White light emission of Mn-doped SnO-ZnO-P$_2$O$_5$ glass containing no rare earth cation

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The authors have demonstrated white light emission of rare earth (RE)-free Mn-doped SnO-ZnO-P$_2$O$_5$ glass. The RE-free glass shows white light emission with a high value of quantum efficiency (QE) comparable to conventional crystalline phosphor. It is notable that the high QE value is attained for RE-free transparent glass, and the broad emission can be continuously tuned by both the amount of activator and the composition of the glass. Since this glass possesses low-melting property, we emphasize that the glass phosphor will lead to the development of a novel inorganic white-light-emitting device in combination with a solid state UV light-emitting source. © 2011 Optical Society of America


Currently, optical materials containing trivalent rare earth (RE) cations have been widely used. These RE cations possess a 4f-4f transition that is hardly affected by the surrounding crystal field, which is characterized by narrow band emission. The strong, sharp emission of RE cation has also been used for white-emitting devices, such as the three narrow emission band type of white fluorescent lamp or the white LED [1]. However, these devices consisting of sharp emission bands possess lower color rendering than the conventional broadband emission device. In addition, RE-free material is favorable from the viewpoint of the uneven distribution of RE on earth. Since the study of phosphor has been supported by advances in LEDs [2–5], a novel phosphor for next-generation LED will be required.

For these reasons, the authors have emphasized that white light emission, constituted of various kinds of wavelengths, can be attained by a RE-free phosphor, for example Sb$^{3+}$, Mn$^{2+}$-doped calcium halophosphate [6]. Although the emission of the phosphor generally possesses two broad emission bands, these emission bands are inherently fixed because of the crystal structure [7]. On the other hand, if glass material without the RE cation shows white light emission comparable to the crystalline phosphor, it will be considered a novel emitting material capable of much broader emission and good formability that is quite important in the industrial manufacturing process. In general, oxide glass has a great ability to incorporate various kinds of atoms; therefore, the coordination fields of the emission center and the resulting emission color can be tuned. Such emitting material is quite different from the conventional RE-doped crystalline phosphor.

In the study, we have focused on the ns$^2$-type emission center as an activator. Since the ns$^2$-type emission centers ($n\geq4$) possess an electron in the outermost shell in both the ground state (ns$^2$) and the excited state (ns$^1$np$^1$), the emission is strongly affected by the coordination field [1,8–11]. Therefore, this type of emission center is suitable for amorphous glass, in which site distribution is much broader than that in crystal. Recently, the authors of this study reported the highest quantum efficiency (QE) for amorphous SnO-ZnO-P$_2$O$_5$ low-melting glass [12]. It is notable that the transparent glass containing no RE cation shows a high UV-excited emission that is comparable to a crystal phosphor such as MgWO$_4$; further, this was the largest efficiency of glass material without RE cation ever reported. The emission is brought about by Sn$^{2+}$, which is the most conventional and harmless ns$^2$-type center [13–16]. Moreover, the emission property of the obtained glass remains unchanged after heat treatment at forming temperature regions, which indicates that the obtained glass is suitable for low-melting glass that can be applied as the sealing material of an LED [17,18]. Since the previous glass showed broad blue emission [12], it is expected that white light emission can be attained by the addition of Mn$^{2+}$ cation, similar to the Sh$^{3+}$, Mn$^{2+}$-codoped calcium halophosphate.

The present MnO-SnO-ZnO-P$_2$O$_5$ glass was prepared according to a conventional melt-quenching method that employs a platinum crucible. Batches consisting of ZnO and (NH$_4$)$_2$HPO$_4$ were first heat treated at 300 °C for 1 h and 800 °C for 3 h to remove NH$_3$ and residual OH groups. The heat-treated glass precursor was mixed with SnO and MnO and then melted at 1100 °C for 30 min at ambient atmosphere. The glass melt was quenched on a steel plate at 200 °C and then annealed at the glass transition temperature, $T_g$, as measured by differential thermal analysis, for 1 h. The photoluminescent (PL) and PL excitation (PLE) spectra were measured at room temperature (r.t.). The emission decay at r.t. was measured using a Quantaurus-Tau (Hamamatsu Photonics) with a 280 nm LED. The absolute QE of the glass was measured using an integrating sphere (Hamamatsu Photonics C9920-02) at r.t. The QE was evaluated using the normalized QE (NQE) that was obtained by normalization of practical phosphor MgWO$_4$ excited by a wavelength of 254 nm. The NQE was calculated using...
emission center (x center) was hardly affected by 5°C, as they and Mn_2 nm). The NQE values and color coordination x shows PL and PLE spectra of the emission center, and the emission band of Mn_μ μ sm glasses (312 and that of sample P center plays roles both in the emission center glasses (312 and the amount of Mn in the glasses was less than nm). It is expected that the is the ab-

\[ E_\text{g} = \frac{P_y \Delta E_s}{P_x \Delta E_y} \]  

where \( P_y \) and \( P_x \) are the area intensity of glass and the standard phosphor MgWO_4, respectively. \( \Delta E_s \) is the absorption of MgWO_4 at 254 nm, and \( \Delta E_y \) is the photon number absorbed by the sample, which was obtained by the difference between the area intensity of blank \( E_\text{go} \) and that of sample \( E_\text{g1} \).

Table 1 shows the chemical composition of the obtained glasses. These glasses were transparent and colorless. The \( T_g \) of these glasses was less than 440°C, as they belong to the so-called “low-melting glass,” whose manufacturing temperature is below 600°C. Figure 1 shows the PL spectra of the \( x \)MnO-2.5SnO-57.5ZnO-40P_2O_5 glass excited by the photon energy of 4.88 eV (254 nm). The value of \( x \) (mol. %) shows the additive amount of MnO. The composition consists of MnO and the glass composition that showed the maximum QE in the previous report [12]. These emission spectra consist of two broad bands of the Sn^{2+} emission center (2.86 eV) and Mn^{2+} center [19] (2.05 eV). It is expected that the Sn^{2+} center plays roles both in the emission center and in the energy donor. The lifetimes (\( \tau_{1/2} \)) of the Sn emission (2.86 eV) of the nondoped glass (\( x = 0 \)) and Mn-doped glass (\( x = 2.0 \)) are 4.5 \( \mu \)s and 2.1 \( \mu \)s, respectively. The change can be explained by the energy transfer using the Dexter’s theory [20]. Peak deconvolution revealed that these two peaks showed little change in the emission band and the half-width, indicating that local coordination of Sn^{2+} and Mn^{2+} was hardly affected by the concentration of MnO.

Figure 2 shows PL and PLE spectra of the 0.5MnO-2.5SnO-\( y \)ZnO-(97.5-y)P_2O_5 glasses (\( y = 55.0, 57.5, 60.0, \) and 62.5). Although the concentrations of the activators were equal in both glasses, the glass containing the larger amount of ZnO exhibited a slightly narrower PLE peak and a smaller Stokes shift. The observed peak shift is due to the difference of coordination field of the Sn^{2+} emission center, and the emission band of Mn^{2+} is almost independent of the composition. It clearly shows that the ns²-type Sn^{2+} emission center is affected by the coordination field. The so-called theoretical basicity of the glass increases with increasing amounts of ZnO [21]; it can thereby be said that the Stokes shift becomes smaller by increasing the optical basicity of the glass. On the other hand, Duffy and Ingram [22] determined the optical basicity of the glass using the experimentally measured peak frequency of the \( ^1S_0 \rightarrow ^3P_1 \) transition of Tl^{+}, Bi^{3+}, and Pb^{2+}. Although they reported no data concerning Sn^{2+}, ns²-type Sn^{2+} can also serve as a probe for estimation of the basicity. The observed peak shift indicates that optical basicity also increased qualitatively by the addition of ZnO. With an increasing amount of ZnO, the PL peak was blueshifted to increase the emission in the UV region. Thus, there was an increase in the relative intensity of red color that was attributed to the emission from Mn^{3+}.

Figure 3 shows chromatic coordination mapping of the SnO-ZnO-P_2O_5 glasses. The inset shows a photograph of the glass phosphors (\( x = 0, 0.7, 2.0 \)) with and without UV light (254 nm). The NQE values and color coordination position of the samples are shown in Table 1. It is notable that these glasses show a high NQE value comparable to that of practical MgWO_4, whose QE value was reported to be greater than 80%. This value enables us to confirm the potential application of the present RE-free glass as phosphor with a high NQE. On the other hand, it is also noteworthy that the color coordination positions are

<table>
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<th>Composition (mol. %)</th>
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<tr>
<td>MnO</td>
<td>SnO</td>
<td>ZnO</td>
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<tr>
<td>0.00</td>
<td>2.5</td>
<td>57.5</td>
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<td>0.10</td>
<td>2.5</td>
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<tr>
<td>0.50</td>
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<tr>
<td>0.70</td>
<td>2.5</td>
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<tr>
<td>1.00</td>
<td>2.5</td>
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<td>2.00</td>
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<td>0.25</td>
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<td>0.50</td>
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<td>55.0</td>
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Their chromatic coordination positions (CCPs) and colors under excitation (4.88 eV; 254 nm) are also shown.

NQE = \( P_y \Delta E_s/P_x \Delta E_y \),

Fig. 1. Correlation between PL intensity excited by 4.88 eV and the amount of Mn in the \( x \)MnO-2.5SnO-57.5ZnO-40P_2O_5 glasses.

Fig. 2. PL and PLE spectra of 0.5MnO-2.5SnO-yZnO-(97.5-y)P_2O_5 glasses.
continuously changed from blue to red with the addition of MnO. In particular, several glasses satisfy the white light emission condition without the RE cation. The emission from Sn$^{2+}$ in the glass showed the maximum PL peak around 420 nm, which is about 60 nm shorter than that of Sb$^{3+}$-doped calcium halophosphate, and therefore no additional blue phosphor was needed to improve the color rendering. This is also a notable advantage of the present Sn$^{2+}$-doped glass phosphor.

From the obtained results, it is suggested that the basicity of the glass affects both the emission center and the following emission color. Since the basicity of oxide glasses is tailored by a great variety of chemical compositions, the emission color is also controlled in a wide range. The present results indicate that the Mn-doped SnO-ZnO-P$_2$O$_5$ glass will be (1) a novel PL material that does not contain an RE cation, which is a benefit for natural resources, (2) a candidate for conventional organic sealant that is damaged by strong UV light, and (3) a novel white LED in combination with deep-UV LED. Although the present glass shows white light emission that is similar to halo calcium phosphate crystal, there are several large differences between the two. First, for a greater number of emission centers, Sn$^{2+}$ can be doped in glass. Second, various kinds of elements can be added to the glass to control the emission properties as well as to improve the mechanical or thermal property. Third, monolithic material can reduce optical loss due to scattering at the interface. Moreover, transparent emission material will meet novel industrial applications. Since organic material as well as an organic–inorganic hybrid cannot be used for deep-UV light sources, inorganic low-melting materials will be important in these applications.

RE cations generally exhibit a high QE value because there is little influence of phonons. We have emphasized that the present RE-free amorphous glass possesses high QE values comparable to RE-doped crystalline phosphor, although it shows a broad emission tunable by the local coordination state. Although we have not yet clarified the mechanism, the present $n^2$-type center appears to be very advantageous from the viewpoint of unique emission mechanisms in a random matrix: the coexistence of high efficiency and broad emission. Recent development of a deep-UV LED [5] clearly suggests a possibility for Hg-free white fluorescent lamps in the near future. RE-free inorganic amorphous materials possessing emission properties by excitation of a UV LED source will be required for the novel practical optical device.

References