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Application of red light-emitting diodes using $Mg_{3.5}Ge_{1.25}O_6$: Mn^{4+} phosphor

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ABSTRACT

$Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} was synthesized by a solid-state reaction and its photoluminescence characteristics were investigated. The synthesized phosphor showed a narrow emission band between 600 and 700 nm with two clear peaks at 632 and 660 nm and two obscure peaks at 626 and 653 nm due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+} ($\lambda_{ex}=405$ nm). Red light-emitting diodes (LEDs) were fabricated through the integration of an InGaN UV chip ($\lambda_{em}=405$ nm) and $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphor in a single package. Red LEDs showed CIE chromaticity with values of $x=0.32$ and $y=0.10$ and the color temperature of 4900 K.

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1. Introduction

Light-emitting diodes (LEDs) have been widely investigated for applications involving alternating lights in both incandescent electric lamps and fluorescent lamps. They are commonly used in electronic elements requiring bright light with a high level of electric power, as they have almost 100% luminescence efficiency, a high electron movement rate, and are capable of functioning at high temperatures [1,2]. In order to apply LEDs as the light source in incandescent electric lamps and fluorescent lamps, it is necessary to fabricate a LED lamp that emits white light. General methods are employed to generate white LED light via the integration of phosphors. One method involves the integration of yellow phosphor, green and orange phosphors, or red phosphors onto a blue LED chip. Another 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 ultraviolet or blue light from GaN (>370 nm) or InGaN (<470 nm) chips must be absorbed and converted [3].

The development of red, green and blue-emitting phosphors had a great impact on the fabrication of LED lamps. There has been great diversity in the manufacture of green and blue-emitting phosphors recently. However, there are not as many red-emitting phosphors thus far. Y_2O_3:Eu^{3+} ($\lambda_{max}=611$ nm) phosphor is a generally known commercial red-emitting phosphor [4]. Red phosphor has been widely investigated in many studies. Through this research investigation, many types of red phosphors have been discovered. Doped MgO–GeO_2 phosphor utilizing Mn ions has led to the development of Mg_4GeO_6, Mg_2GeO_4, and $MgGeO_3$ with an excitation wavelength at 254 nm. Both Mg_2GeO_4, and $MgGeO_3$ have broad band due to the $^4T_1 \rightarrow {}^6A_1$ transition of Mn^{2+}. Mg_4GeO_6 has a narrow band due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+}. These phosphors are not used as their LEDs excitation wavelength is 254 nm. Hence, the interest here is focused on a germinate-based red phosphor with high luminescence and efficiency with excitations at 405 and 450 nm for light-emitting diodes [5,6].

2. Experimental

Red phosphor was synthesized from solid powders ($\geq 99.9\%$) of MgO, MgF_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 oven at 100 °C. The mixed powder was heated to different temperatures for 3 h in air condition. In order to determine the crystal property, a Rigaku (D/MAX-2200V) X-ray diffraction (XRD) system with Cu-Kα radiation (Ni filter) was utilized. The luminescence characteristics of samples at room temperature were obtained using a spectrometer equipped with an Xe-lamp, PMT, and monochromators. The size and morphology were observed via scanning electron microscopy (SEM-JSM-6360, JEOL Corporation Japan). Platinum was electroplated onto the sample surface before the SEM observation. The red LEDs were fabricated from an InGaN-based UV LED chip and $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} red phosphor in a single package using a transparent epoxy resin. The photoluminescence characteristics of the red LEDs were

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verified using a PR-650 Spectrascan SpectraColorimeter with a 50 cm single-grating monochromator under a forward bias current of 20 mA.

3. Results and discussion

XRD patterns with varying temperatures and SEM images are shown in Fig. 1a. Although the Mg_2GeO_4 (JCPDS Card no. 36-1479) phase at 900 °C is shown, an increase at 1000 °C was seen for the mixed phase with $Mg_{3.5}Ge_{1.25}O_6$ (JCPDS Card no. 47-0304) and the Mg_2GeO_4 phase. However, an increase at 1100 °C was seen with the $Mg_{3.5}Ge_{1.25}O_6$ phase. The effect of the mixed phases was significant. As can be seen in Fig. 2b, a difference in the photoluminescence intensity can clearly be observed. The dimension ratio of the photoluminescence spectrum, fired at 900 °C, was calculated as approximately 19% compared to the spectrum fired at 1000 °C. However, sample phosphors heated at a higher temperature of 1100 °C showed a ratio of approximately 68%. The structure of germanate Mg_2GeO_4 phosphor in Fig. 1c is orthorhombic (space group Pmnb, $a=6.0374$ (3) Å, $b=10.3188$ (4) Å, and $c=4.9142$ (2) Å) and consists of a zigzag-chained GeO_4 tetrahedron arranged in layers horizontal to the *b*-axis. The GeO_4 tetrahedron has a bond length in the range of 1.744 (14)–1.807 (21) Å. The Mg atoms occupy two sites in the structure. One Mg atom exists as a lone atom without the bonding in the structure. The other Mg atom exists with an Mg–O bond that is part of the zigzag-chained GeO_4 tetrahedron shape. Thus, the lone Mg atom plays the role of a luminescence center as it is substituted by a Mn^{4+} ion (activator). The germinate $Mg_{3.5}Ge_{1.25}O_6$ phase in Fig. 1b is orthorhombic (space group Pbam, $a=10.2230$ (3) Å, $b=14.512$ (1) Å, and $c=5.9460$ (2) Å) and consists of a GeO_4 tetrahedron and a GeO_6 octahedron. The GeO_4 tetrahedron and the GeO_6 octahedron have a bond length in the range of 1.723 (3)–1.783 (3) Å and 1.899 (3)–1.018 (3) Å, respectively. In the unit cell, Mg atoms have two sites with a non-bonding atom and Mg–O bonding. In the Mg_2GeO_4 and $Mg_{3.5}Ge_{1.25}O_6$ structures, Mg atoms have different environmental conditions. Although, the Mn^{4+} activator was substituted in the Mg site, the two structures have different environmental conditions around the Mg atom. The reason of this is the difference in intensity. Thus, phosphor with mixture phases showed better photoluminescence intensity than phosphor solely with the $Mg_{3.5}Ge_{1.25}O_6$ phase. The size and morphology of the $Mg_{3.5}Ge_{1.25}O_6{:}Mn^{4+}$ red phosphor is shown in Fig. 1b. The sample particles showed good quality in terms of their crystallinity as they were polygonal-like shaped and are approximately 5–10 μm in size. This size is useful in LED applications.

The photoluminescence characteristics of the $Mg_{3.5}Ge_{1.25}O_6{:}Mn^{4+}$ samples as a function of the Mn concentration are shown in Fig. 2a. The emission peak of $Mg_{3.5}Ge_{1.25}O_6$ is not affected by the increase in Mn^{4+} concentration, however, the emission intensity depends on the Mn^{4+} concentration. In this figure, the results show typical concentration quenching, and the typical Mn^{4+} concentration is determined to be about 0.005 mol. Precisely, more than a normal quantity of the dopants was added, which suddenly reduced the photoluminescence intensity due to the change in the structural heterogeneity and chemical complexity up to a 0.005 mol concentration [7].

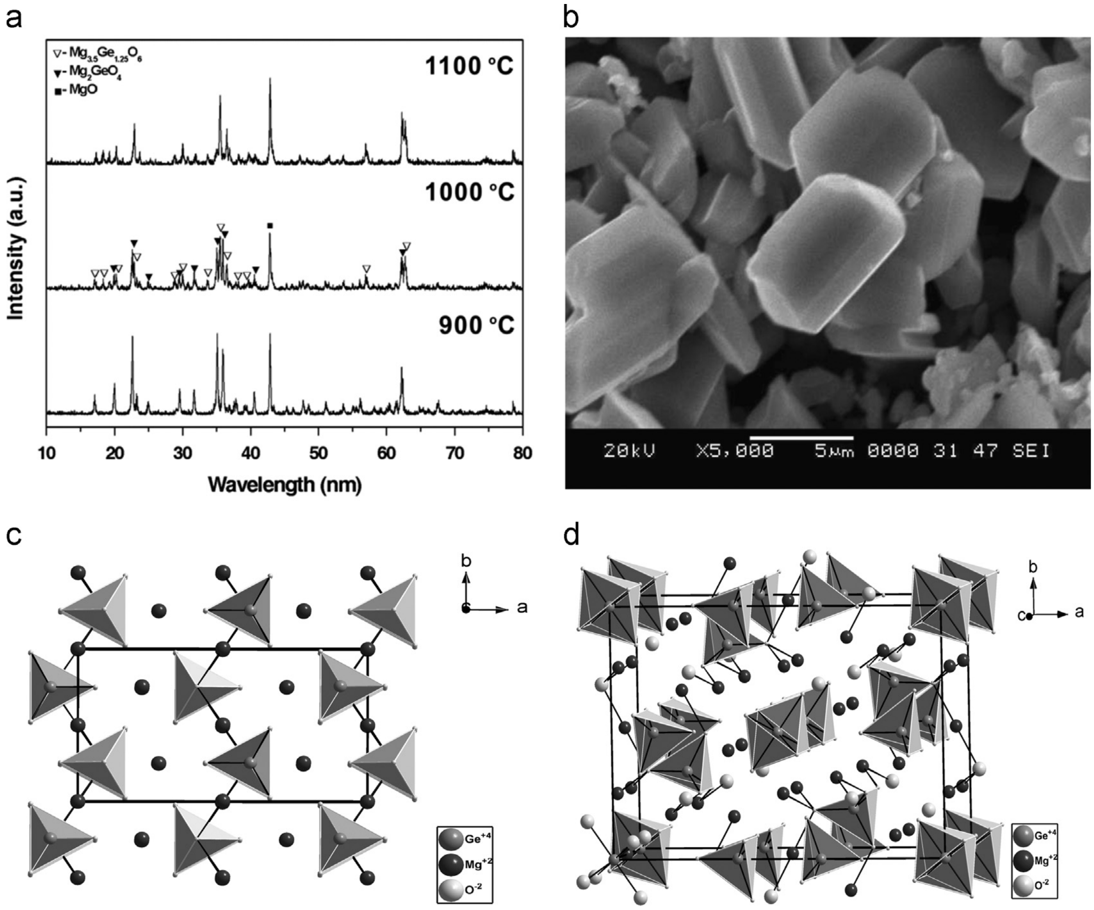

Fig. 1. (a) XRD patterns of the $Mg_{3.5}Ge_{1.25}O_6{:}Mn^{4+}$ samples heat-treated at different temperatures: 900 °C, 1000 °C, and 1100 °C, (b) SEM image at 1000 °C of the sample, (c) the crystal structure of Mg_2GeO_4, and (d) the crystal structure of $Mg_{3.5}Ge_{1.25}O_6$.

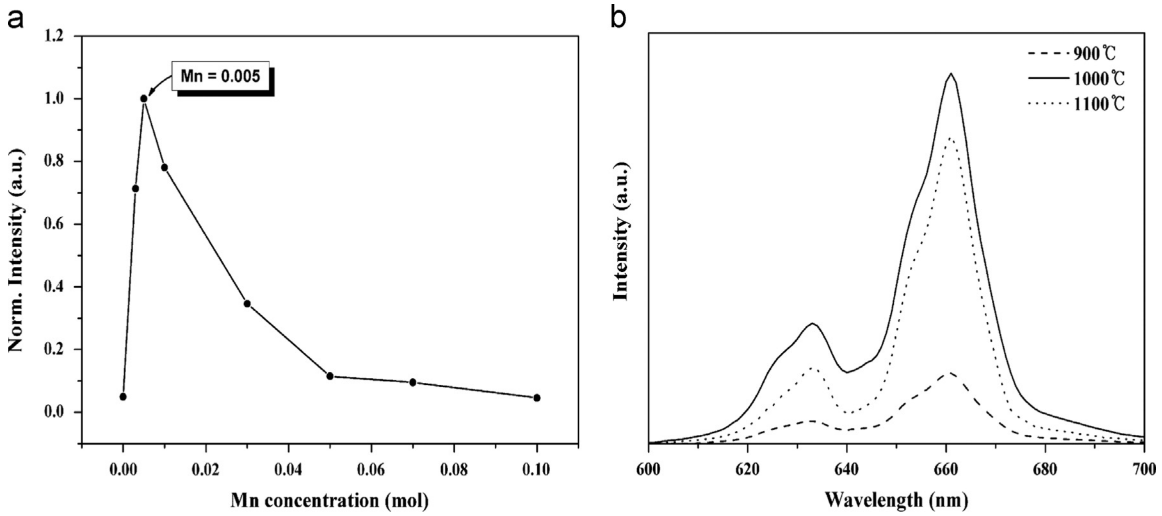

Fig. 2. (a) PL emission intensities of $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphors as a function of the Mn^{4+} concentration, and (b) PL emission spectra of $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphor as a function of the different firing temperatures.

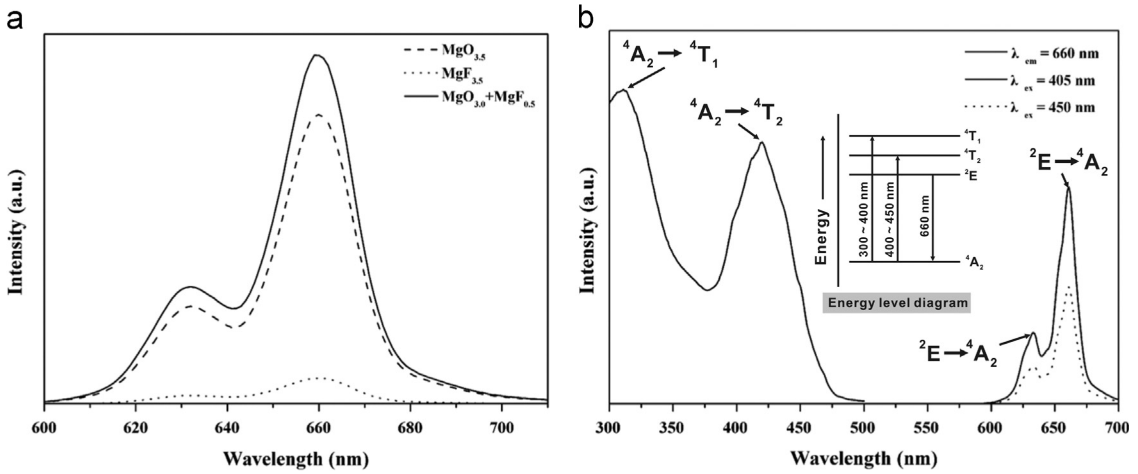

Fig. 3. (a) Effect of the addition of 0.5 MgF_2 on the PL emission intensities, and (b) typical emission and excitation spectra of $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphor and the energy diagram of Mn^{4+}.

The photoluminescence intensity depending on the temperature is shown in Fig. 2b for the phosphors synthesized under conditions of 0.005 mol Mn^{4+} ion concentrations with temperatures ranging from 900 °C to 1100 °C with excitation at 405 nm. As can be seen in Fig. 2b, the phosphors have the maximum emission peaks at 660 nm ($\lambda_{ex}=405$ nm). However, a difference in the photoluminescence intensity can clearly be observed. The dimension ratio for phosphor, fired at 1000 °C was calculated as the maximum value. Thus, the sample fired at 1000 °C has the most suitable photoluminescence characteristics. The excitation spectrum of sample showed two bands. The first band is in the range of 300–380 nm, which is attributed to the transition $^4A_2 \rightarrow {}^4T_1$ of Mn^{4+} as shown in the inset of Fig. 3b. The second band is in the range of 380–450 nm, which is attributed to the transition $^4A_2 \rightarrow {}^4T_2$ of Mn^{4+}. Under 405 or 450 nm excitations, photoluminescence spectra showed a narrow emission band between 600 nm and 700 nm with two clear peaks at 632 and 660 nm and two obscure peaks at 626 and 653 nm due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+} [9].

Thorington [8] reported that the photoluminescence intensity of Mg_4GeO_6:Mn^{4+} phosphor increased by adding MgF_2. The effect of MgF_2 on the photoluminescence properties of $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} is shown in Fig. 3a. MgF_2 was fixed at a 0.5 mol concentration and was added to replace MgO. The prepared sample with only MgF_2 or MgO showed a maximum peak intensity at 660 nm at a dimension ratio of approximately 7% and 83% in comparison with a prepared sample of MgO and MgF_2. The reason for the improvement in the photoluminescence intensity after adding MgF_2 is the increase in the concentration of oxygen vacancies associated with Ge^{4+} ions [5].

The typical emission and excitation spectra of the $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphor is shown in Fig. 3b. The emission spectra of $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} show a double sharp band at 632 and 660 nm. In addition, two emission spectra were measured between 500 and 700 nm at excitation wavelengths of 405 and 450 nm. The measured emission spectrum of phosphor excited at 405 nm is enhanced by 45% compared to phosphor at 450 nm in terms of the dimension ratio. $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphor showed a broad excitation wavelength ranging from 300 to 500 nm. As can be seen from this figure, two sharp bands exist in the excitation spectrum with maxima at 311 and 420 nm. $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} red phosphor has a suitable intensity for application in InGaN-based red LEDs.

A red LED was prepared through the integration of an InGaN UV LED chip and $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} red phosphor into a single

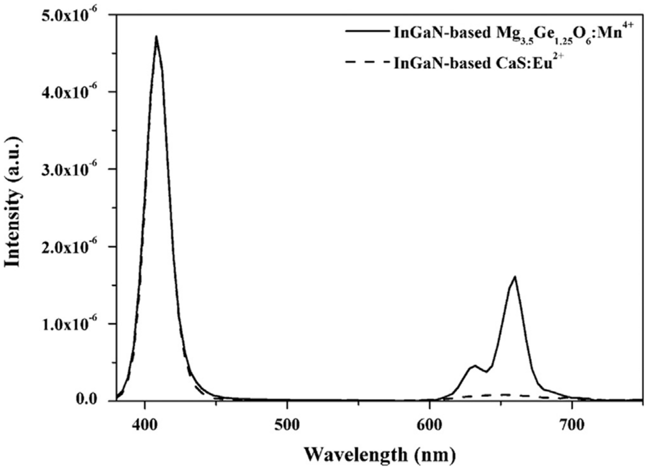

Fig. 4. Emission spectra of the red-emitting InGaN-based CaS:Eu^{2+} LED and InGaN-based $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} LED under a 20 mA drive current.

package. The emission spectra of the InGaN (405 nm chip)-based CaS:Eu^{2+} LED and the InGaN (405 nm chip)-based Mg_3GeO_5:Mn^{4+} LED are shown in Fig. 4. In the case of the InGaN-based CaS:Eu^{2+} LED, two distinct emission bands from the InGaN-based LED and the CaS:Eu^{2+} phosphor were clearly resolved at 408 (very strong peak) and 652 nm (very weak peak). In contrast, the InGaN-based $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} LEDs showed three bands at 408, 632, and 660 nm. However, two peaks at 626 and 653 nm due to the $^2E \rightarrow {}^4A_2$ transition of Mn^{4+} do not show the emission spectrum of a red LED due to the strong blue emission (408 nm). The 408 nm emission band occurred due to a radiative recombination from an InGaN active layer. This emission band at 408 nm served as the excitation source of the phosphors. The red emission band at 632 and 660 nm was due to $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphor. The excitation of red emission bands by the emission at 408 nm appears as a red light to the naked eyes. The fabricated red LED in this study showed CIE chromaticity (CIE $x=0.32$ and CIE $y=0.10$) and a color temperature of 4900 K. This sample LED lacked color purity; however, this investigation has led to a new possibility for replacement devices in the industry.

4. Conclusion

In the present work, $Mg_{3.5}Ge_{1.25}O_6$:Mn^{4+} phosphors were successfully synthesized in terms of red and high photoluminescence through a conventional solid-state method. Phosphor fired at 1000 °C with the most suitable qualities had a 0.005 mol Mn^{4+} concentration in an air oxidation condition. The synthesized phosphors showed a good photoluminescence property of 660 nm ($\lambda_{ex}=405$ nm). In addition, the sample particles had a polygonal-like shape and were approximately 5–10 μm in size. This size was suitable for LED applications. The photoluminescence property of this sample was investigated based on the development of a red LED through the integration of an InGaN UV LED chip ($\lambda_{em}=405$ nm) and synthesized phosphor into a single package. The red LED showed CIE chromaticity with x and y values of 0.32 and 0.10, respectively, and a color temperature of 4900 K.

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References

[1] Park JK, Lim MA, Kim CH, Park HD, Park JT, Choi SY. Applied Physics Letters 2003;82:683–5.
[2] Xie RJ, Hirosaki N. Science and Technology of Advanced Materials 2007;8:588–600.
[3] Yamada M, Narukawa Y, Mukai T. Japanese Journal of Applied Physics 2002;41: L246–L248.
[4] Wenjing L, Yuhua W, Mingqi Z, Yunxian Z. Materials Letters 2013;96:42–4.
[5] Iwasaki M, Kim DN, Tanaka K, Murata T, Morinaga K. Science and Technology of Advanced Materials 2003;4:137–42.
[6] Hongmei Y, Jianxin S, Menglian G, Hongbin L. Materials Letters 2010;64:1034–6.
[7] Dexter DL. Journal of Chemical Physics 1953;21:836–50.
[8] Thorington L. Journal of the Optical Society of America 1950;40:579–83.
[9] Xu YD, Wang D, Wang L, Ding N, Shi M, Zhong JG, et al. Journal of Alloys and Compounds 2013;550:226–30.