Synthesis and Luminescent Property Investigation of the Mg_4GeO_2:Mn for LEDs

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Abstract

In this report, Manganese doped magnesium germanate (Mg_4GeO_2:Mn) phosphor has been synthesized by the solid state method. Also, this phosphor was prepared by simple process under an air atmosphere for oxidation of Mn. The prepared phosphor shows a main luminescent peak at 661nm. Therefore, this phosphor is possible to be applicable to white LED lamp by GaN or InGaN chips.

1. Introduction

The light emitting diodes (LEDs) is widely investigated for alternation of the incandescent electric lamps and fluorescent lamps. There are widely used in electronic elements requiring a high light rate and with a high level of electric power, as LEDs have nearby 100% luminescence efficiency, a high electron movement rate, and function at high temperatures. In order to apply LEDs for a light source of the incandescent electric lamps and fluorescent lamps, it is basically to fabricate a LED lamp which emits white light. General methods are employed to generate white LED light by using integration of phosphors. One method is the integration of yellow phosphor or green and orange or red phosphors on a blue LED chip. The other method is the accumulation of two (blue and yellow) or three (red, green and blue) phosphors on an ultraviolet (UV) chip. In order to use phosphors for white LEDs, part of the commonly ultraviolet or blue light from GaN (>370nm) or InGaN(<470nm) chips must be absorbed and converted.

The red, green and blue-emitting phosphors development has a great regard for fabrication of LED lamp. At this point in time, a diversity of green and blue-emitting phosphors is developed. However, a variety of red-emitting phosphor has not developed so far. The $Y_2O_3:Eu^{3+}$ (λ_{max}=611nm) phosphor becomes generally known commercial red-emitting phosphor. The red phosphor was widely investigated through many researcher groups in world. By this time, many sorts of red phosphors were discovered. Thus, I concern about the magnesium germinate phosphor using Plasma display panels (PDPs). The Eu-activated magnesium germinate has the red emission. Using activator with Mn, magnesium germinate show variation of emission property.[1-2]

2. Experimental

The red phosphor $Mg(1)_{3.5-x}$ $Mg(2)_{0.5}GeO_2:Mn_x$ was synthesized from solid powders ($\geq$ 99.9 %) of MgO(1), MgF_2(2), GeO_2, and MnO_2 using a solid-state reaction method. Initially, appropriate proportions of the raw materials were mixed in acetone and dried in an air oven at 100℃. The mixed powder was heated to different temperatures for 3h under an air condition for $Mn^{2+} \rightarrow Mn^{4+}$. In order to determine the crystal property of the prepared phosphor, a Rigaku (D/MAX-2200V) X-ray diffraction (XRD) system with Cu $K\alpha$ radiation (Ni filter) was utilized. The luminescence characteristics of the synthesized samples at room temperature were obtained by a spectrometer equipped with Xe-lamp, PMT, and monochrometers. The size and morphology of the prepared phosphors were observed by scanning electron microscopy (JSM-6360, JEOL Corporation Japan). The platinum was coated onto the sample surface by electric power before SEM observation.

3. Results and discussion

The photoluminescence intensity with variations of the temperature is shown for the phosphors synthesized under conditions of 0.005 mol Mn^{4+} ion concentration between temperatures of 900℃ and 1200℃ with excitation at 405 nm (Fig. 1). The photoluminescence spectra of sample phosphors were shown narrow emission band between 600 nm and 700 nm with clear two peaks at 633, 661 nm and obscure two peaks at 626, 653 nm due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+}.[4]

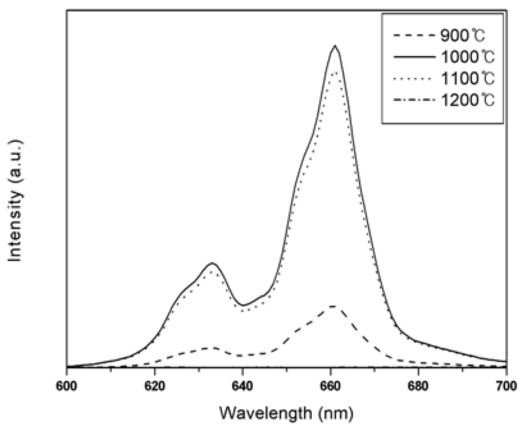

Fig 1. PL emission spectra of $Mg_4GeO_2:Mn^{4+}$ phosphor as a function of different firing temperatures

The XRD pattern with variation of the temperature is shown Fig.2. Although the Mg_2GeO_4 (JCPDS card No. 36-1479) phase at 900℃ show, an increase at 1000℃ was shown for the mixed phase with $Mg_{3.5}Ge_{1.25}O_6$ (JCPDS card No. 47-0304) and Mg_2GeO_4 phase. But, an increase at 1100℃ was shown the $Mg_{3.5}Ge_{1.25}O_6$ phase. The effect of the mixed phases was significant. As can be seen in Fig.1 , a difference in the photoluminescence intensity was clearly observed. The dimension ratio for the spectrum, fired at 900℃ was calculated approximately 19%, compared to the spectrum fired at 1000℃. However, the sample phosphors heated at higher temperature, like 1100 and 1200℃ showed the same at be approximately 90 and 1 %, respectively.[3]

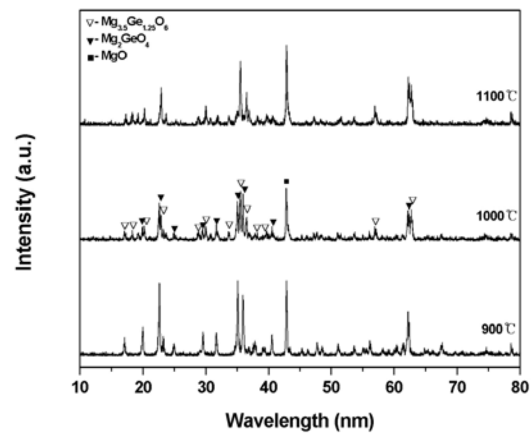

Fig 2. XRD patterns of $Mg_4GeO_2:Mn^{4+}$ samples heat-treated with different temperatures: 900℃, 1000℃, 1100℃.

The photoluminescence characteristics of the Mg_4GeO_2:Mn samples as a function of the Mn^{4+} concentration are shown in Fig3. In this figure, the best optimum condition of the sample obtained at 0.005 mol Mn^{4+} concentration. The increasing Mn^{4+} concentration, the photoluminescence intensity was shown a rapid decrease from 0.01 mol and 0.03 mol as approximately 11% and 4%. However, 0.05 mol and 0.07 mol Mn^{4+} concentrations were shown intensity as approximately 77 % and 34% in comparison with 0.005 mol samples. This intensity variation is the result of concentration quenching. Precisely, more than a normal quantify of the dopants were added and the photoluminescence intensity was suddenly reduced due to change in the structural heterogeneity and chemical complexity until 0.03 mol concentration. But, 0.05 and 0.07 mol concentration was broken this phenomena.

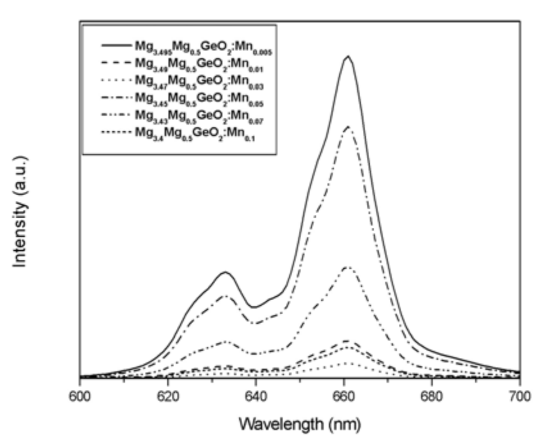

Fig 3. PL emission intensities of $Mg_4GeO_2:Mn^{4+}$ phosphors as a function of the Mn^{4+} concentration.

The size and morphology of $Mg_4GeO_2:Mn^{4+}$ red phosphor was shown Fig. 4. The sample particles showed good quality of crystallinity that were polygonal (cubic)-like shape with the size about 5 ~ 10 μm.

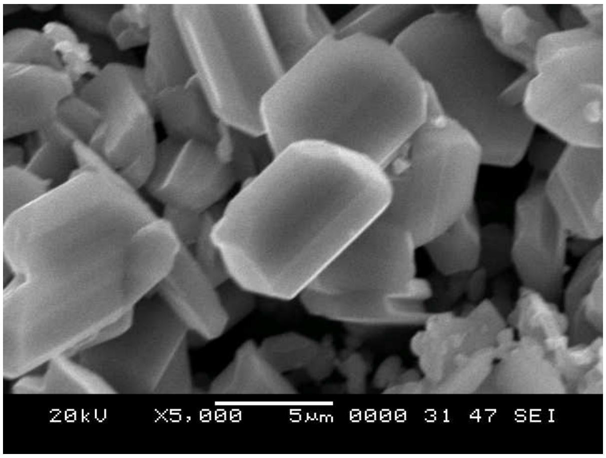

Fig 4. SEM image of $Mg_4GeO_2:Mn^{4+}$ samples

4. Summary

$Mg_4GeO_2:Mn^{4+}$ phosphor was prepared by solid state method through using raw materials under the air condition. When we obtained the best synthesis condition at 0.005 mole of Mn^{4+} concentration, at 1000℃ heat-treated temperature and for 3 hours. Prepared phosphor shows 661 nm main wavelength. And we can confirm the possibility to be applied to red phosphor for white LEDs.

5. References

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