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Fluorescence properties of Mn^{4+} in $CaAl_{12}O_{19}$ compounds as red-emitting phosphor for white LED

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Abstract

Red fluorescence properties of Mn^{4+} ions in $CaAl_{12}O_{19}$ compounds prepared by the solid-state reaction were investigated in order to seek a candidate for red-emitting phosphor of white LED. The fluorescence spectrum of $CaAl_{12}O_{19}$:Mn^{4+} consists of main peak at 656 nm with three satellite peaks due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+}. The excitation spectrum exhibits a broad band between 250 and 550 nm with three peaks occurring around 338, 398, and 468 nm. The fluorescence intensity excited at 400 nm, which correspond to the wavelength of GaN-based LEDs, is about 80% compared with the excitation spectrum peak at 338 nm. The measured chromaticity of red fluorescence is $x = 0.728$, $y = 0.269$. $CaAl_{12}O_{19}$:Mn^{4+} would be suitable for red-emitting phosphor of white LED because $CaAl_{12}O_{19}$:Mn^{4+} is excellent in the excitation spectral profile and the chromaticity. The effect of CaF_2 and MgF_2 additions on the relative fluorescence intensity of $CaAl_{12}O_{19}$:Mn^{4+} is discussed in terms of the flux and charge compensation effects.

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1. Introduction

Nowadays, fluorescent lamps are most widely used and are produced in the largest quantity for lighting [1]. Fluorescent lamps employing the blue-, green-, and red-emitting phosphors of

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$BaMgAl_{10}O_{17}:Eu^{2+}$, $LaPO_4:Tb^{3+}$, Ce^{3+}, and $Y_2O_3:Eu^{3+}$ and mercury-radiated UV light at 254 nm as an exciting source for phosphor generate white lights with high color rendering. The fluorescent lamps are one of the energy-saving lighting because a lamp luminous efficiency of nearly $100\,lm \cdot W^{-1}$ has been attained. However, alternative energy-saving lightings are necessary due to an environmental problem of mercury.

To solve the above problem, a new kind of energy-saving lighting so-called white LED was contrived [2] since GaN-based near ultraviolet light-emitting diodes (NUV LEDs) were developed. White LEDs consist of blue-, green-, and red-emitting phosphors and a NUV LED as an exciting source for phosphor instead of mercury. NUV LEDs drive most efficiently while radiating a NUV light around 400 nm [2], so that exciting wavelength is shifted to longer wavelength compared with mercury. Therefore, new phosphors which can be excited at 400 nm efficiently are indispensable for white LEDs because phosphors for fluorescent lamps such as $BaMgAl_{10}O_{17}:Eu^{2+}$, $LaPO_4:Tb^{3+}$, Ce^{3+}, and $Y_2O_3:Eu^{3+}$ cannot be excited by NUV LEDs. White LEDs have been produced by way of trial due to development of blue-, green, and red-emitting phosphors of (Sr, Ca, Ba, Mg)$_{10}(PO_4)_6Cl_2:Eu^{2+}$, ZnS:Cu, Al, and $La_2O_2S:Eu^{3+}$. However, the white LED has disadvantages over fluorescent lamps: the lamp luminous efficiency is less than $30\,lm \cdot W^{-1}$ and the color rendering is low [2]. The low-lamp luminous efficiency and low color rendering are caused by low luminance and undesirable chromaticity of red-emitting phosphor $La_2O_2S:Eu^{3+}$ [2]. Therefore, red-emitting phosphors with high luminance and satisfactory chromaticity are required to improve the lighting properties of white LEDs.

The purpose of this work is to develop the red-emitting phosphor for white LEDs based on Mn-ions-doped oxide compounds. As a result, Mn^{4+}-doped $CaAl_{12}O_{19}$ exhibits red fluorescence with satisfactory chromaticity. The effect of CaF_2 and MgF_2 addition on the relative fluorescence intensity of $CaAl_{12}O_{19}:Mn^{4+}$ is discussed in terms of flux and charge compensation effects.

2. Experimental procedure

2.1. Selection of red-emitting phosphor composition

The combination of an active ion and a matrix compound is important for development of phosphor. Active ions are classified broadly into lanthanide ions and transition metal ions [3]. The 4f electronic energy levels of lanthanide ions are not affected much by the matrix because of shielding effect by outer $5s^2$ and $5p^6$ electrons. This feature is in strong contrast with transition metal ions whose 3d electrons, located in an outer orbit, are heavily affected by the matrix. Consequently, transition metal ions are suitable for an active ion of red-emitting phosphor because the red fluorescence peak position and the chromaticity can be control by matrix composition. Especially, peak wavelengths of fluorescence bands and strong absorption bands due to Mn^{4+} exist in the range 640–700 nm and in the visible to NUV region in oxide compounds [4], respectively. Therefore, we select Mn^{4+} as active ion for red-emitting phosphor of white LEDs in this study.

It is well-known that $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2:Mn^{4+}$ show deep red fluorescence and the best chromaticity among the Mn^{4+} phosphors [4,5]. Mn^{4+} ions would substitute the six-oxygen coordinated Ge^{4+} sites in the $3.5MgO \cdot 0.5MgF \cdot GeO_2$ matrix because Mn^{4+} and Ge^{4+} ions have the same valence state, and ionic radius ($r_{Mn^{4+}} = r_{Ge^{4+}} = 67\,pm$) [4,5]. However, $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2:Mn^{4+}$ is currently being used only for lamps with special application because raw materials of germanium are very costly. We sought for a new matrix, which provides a similar environment surrounding Mn^{4+} in the $3.5MgO \cdot 0.5MgF_2 \cdot GeO_2$ matrix; consequently, we select magnetplumbite structure $CaAl_{12}O_{19}$ compound [6,7] for matrix of Mn^{4+}. In the $CaAl_{12}O_{19}$ Mn^{4+} ions would substitute the six-oxygen coordinated Al^{3+} ($r_{Al^{3+}} = 68\,pm$) sites; thus $CaAl_{12}O_{19}:Mn^{4+}$ would be expected to exhibit red fluorescence with satisfactory chromaticity. The fluorescence properties of $CaAl_{12}O_{19}:Mn^{4+}$ have been reported in the literature [8,9]. However, the fluorescence properties of $CaAl_{12}O_{19}:Mn^{4+}$ for white LEDs are not well understood. In this study, the fluorescence