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Correlation between emission property and concentration of Sn²⁺ center in the SnO-ZnO-P₂O₅ glass

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Abstract: The authors report on the correlation between the photoluminescence (PL) property and the SnO amount in SnO-ZnO-P₂O₅ (SZP) glass. In the PL excitation (PLE) spectra of the SZP glass containing Sn²⁺ emission center, two S₁ states, one of which is strongly affected by SnO amount, are assumed to exist. The PLE band closely correlates with the optical band edge originating from Sn²⁺ species, and they both largely red-shifts with increasing amount of SnO. The emission decay time of the SZP glass decreased with increasing amount of SnO and the internal quantum efficiencies of the SZP glasses containing 1~5 mol% of SnO are comparable to that of MgWO₄. It is expected that the composition-dependent S₁ state (the lower energy excitation band) governs the quantum efficiency of the SZP glasses.

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1. Introduction

White light emitting device using light emitting diode (LED) is strongly desired as a next-generation light source because of the low electrical power consumption, the long lifespan and so on. Therefore, it will replace the conventional white fluorescent lamp in near future. Although various kinds of phosphors are actively developed all over the world, the host materials for these phosphors, such as silicone, still have a limitation against a high power or short wavelength excitation light source because of the degradation. Therefore, we would like

to emphasize that low-melting inorganic glass can be applied as sealant for high intensity and shorter wavelength excitation white LED.

Based on such background, we have proposed a novel white LED device consisting of inorganic glass phosphor and LED source, and selected SnO-ZnO-P₂O₅ glass system as a potential candidate [1–5]. This glass is known as a low-melting glass that is used as a sealant of electronic devices [6, 7]. If LED-sealing inorganic material itself shows light emission, *i.e.* spectrum conversion, it will be a novel light emitting device possessing both transparency and chemical durability. On the other hand, it has been reported that Sn-doped ZnO-Al₂O₃-P₂O₅ glass exhibits an emission property via the absorption of ultraviolet (UV) light [8]. The origin of the emission by UV excitation is Sn²⁺ belonging to an ns² type emission center. Since the ns² type emission centers ($n \geq 4$), such as Sn²⁺, Sb³⁺, Hg⁰, Tl⁺, Pb²⁺, and Bi³⁺, possess electrons in the outermost shell in both the ground state (ns²) and the excited state (ns¹np¹), the emission is strongly affected by the coordination field [9]. Therefore, the broad emission of ns² type emission center, which is quite different from sharp emission of conventional rare earth (RE)-containing phosphors, is suitable for broad-band white light emission.

Recently, our group has reported that SnO-ZnO-P₂O₅ low-melting glasses show light emission by UV excitation [2]. The oxide glass prepared by conventional melt-quenching method showed white ~blue emission depending on the amount of SnO. It is notable that the transparent oxide glass containing no RE cation shows intense UV-excited emission comparable to crystal phosphor such as MgWO₄; in other words, this shows the largest efficiency among glass materials without RE cation ever reported. In addition, we have also demonstrated the UV-excited white light emission property of MnO-codoped SnO-ZnO-P₂O₅ glasses [2, 3]. The white light emission consisting of broad bands can be tailored by addition of Mn²⁺ emission center instead of RE. It is notable that high efficiency comparable to the practical crystalline phosphor was also attained.

However, the emission property of the glass, especially correlation between the emission property and the amount of SnO, has not been clarified yet. In the previous study, we examined the emission property of the SnO-ZnO-P₂O₅ glasses prepared by melt-quenching method, and reported that substitution of ZnO by SnO significantly affects the PLE peak in the SnO-ZnO-P₂O₅ glasses [1]. Although it was found that the PLE peak shifted depending on the SnO concentration, the concentration range previously studied [1] (1 ~40 mol%) is not enough to discuss the details of emission properties. In addition, spectral shape of the emission has not been discussed yet. Moreover, the previous samples were prepared using an alumina crucible [1], the contamination by Al₂O₃ from the crucible, which may affect the coordination field of the emission center, cannot be avoided. Therefore, in the present study, we report the correlation between the SnO amount and the emission property of the SnO-ZnO-P₂O₅ (SZP) glass in the concentration range from 0.1 to 7.5 mol% SnO in order to obtain RE-free amorphous phosphors with high efficient and broad emission.

2. Experimental

The SnO-ZnO-P₂O₅ (SZP) glasses were prepared by a conventional melt-quenching method using a platinum crucible [4]. The chemical composition of the SZP glass was fixed at xSnO-60ZnO-40P₂O₅ (in mole%, $x = 0 \sim 7.5$). Batches consisting of ZnO and (NH₄)₂HPO₄ were initially calcined at 800°C for 3 h in an ambient atmosphere. The calcined solid was mixed with SnO at room temperature (r. t.) and then melted at 1100°C for 30 min in an ambient atmosphere. The glass melt was quenched on a steel plate kept at 200°C and then annealed at the glass transition temperature T_g for 1 h. The samples were mechanically polished to obtain mirror surface.

The T_g was determined by differential thermal analysis (DTA) operated at a heating rate of 10 K/min using TG8120 (Rigaku). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at r.t. using 850 fluorescence spectrophotometer (Hitachi). The absorption spectra were measured at r.t. using U3500 spectrophotometer (Hitachi). The emission decay at r.t. was measured using a Quantaaurus-Tau (Hamamatsu Photonics) whose excitation light source was 280 nm LED operated at a frequency of 10 kHz.

The absolute quantum efficiency of the glass was measured using an integrating sphere C9920-02 (Hamamatsu Photonics) at r.t.

The quantum efficiency (QE) was normalized with respect to practical phosphor MgWO_4 (3N) excited by a wavelength of 254 nm. The normalized quantum efficiency (NQE) that was calculated using Eq. (1):

$$NQE = P_g \Delta E_s / P_s \Delta E_g, \quad (1)$$

where P_g and P_s are the PL peak area of glass and the standard phosphor MgWO_4 , respectively; ΔE_s and ΔE_g are the photon number absorbed by MgWO_4 at 254 nm and the sample, respectively, and both are obtained by the difference between the peak area of blank and that of sample. The authors have confirmed that there was no difference in NQE between the bulk sample and the powdered sample.

3. Results and discussion

Figure 1 shows the variation of T_g with SnO amount in the $x\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$ (SZP) glass. The T_g decreased with increasing amount of SnO. The observed change of the T_g values indicates that SnO is homogeneously dispersed in the glass network and plays a role of a network modifier to decrease the network dimension.

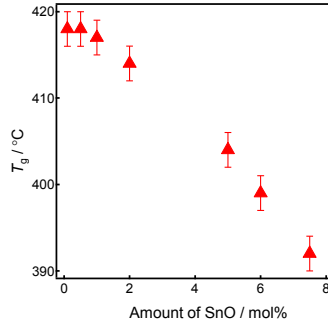


Fig. 1. Glass transition temperature T_g of the $x\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$ (SZP) glasses as a function of SnO amount.

The obtained glasses were colorless and transparent. We have already reported that Sb_2O_3 -added zinc phosphate glass, which also contained ns^2 type Sb^{3+} emission center, was yellow-colored by addition of 1 mol% of Sb_2O_3 [5]. Since the present glasses were colorless even when 5 mol% SnO was added, SnO-addition to zinc phosphate glass has an advantage over Sb_2O_3 -addition. First, we have examined the correlation between the PLE peak and the optical absorption band. Figure 2(a) shows the optical absorption and PLE spectra of the SZP glasses containing different amounts of SnO ($x = 0, 0.1, 1.0, \text{ and } 5.0$). The PLE spectra were measured at the peak photon energy of each PL spectrum. The optical band edge energy of $60\text{ZnO}-40\text{P}_2\text{O}_5$ glass is over 6 eV, which is much larger than that of Sn-doped glasses. It was reported that binding energy of the $\text{Zn}2p_{3/2}$ electrons in zinc phosphate glass is higher than that measured for ZnO powder [10]. We speculate that the observed band edge is strongly affected by the coordination state of zinc in the phosphate glass, although the actual coordination state has not been confirmed yet. It is notable that addition of a small amount of SnO (0.1 mole%) brings about a large peak shift of PLE band, which clearly indicates that the PLE band derives from a Sn^{2+} species. Therefore, it can be said that a strong absorption band of the Sn^{2+} species exists within the band gap of the host zinc phosphate glass. Comparing the absorption spectra with the PLE spectra, we notice that the main excitation band position locates in the vicinity of the optical band edge. It is also found that both the PLE peak energy providing the maximum PL intensity and the optical absorption edge red-shift with increasing amount of SnO. Here, we introduce the optical band edge E_{gopt} which is evaluated by the

extrapolation of linear portion of the absorption coefficient within the region of 30 cm^{-1} . Figure 2(b) shows a plot of the peak energy of PLE vs. the E_{gopt} . There is a clear linear relation between them, indicating that a Sn^{2+} species is the origin of both the absorption edge and the PLE band, and gives strong emission under irradiation with a light whose photon energy corresponds to the optical band gap of Sn^{2+} center.

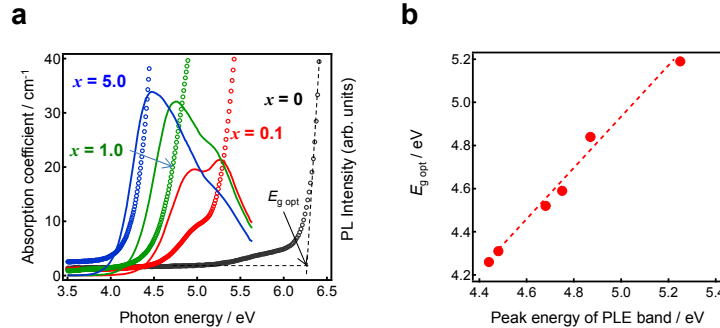


Fig. 2. (a) Optical absorption and PLE spectra of the SZP glasses containing different amounts of SnO ($x = 0, 0.1, 1.0,$ and 5.0). (b) Relation between the peak energy of PLE band and the E_{gopt} .

Figure 3(a) shows the normalized PL and PLE spectra of the SZP glasses containing different amounts of SnO ($x = 0.1, 1.0,$ and 5.0). The PL spectra were measured by excitation with a light at the peak energy of each PLE spectrum. It is found that the SZP glasses show broad emission in the range from 2 to 4 eV, which is characteristic of a parity-allowed ns^2 -type emission center. In addition, the peak energy and the bandwidth of PL spectra depend on the SnO amount, that is, with increasing amount of SnO, the peak energy of PL spectra increases and the bandwidth becomes slightly narrower. In the previous paper [5], we demonstrated that the emission of the $1\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$ glass is mainly due to T_1-S_0 relaxation with a lifetime of the microsecond order. Considering the previous result [5], it is suggested that energy level distribution at the T_1 state of Sn^{2+} center becomes narrower in a Sn-rich glass. On the other hand, it seems that these PLE spectra consist of two bands, and the peak area of each band depends on the amount of SnO. In order to clarify this behavior, the PLE spectra are deconvoluted into two bands using the Gaussian functions. For an example, the deconvoluted two bands are shown using the broken lines for the SZP glass ($x = 0.1$). Considering the previous finding that Sn^{2+} in a silica glass possesses the S_1 band at 4.9 eV [11], we assume that there are two different Sn^{2+} emission centers which give two S_1 bands. For convenience, the higher energy band is called S_1 band and the lower one S_1' band. The higher energy band (S_1) at 5.2~5.3 eV is almost unchanged, whereas the lower band (S_1') red-shifts with increasing amount of SnO. The emergence of Sn^{2+} emission band S_1' at lower photon energy by increasing SnO amount suggests that a local structure different from the one providing the S_1 band (5.2 eV) is the origin of the band. The peak area ratio S_1'/S_1 increases with increasing SnO, indicating the lower energy band S_1' is a strongly concentration-dependent excitation band. Figure 3(b) shows the concentration dependence of peak energies of PL and PLE bands of the SZP glasses together with that of the Stokes shift that corresponds to the peak energy difference between the PLE and PL bands. With increasing amount of SnO, the excitation peaks red-shifts but the emission peaks blue-shifts, resulting in the decrease of the Stokes shift. Since it is expected that decrease of the Stokes shift brings decrease of energy loss by UV excitations, effective emission can be available.

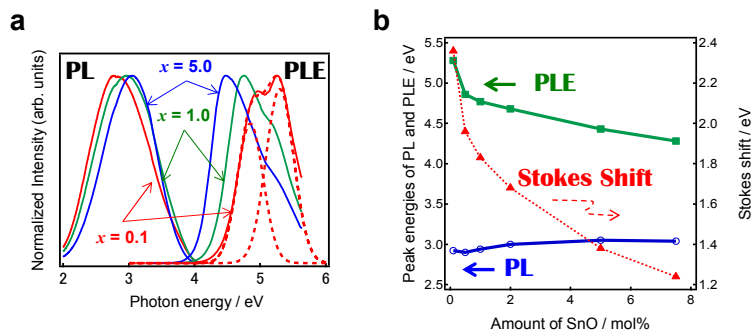


Fig. 3. (a) Normalized PL and PLE spectra of the SZP glasses containing different amounts of SnO ($x = 0.1, 1.0,$ and 5.0). Dashed lines show that PLE spectra can be deconvoluted into two S_1 bands. (b) Composition dependence of peak energies of PL and PLE bands and the Stokes shift of the SZP glasses.

Figure 4 shows PL-PLE contour plots of the SZP glasses ($x = 0, 0.1, 0.5, 1.0, 5.0$ and 6.0) using an intensity axis on a linear scale. The $60\text{ZnO}-40\text{P}_2\text{O}_5$ glass ($x = 0$) shows no emission, and the Sn-containing glasses shows broad emission in the range from 2 to 4 eV. In each figure, the photon energy of excitation is plotted as ordinate and that of emission as abscissa, and emission intensity axis is shown on an identical linear scale using colors. From these figures, we can easily understand the red-shift of PLE peak and the generation of S_1' state on the lower excitation energy side with increasing SnO amount. In addition, it is observed that either excitation to S_1 state or S_1' state (at different excitation energy) gives similar emission spectra. Emission intensity of these glasses takes the maximum value in the range of from 1

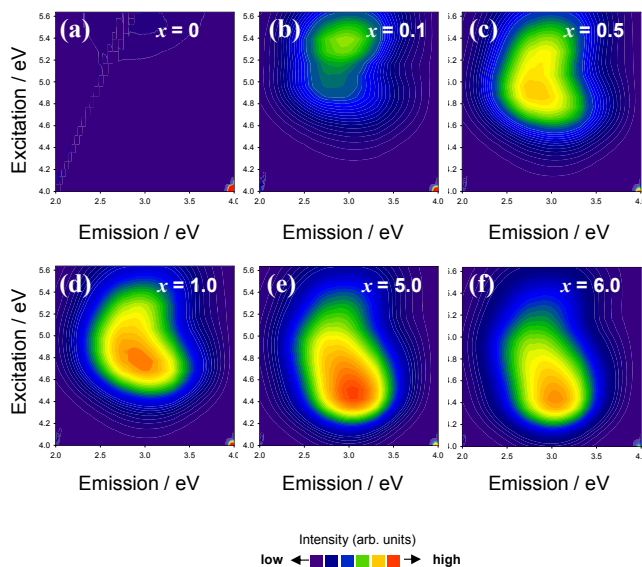


Fig. 4. PL-PLE contour plots of the SZP glasses ($x =$ (a) 0, (b) 0.1, (c) 0.5, (d) 1.0, (e) 5.0 and (f) 6.0) whose emission intensity is shown on an identical linear scale using colors.

to 5 mole% SnO, and then, with further increasing amount of SnO, the intensity decreases, indicating that concentration quenching occurs by addition of more than 6 mole% SnO. It is notable that the concentration of Sn^{2+} emission center in the SZP glass where concentration quenching takes place is much higher than that of conventional emission centers such as RE

cations. Although the mechanism has not been clarified yet, the ionic host phosphate glasses may prevent aggregation of Sn^{2+} cations to cause the emission quenching.

Figure 5 shows the emission decay curves of the SZP glasses containing different amounts of SnO. The SZP glass ($x = 1.0$) shows single exponential-like decay possessing a lifetime ($\tau_{1/e}$) of 5.2 μs . On the other hand, decay curve of the SZP glass ($x = 5.0$) is slightly deviated from a single exponential decay, and the lifetime $\tau_{1/e}$ is about 3.5 μs , which is shorter than that of the low-doped sample. In the previous report [3], the lifetime $\tau_{1/e}$ of the 2.5SnO-57.5ZnO-40P₂O₅ was 4.5 μs . The lifetime of the SZP glass, therefore, decreases with increasing SnO amount. We will discuss the emission decay dynamics in detail in a separated paper.

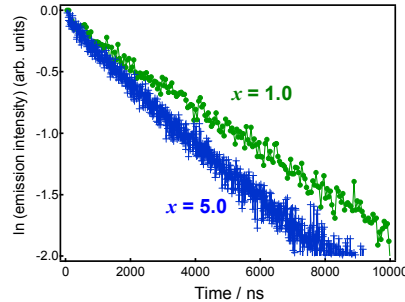


Fig. 5. Emission decay curves of the SZP glasses containing different amounts of SnO.

Here, the emission mechanism of the $x\text{SnO}-60\text{ZnO}-40\text{P}_2\text{O}_5$ glass is discussed based on the present results. Figure 6 shows plausible energy schemes for photoluminescence process of Sn^{2+} in the 0.1SnO-60ZnO-40P₂O₅ and 5SnO-60ZnO-40P₂O₅ glasses. In the case of 0.1SnO-60ZnO-40P₂O₅ glass, the peak photon energies for S_0-S_1 excitation and T_1-S_0 relaxation are 5.3 eV and 2.9 eV, respectively. On the other hand, the peak photon energy for S_0-S_1 excitation in the 5SnO-60ZnO-40P₂O₅ glass is 4.4 eV, which is lower than that in the glass containing lower amount of SnO. In the glass phosphor, there are two excitation states: one is S_1 state at a photon energy of 5.3 eV, and the other is S_1' state whose peak energy strongly depends on the SnO concentration. It is easily understood that the smaller the Stokes shift becomes, the more effective the emission process takes place. Therefore, it is expected that the high quantum efficiency of the present glass, which is comparable to crystalline phosphor, is attained by the unique energy scheme.

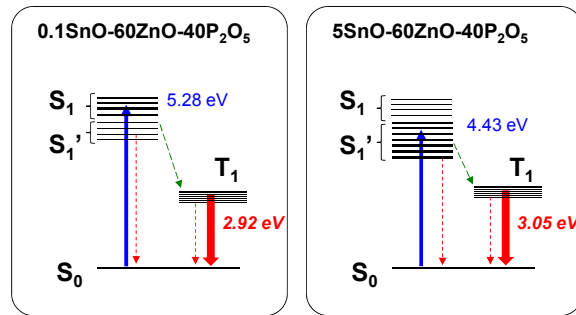


Fig. 6. Plausible energy scheme for photoluminescence process of Sn^{2+} in the 0.1SnO-60ZnO-40P₂O₅ and 5SnO-60ZnO-40P₂O₅ glasses. Solid and dashed lines show radiative and non-radiative processes, respectively.

Table 1 shows the normalized quantum efficiency of the SZP glass, which is calculated using the value of MgWO₄ crystalline phosphor. The efficiency of the SZP glasses containing 1 ~5 mole% shows a very high value comparable to that of MgWO₄ phosphor, suggesting that

concentration quenching was not observed in the present phosphate glass of which the concentration of Sn^{2+} emission center is as high as 5 mole%, which is much higher compared to the case for usual crystalline phosphors. The color chromaticity coordinates of the glasses are shown in Fig. 7. The emission color of the 0.1SnO-containing glass is white-blue, and becomes closer to blue with increasing amount of SnO. Therefore, we can control the emission properties of the glass phosphor to a certain extent by changing the amount of SnO.

Table 1. Normalized quantum efficiency of the SZP glasses containing different amounts of SnO. The quantum efficiency is normalized to the value of MgWO_4 crystalline phosphor.

Amount of SnO, x / mole%	Excitation energy / eV	Normalized quantum efficiency / % ($\pm 2\%$)
0.1	5.04	74
0.5	4.86	91
1.0	4.77	100
2.0	4.68	100
5.0	4.43	100
6.0	4.40	84
7.5	4.28	63

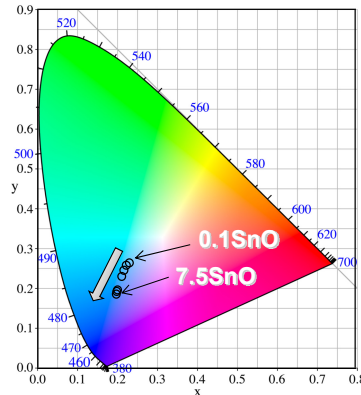


Fig. 7. Color chromaticity coordinates of the SZP glasses.

The importance of the present study is to have elucidated the possibility of tuning the emission property by changing the local coordination field of Sn^{2+} emission center. In addition, it is notable that the SZP glass containing high amount of SnO shows quite high quantum efficiency comparable to MgWO_4 phosphor. Although the coordination states of two S_1 states have not been clarified yet, the lower excitation band that closely correlates with the absorption edge has particularly a key for the broad emission. As we have demonstrated, the intrinsic emission properties of ns^2 -type emission centers are useful for designing white light emission. Further study for clarification of the emission centers will open a novel amorphous emission device containing no RE cation.

4. Conclusion

We have demonstrated deep-UV-induced PL properties in $\text{SnO-ZnO-P}_2\text{O}_5$ (SZP) glasses. The T_g of the SZP glass decreased with increasing amount of SnO, indicating that addition of SnO results in lower dimensional glass network. Both the peak position of PLE band and the optical absorption edge decreased in photon energy with increasing amount of SnO, indicating a strong correlation between them. The broad emission of the Sn^{2+} center is strongly affected by the coordination field, in other words, the chemical composition of the

glass. We found that two excitation bands, S_1 and S_1' , exist and that the two bands depended on the SnO concentration. The emission decay indicates that emission quenching occurs in the SZP glass containing higher than 5mol% SnO. The internal quantum efficiency indicates that the concentration dependent PLE band (S_1') is also attributed to the allowed excitation band. The large shift of S_1' band is characteristic of the present RE-free SnO-ZnO-P₂O₅ glass.

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