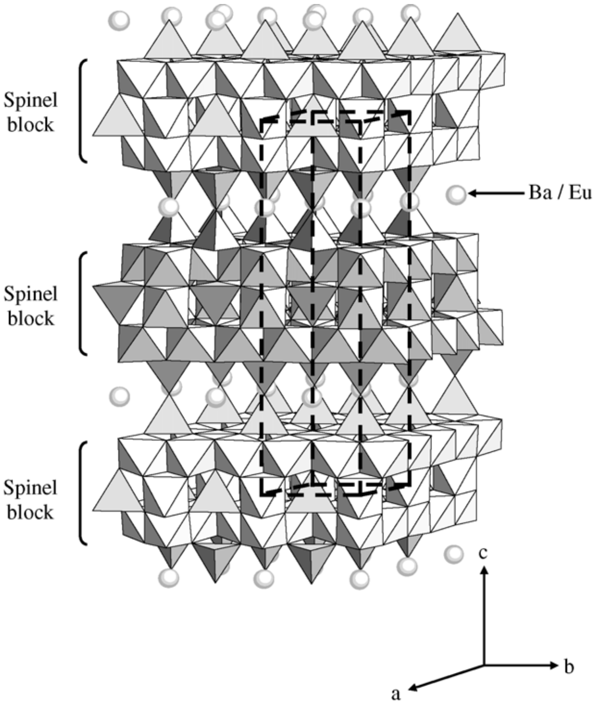

Fig. 1. Crystal structure of BAM.

2.3. New borophosphate blue phosphor $Sr_6BP_5O_{20}:Eu^{2+}$

Fig. 1 shows the crystal structure of the BAM blue VUV phosphor. It is similar to the β-alumina ($NaAl_{11}O_{17}$) structure, with high sodium ionic conductivity. Goto et al. reported that BAM shows ionic conductivity at high temperature [9]. Therefore, BAM is essentially an unstable compound in high temperature and plasma. New phosphors with a rigid crystal structure should be designed.

Most VUV phosphors belong to the class of silicates, aluminates, and borates. These phosphors have a relatively strong absorption band in the VUV region because of strong covalent characteristics of Si–O, Al–O, and B–O bonds. These materials are attractive candidates for VUV phosphors for plasma display panels and mercury-free fluorescent lamps. For example, a red VUV phosphor (Y, Gd)$BO_3:Eu^{3+}$ absorbs the VUV photons efficiently and has good chemical stability [10]. Luminescent properties under VUV (147 nm) excitation were investigated for a new Eu^{2+} doped borophosphate phosphor. The new phosphor has a relatively strong

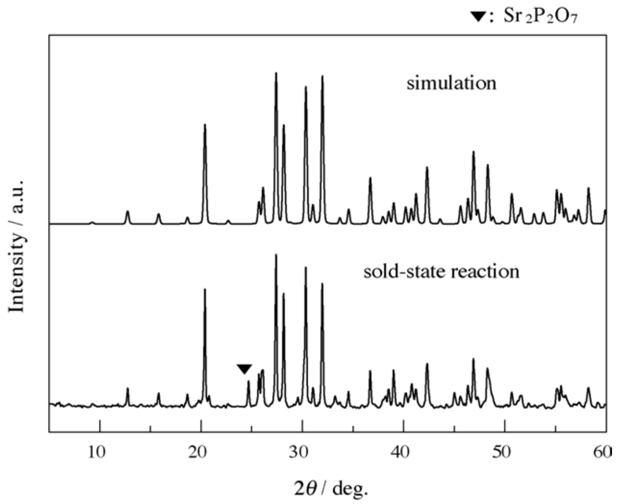

Fig. 2. X-ray diffraction patterns of SBP.

absorption band in a short wavelength region because of the strong covalent characteristics of B–O and P–O bonds.

Powder samples of the new borophosphate, $Sr_6BP_5O_{20}$:Eu^{2+} (SBP), were synthesized by conventional solid state reaction. Fig. 2 shows its X-ray diffraction patterns. The SBP contains small amount of the impurity $Sr_2P_2O_7$. The SBP crystal structure is shown in Fig. 3. This compound is an isomorph of $Pb_6BAs_5O_{20}$ [11]. The anion framework in this compound is complex: it resembles a propeller, with a central $[BO_4]$ tetrahedron surrounded by an array of four $[PO_4]$ tetrahedrons. The excitation energy is transferred from the surrounding propeller to the luminescence center Eu^{2+} ion. This mechanism is similar to the antenna effect in luminescent complex between a rare-earth and an organic ligand [12].

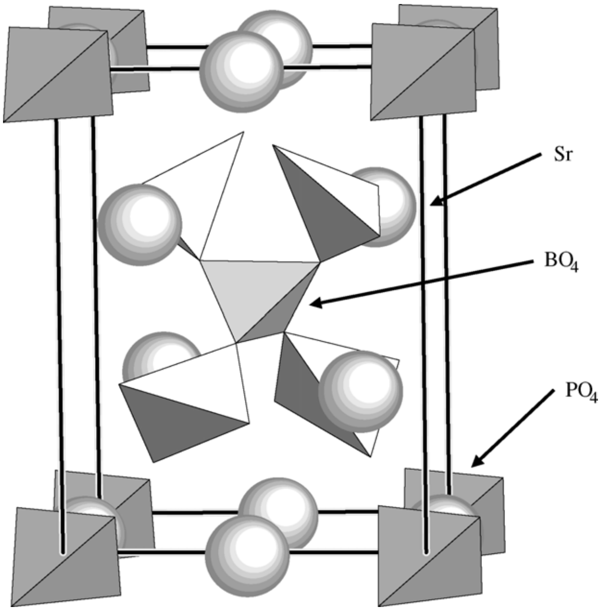

Fig. 3. Crystal structure of SBP.

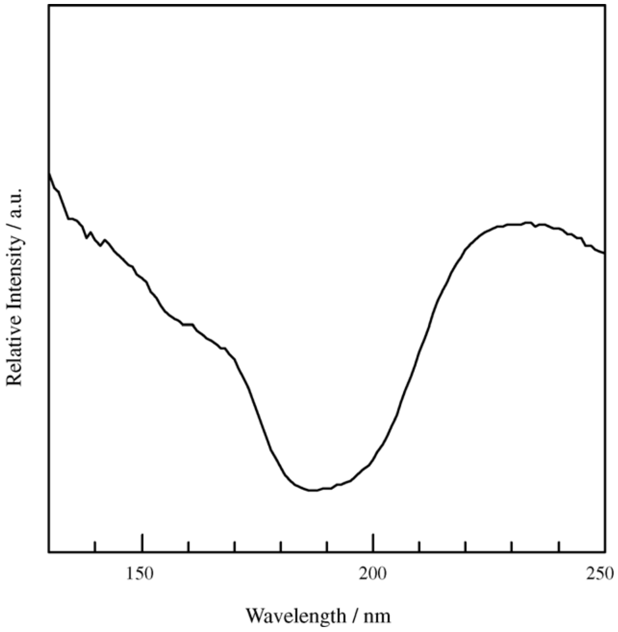

Fig. 4. VUV excitation spectrum of SBP.

The VUV excitation spectrum and the emission spectrum of the SBP are shown in Figs. 4 and 5, respectively The broad excitation absorption band around 147 nm and broad cyan emission (476 nm) were confirmed. The fundamental absorption band edge of the SBP is present around 180 nm. Therefore, the SBP efficiently absorbs the VUV photons. The composition $(Sr_{0.99}Eu_{0.01})_6BP_5O_{20}$, shows its highest luminance under VUV excitation (147 nm), which corresponds to 216% that of the commercial BAM phosphor as a reference. Therefore, this borophosphate phosphor is an attractive candidate for a new VUV phosphor for a mercury-free fluorescent lamp.

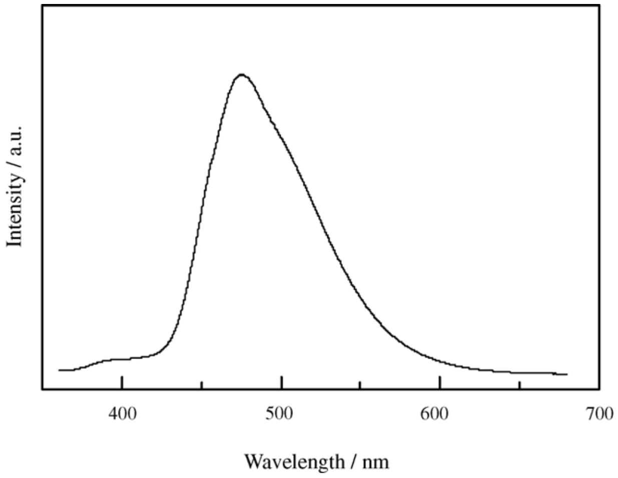

Fig. 5. Emission spectrum of SBP.

3. Development trend for recent VUV excitation phosphors

Through the millennium project, other colored VUV phosphors have also been developed. A new red VUV phosphor, Na(Gd, Y)GeO_4:Eu^{3+}, with an ordered olivine-type structure was designed with a similar design philosophy of the SBP. The emission center was surrounded by an isolated polyanion matrix [13]. However, direct excitation of trivalent europium ions is inefficient because of the forbidden nature of their electronic transitions. Therefore, a concentration-quenching phenomenon results from migration of excitation energy among the emission ions in many highly Eu^{3+} doped phosphors. This phenomenon can be overcome for compounds with large separations and low-dimensional arrangements of rare earth ions. The VUV phosphors engender numerous problems including phosphor deterioration, surface damage, and poor excitation efficiency. These problems should be resolved by a new design concept such as a new excitation mechanism "quantum cutting" [14–16] and new materials offering new crystal structures. "Research and development of phosphors for mercury-free lamp" is underway.

Acknowledgement

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