

Preparation of rare-earth-free oxide glass phosphors

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Light emission in rare earth (RE)-free SnO–ZnO–P₂O₅ glasses is demonstrated. The RE-free transparent phosphate glasses show light emission with high quantum efficiency (QE) values, comparable to conventional crystalline phosphors, by excitation with deep-UV light. The broad emissions of the RE-free transparent glasses can be continuously tuned by both the amount of activator and the composition of the glasses, without reduction of the QE values. For future emitting devices, we believe that the low-melting glasses will constitute one of the most industrially favorable inorganic materials possessing transparency and emitting properties.

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1. Introduction

Recently, the strong, sharp emissions of rare earth (RE) cations have been used in the white light-emitting diodes (LED).¹⁾ Since conventional fluorescent lamp containing Hg vapor generates heat, the trend shifts to LED that has much longer lifetime compared with the conventional devices. However, there are mainly two problems in the blue and UV LED applications shown in Fig. 1. First point is low color rendering. White light-emitting devices comprising the sharp emission bands of REs usually have the problem of color rendering that is lower than conventional broadband emission devices. Second is the device structure. Although various kinds of RE-doped phosphors have been actively developed worldwide, the host materials (sealant) for these phosphors, such as silicone, still remain limited with respect to high-power or short-wavelength excitation light sources, because of degradation. Thus, a novel, inorganic, low-melting material will be needed as an alternative to organic sealing materials in the future. In addition, RE-free materials have been extensively examined because there is uncertainty about the stability of RE supplies in the future. If a transparent glass material without a RE cation emits white light comparable to a crystalline phosphor, it would be considered a novel emitting material capable of good formability, which is quite important in the industrial manufacturing process. In addition, the emission color can also be widely tuned because various kinds of emission centers can be incorporated in the glass network, which is quite different from the conventional RE-doped crystalline phosphor. Therefore, we have focused our efforts on RE-free glass phosphors that can be used in white fluorescent lamps.

Since white light emission is composed of various wavelengths, it can be attainable by RE-free phosphors: for example, the Sb³⁺, Mn²⁺-doped calcium halophosphate, [Ca₅(PO₄)₃(F,Cl):Sb³⁺, Mn²⁺].²⁾ In the halophosphate crystal, broad white light emission is attained using Sb³⁺ and Mn²⁺ cations, in which the emission of Mn²⁺ cation is sensitized by Sb³⁺ cations via an energy transfer process. Although several cations have been used

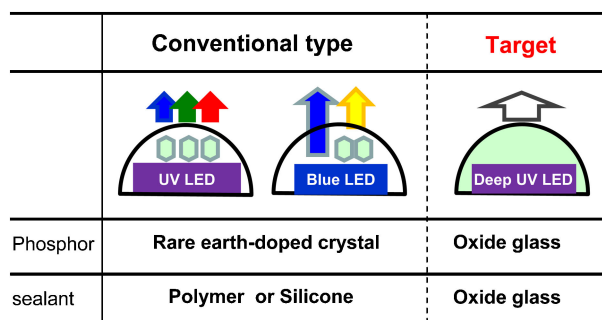


Fig. 1. (Color online) Schematic image of white LEDs: conventional type and the target of the present study.

as an emission center, it is necessary to select an emission center exhibiting the parity allowed excitation, i.e. the high transition probability, to attain high performance for practical application using amorphous materials. Therefore, we have selected ns²-type emission center, which possesses the allowed transition, and low-melting phosphate glass to prepare a next generation emitting materials. In the following sections, ns²-type emission center is first introduced before our recent results. Secondly, results of low-melting phosphate glasses containing Sn²⁺ emission center are shown. Thirdly, the author compares emission properties of two ns²-type emission centers: Sn²⁺ and Sb³⁺. Finally, demonstration of white light emission using Sn²⁺ and Mn²⁺ cations is described.

2. Luminescence of ns²-type emission center

The ns²-type ions ($n = 4, 5, 6$) is a technical term of ions exhibiting ns² electron configuration in the ground state and ns¹np¹ in the excited state. Table 1 shows several ns²-type ions whose emission property has been reported in alkali halides³⁻⁷⁾ and several oxides.^{2),8)-17)} In particular, excitation and emission spectra of Tl⁺-incorporated alkali halides have been most minutely reported.^{3),4)} The characteristics of these ions are (1) parity allowed excitation (¹S₀ → ¹P₁), and spin-forbidden relaxation (³P₁ → ¹S₀) whose decay is the order of microseconds, and (2) broad emission with large Stokes' shift especially in the case

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Table 1. References of ns²-type ions exhibiting luminescent property in crystals

(ns) ²	Ion species	Alkali halides ^{3),4)}	Oxides
	Sn ²⁺	NaCl, ⁵⁾ KCl, ⁵⁾ RbCl ⁵⁾	Ca ₃ (PO ₄) ₂ , ⁸⁾ Sr ₂ P ₂ O ₇ , ⁹⁾ SrB ₆ O ₁₀ ¹⁰⁾
(5s) ²	Sb ³⁺	KCl, ⁶⁾ KI ⁶⁾	Ca ₅ (PO ₄) ₃ (F,Cl) ^{2), 11)-13)} YPO ₄ ¹⁴⁾
	Tl ⁺	NaCl, ⁵⁾ KCl ⁵⁾	BaSiO ₃ , ¹⁵⁾ (Ca,Zn) ₃ (PO ₄) ₂ ¹⁶⁾
(6s) ²	Pb ²⁺ Bi ³⁺	NaCl, ⁵⁾ KCl, ⁵⁾ RbCl ⁵⁾ KCl ⁷⁾	BaSi ₂ O ₅ , ¹⁵⁾ BaFSiO ₃ , ¹⁵⁾ YPO ₄ ¹⁷⁾

of Sn²⁺ and Sb³⁺ centers. Because of the large transition probability, Sb³⁺ doped calcium halophosphate has been used as a practical phosphor for white fluorescent lamps.²⁾ The emission of ns²-type cation is strongly affected by the coordination field, because the emission centers possess electrons in the outermost shell in both the ground state and the excited state.¹⁾ Considering the site distributions of amorphous glasses and crystals, it could be said that this type of emission center is suitable for amorphous glass.

3. Preparation of Sn²⁺-doped zinc phosphate glass and its emission property

We focus on glasses with the principal chemical composition SnO–ZnO–P₂O₅ (SZP), which have been industrially applied, owing to their low-melting properties, in the sealing of electronic devices such as LEDs.^{18),19)} These glasses will be potential candidates for Pb-containing low-melting glasses, not only because of their low-melting properties,^{20),21)} but also because they contain no hazardous cations.²²⁾ On the other hand, it was also reported that Sn-doped ZnO–Al₂O₃–P₂O₅ glass exhibited emission properties via the absorption of UV light.²³⁾ In addition, tin in float glasses is used as a marker to determine the free plane by irradiation of UV light.²⁴⁾ Therefore, it is expected that Sn²⁺-containing zinc phosphate glass can exhibit both low-melting and light emitting properties.

Among several zinc phosphate glasses, 60ZnO–40P₂O₅ glass (mole %) has been selected as a base glass, because the structure has been examined by XPS,²⁵⁾ ³¹P NMR,²⁶⁾ X-ray diffraction,²⁷⁾ HPLC analysis,²⁸⁾ Raman and IR,²⁹⁾ and molecular dynamics calculation.³⁰⁾ Starting materials of the SZP glasses were SnO, ZnO, and (NH₄)₂HPO₄. Although ammonium phosphate is a commercially available solid-state chemical used as a starting material for P₂O₅, it has often been observed that the used crucible is damaged during the conventional melt process.³¹⁾ This is a clear sign that these glasses contain Al₂O₃ or SiO₂ eluted from the crucible, which is likely to affect the physical properties of the obtained glass and renders the glass composition less certain.^{32),33)} Although SZP glasses are prepared using either alumina or platinum crucibles, it would be desirable to establish a preparation scheme using ammonium phosphate with a Pt crucible for the refined design. We have demonstrated that a sintering process (~800°C) using ZnO and (NH₄)₂HPO₄, in which zinc phosphate crystallites such as α-Zn₂P₂O₇ was formed to reduce amounts of OH groups, is the key to prevent damage to a Pt crucible.³⁴⁾ Therefore, this process is important for the fabrication of contaminant-free phosphate glass using ammonium phosphate as a starting material.

The colorless SZP glasses prepared by a melt-quenching method show the glass transition temperatures, *T*_gs, that are less

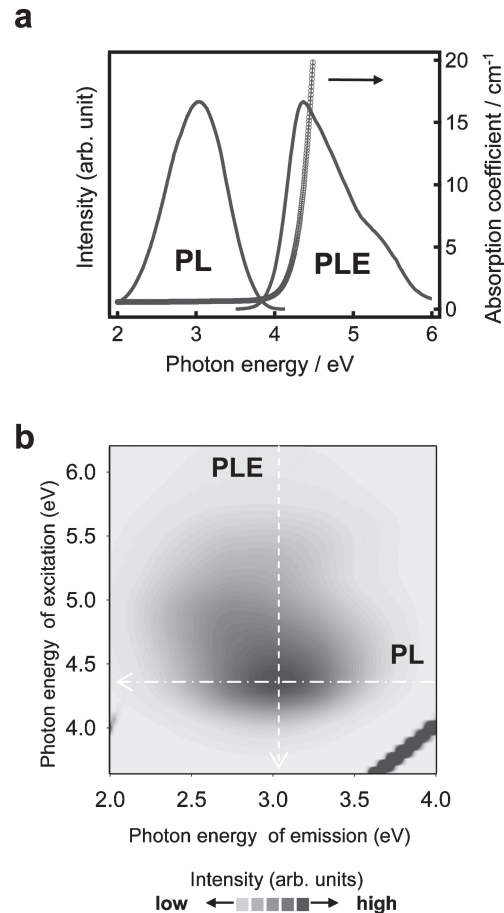


Fig. 2. Optical property of the 5SnO–55ZnO–40P₂O₅ glass. (a) Normalized PL and PLE spectra of the glass together with absorption spectrum of the glass. (b) Contour plot of the glass using an intensity axis on a linear scale.

than 420°C. The *T*_g increases with decreasing amounts of P₂O₅ and SnO. **Figure 2(a)** shows normalized photoluminescence (PL) and PL excitation (PLE) spectra of the 5SnO–55ZnO–40P₂O₅ glass together with its absorption spectrum. Comparison of the absorption spectrum with the PLE spectrum shows that the strongest emission spectrum is obtained by excitation using the wavelength of the optical band edge. Through examination of the PL properties of other SZP glasses, it is found that both the maximum PLE position that induced the maximum PL intensity and the optical band gap are blue shifted with decreasing amounts of SnO. Since 60ZnO–40P₂O₅ glass shows no emission, it is indicated that the emission origin in the SZP glasses is the Sn species. Figure 2(b) shows a contour plot of the 5SnO–55ZnO–40P₂O₅ glass with the photon energy of excitation (ordinate) and emission (abscissa), using an intensity axis on a linear scale. A broad emission is observed at the UV light excitation of 4.1–4.5 eV (300–275 nm), and the Stokes shift is about 1.3 eV. The photon energy for excitation decreases with increasing amounts of SnO, whereas the quantum efficiency (QE) reaches a maximum near 2.5 mol % Sn. Notably, transparent 2.5SnO–57.5ZnO–40P₂O₅ glass shows a maximum emission of the QE (over 80%) without any additives, such as RE cations.³⁵⁾ This tendency is roughly correlated with the change in the chromatic coordination of the glass. **Figure 3** shows the chromaticity coordinates of the SZP glasses together with photographs of (1) 40SnO–30ZnO–30P₂O₅, (2) 30SnO–30ZnO–40P₂O₅, and (3)

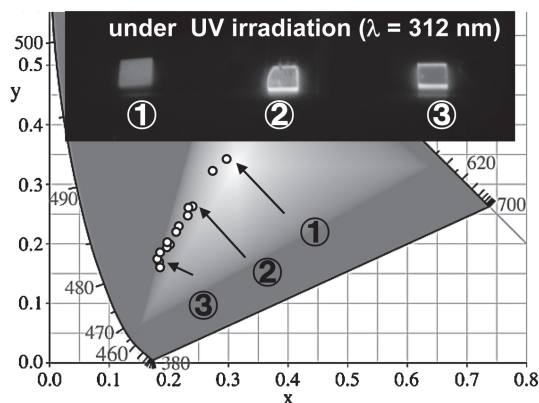


Fig. 3. Chromaticity coordinates of the SnO-ZnO-P₂O₅ glasses. Inset shows a photograph of (1) 40SnO-30ZnO-30P₂O₅ glass, (2) 20SnO-30ZnO-40P₂O₅ glass, and (3) 5SnO-55ZnO-40P₂O₅ glass under exposure to a wavelength of UV light ($\lambda = 312$ nm). Tendency of the QE value is roughly correlated with that of chromatic coordination of the glass.

5SnO-55ZnO-40P₂O₅. Glass (1) exhibits a weak white emission, whereas glass (3) produces a strong blue emission. Because the oxidation state of Sn in glass (3) is estimated at $89 \pm 1\%$ (Sn²⁺): $11 \pm 1\%$ (Sn⁴⁺) by Mössbauer spectroscopy,³⁶⁾ it is expected that Sn²⁺ would strongly affect both the transparency and QE of the glass. It is confirmed that the PL properties are maintained after heat treatment at $T_g + 100$ K, the temperature at which most glasses offer workability in air. Moreover, no devitrification is observed in these glasses after heat treatment. The chemical durability demonstrated by the present SZP glass in the industrial formation process ensures its potential for sealing applications. It is reported that twofold-coordinated Sn in SiO₂ shows two emission bands: an α -band [singlet (S_1)-singlet (S_0), ~ 4.1 eV] and a β -band [triplet (T_1)-singlet (S_0), ~ 3.1 eV].^{37,38)} Since the emission decay constant $\tau_{1/e}$ was 4.5 μ s, which is a typical decay time for T_1 - S_0 relaxation, the observed emission is probably due to the T_1 - S_0 relaxation of twofold Sn²⁺ center. On the other hand, the QE decreased as the amount of Sn in the glass increased, which is an indication of concentration quenching. Because the glass showed stable emission properties after the formation process, it is a promising candidate for use as a sealing material for various types of optoelectronic devices.

4. Comparison of Sn²⁺ and Sb³⁺ emission centers in zinc phosphate glass

As mentioned above, Sb³⁺, Mn²⁺-codoped calcium halophosphate is a practical phosphor for white fluorescent lamps.²⁾ On the other hand, Sb₂O₃ is used as a fining agent in glass preparation because its oxidation state can be changed upon the release or capture of oxygen in the glass melt.³⁹⁾ Sb³⁺ has thus far received little attention as an emission center in conventional glass science, although the emission of Sb³⁺ has been described.^{40,41)} Since it was reported that Sb³⁺-doped zinc phosphate was also a potential substitute for Pb-based glasses in sealing applications,⁴²⁾ it is worthwhile to examine Sb³⁺-doped ZnO-P₂O₅ glass to discuss the differences between Sn²⁺ and Sb³⁺ emission centers.⁴³⁾

One of the differences between the Sb³⁺ and Sn²⁺ emission centers is effect of a preheating treatment before glass melting on coloration of the glasses. If the starting materials are preheated at 500°C, the obtained Sb³⁺-doped glass is transparent as shown in Fig. 4(a). On the other hand, the formation of Sb nanoparticles is observed in the glass preheated at 300°C, as shown in Fig. 4(b).

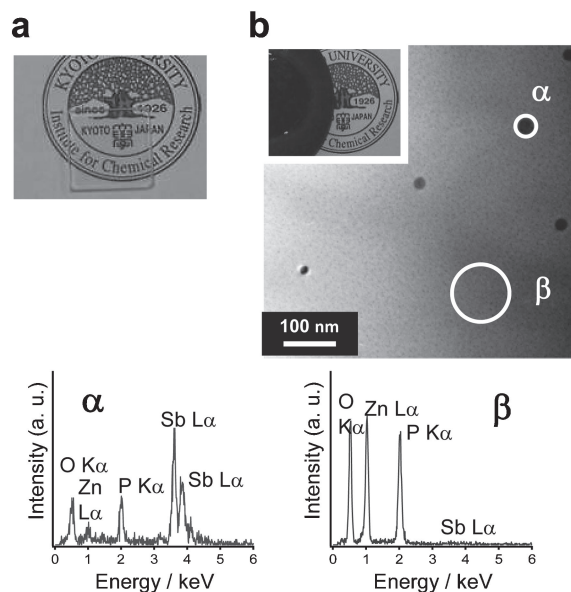


Fig. 4. (a) Photograph of the 1.0SbO_{3/2}-60ZnO-40P₂O₅ glass prepared by 1100°C melting with pre-heat-treatment at 500°C. (b) TEM image of the 1.0SbO_{3/2}-60ZnO-40P₂O₅ glass prepared by 1100°C melting with pre-heat-treatment at 300°C. EDX patterns of two parts (α) (β) are also shown.

Since reducing conditions have been reported to facilitate the precipitation of metal nanoparticles in glass materials,^{44,45)} it is speculated that Sb³⁺-doped glass is easily affected by the reductive species to change the valence during melt quenching, which is not observed in the Sn²⁺-doped glass.

Figure 5(a) shows the normalized PL and PLE spectra of the x SbO_{3/2}-60ZnO-40P₂O₅ glasses. The 1.0SbO_{3/2}-60ZnO-40P₂O₅ glass shows the strongest emission intensity among these glasses. The PL spectra most likely consists of two bands at 2.95 and 2.11 eV, and the peak area ratio of the peak at 2.11 eV decreases with increasing amounts of SbO_{3/2}. Comparison of the absorption spectrum with the PLE spectrum shows that the strongest emission is obtained by excitation using the wavelength of the optical band edge, and the optical band edges and the PLE peak energies of the x SbO_{3/2}-60ZnO-40P₂O₅ glasses are red shifted with increasing amounts of SbO_{3/2}, which is also observed in the SnO-ZnO-P₂O₅ glass. However, although both emission centers adopt the 5s² electron configuration, the emission properties of the Sb-doped glass are quite different from those of the Sn²⁺-doped glass. One of the differences between the Sb³⁺ and Sn²⁺ emission centers is the amount of added species. The SbO_{3/2}-ZnO-P₂O₅ glass can contain less than 2 mol % Sb³⁺ without any decrease in transparency, as opposed to the previous Sn²⁺-doped glasses that can contain more than 5 mol % Sn²⁺.⁴⁶⁾ The broad absorption tail in the 2SbO_{3/2}-60ZnO-40P₂O₅ indicates defects due to the presence of excess Sb cations. Figures 5(b) and 5(c) show the PL-PLE contour plots of 1.0SbO_{3/2}-60ZnO-40P₂O₅ glass and 1.0SbO_{3/2}-60ZnO-40P₂O₅ glass, respectively. The emission color of the Sb³⁺-doped glass is slightly pink, and is different from the blue color derived from the Sn²⁺-doped glass. As shown in Fig. 5(b), the emission at the maximum peak intensity for Sb³⁺ is located at 2.97 eV, with a bandwidth of about 1.5 eV. Although the photon energy for excitation of Sb³⁺ is higher than that of Sn²⁺, the emission of Sb³⁺ corresponds to a lower emission band energy and a broader bandwidth than that of Sn²⁺, as shown in Fig. 5(c). In addition,

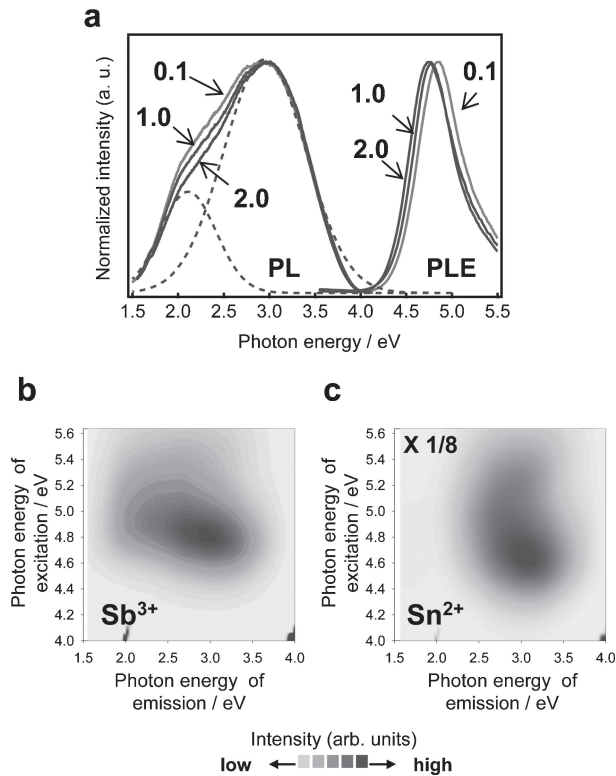


Fig. 5. Normalized PL and PLE spectra of $x\text{Sb}_{0.3/2}\text{-60ZnO-40P}_2\text{O}_5$ glasses. Dotted lines indicate the deconvoluted emission bands of the $2.0\text{Sb}_{0.3/2}\text{-60ZnO-40P}_2\text{O}_5$ glass. PL-PLE contour plot of the $1.0\text{Sb}_{0.3/2}\text{-60ZnO-40P}_2\text{O}_5$ glass (b) and the $1.0\text{SnO-60ZnO-40P}_2\text{O}_5$ glass (c).

Table 2. Emission properties of the $1.0\text{Sb}_{0.3/2}\text{-60ZnO-40P}_2\text{O}_5$ and the $1.0\text{SnO-60ZnO-40P}_2\text{O}_5$ glasses. These glasses were prepared by 1100°C melting with pre-heat-treatment at 500°C

ns ² emission center	Sb ³⁺	Sn ²⁺
Peak energy of excitation/eV	4.77	4.61
Peak energy of emission/eV	2.97	3.06
Band width of emission/eV	~1.5	~1.0
$\tau_{1/e}/\mu\text{s}$	2.5	5.3

the $1.0\text{Sb}_{0.3/2}\text{-60ZnO-40P}_2\text{O}_5$ glass shows non-exponential decay with a lifetime ($\tau_{1/e}$) of $2.5\ \mu\text{s}$, which is half the lifetime of the $1.0\text{SnO-60ZnO-40P}_2\text{O}_5$ glass, in which single exponential-like decay is observed. The non-exponential intensity decay of Sb^{3+} indicates that a quenching site exists in the glass. The broad emission of Sb^{3+} is suitable for white light emission via excitation by a deep-UV LED. As shown in **Table 2**, the Sn^{2+} emission center is more favorable as a longer excitation light source, whereas emission of Sb^{3+} is advantageous from the viewpoint of broader emissions capable of achieving high color rendering. However, from viewpoint of practical application, emission intensity of Sb^{3+} is much weaker than that of Sn^{2+} , which confirm that Sn^{2+} emission center is the most suitable for the present phosphate glass system.

5. White light emission of Sn^{2+} , Mn^{2+} -codoped zinc phosphate glass

Since the SZP glasses show a broad and strong blue emission, it is expected that a white light emission can be attained by the addition of Mn^{2+} cation, similar to the Sb^{3+} , Mn^{2+} -codoped calcium halophosphate.²⁾ By preparation of a series of Sn^{2+} , Mn^{2+} -

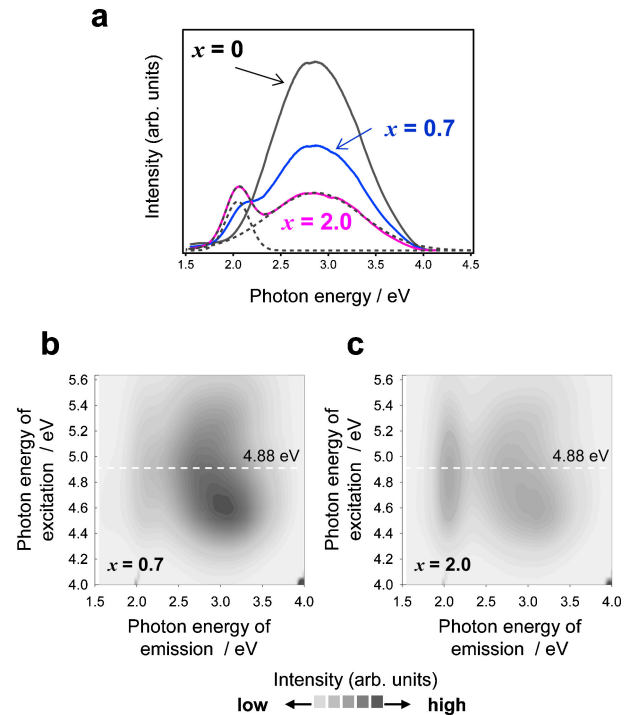


Fig. 6. (Color online) (a) PL spectra of the $x\text{MnO-2.5SnO-57.5ZnO-40P}_2\text{O}_5$ glasses excited by $4.88\ \text{eV}$. PL spectra can be deconvoluted into two bands: $2.86\ \text{eV}$ (Sn^{2+}) and $2.05\ \text{eV}$ (Mn^{2+}). PL-PLE Contour plots of the $2.5\text{SnO-57.5ZnO-40P}_2\text{O}_5$ glasses with different amounts of MnO . (b) 0.7 , and (c) 2.0 mol%. Linear scale is used for the intensity axis.

codoped zinc phosphate glasses, we demonstrate that a white fluorescent lamp is attained by combining UV light and a RE-free amorphous glass phosphor.^{47),48)}

Figure 6(a) shows the PL spectra of the $x\text{MnO-2.5SnO-57.5ZnO-40P}_2\text{O}_5$ glass excited by a photon energy of $4.88\ \text{eV}$ ($254\ \text{nm}$). This glass composition consisted of MnO and the SZP glass composition, which showed the maximum QE.³⁵⁾ The emission spectra consist of two broad bands: a Sn^{2+} emission center at $2.86\ \text{eV}$ and a Mn^{2+} ($3d^5$) center at $2.05\ \text{eV}$. The emission decay constants $\tau_{1/e}$ of the Sn emissions ($2.86\ \text{eV}$) of the $x\text{MnO-2.5SnO-57.5ZnO-40P}_2\text{O}_5$ glasses ($x = 0, 0.7, \text{ and } 2.0$) at room temperature are $4.5\ \mu\text{s}$ ($x = 0$), $3.5\ \mu\text{s}$ ($x = 0.7$), and $2.1\ \mu\text{s}$ ($x = 2.0$), with an excitation wavelength of $280\ \text{nm}$. Since the shape of the decay curves changes from exponential to non-exponential, it can be concluded that the Sn^{2+} center plays roles both in the emission centers and in the energy donors to Mn^{2+} . Figures 6(b) and 6(c) show PL-PLE contour plots of the $x\text{MnO-2.5SnO-57.5ZnO-40P}_2\text{O}_5$ glasses ($x = 0.7, \text{ and } 2.0$). The mapping suggests that the coordination state of Sn^{2+} was almost unchanged in the zinc phosphate glass by the addition of Mn^{2+} , although the emission intensity is decreased by energy transfer. Comparing the absorption spectrum with the PLE spectrum, the present excitation at $4.88\ \text{eV}$, which is higher than the optical band edge, is the most suitable position for the Mn^{2+} center but not for the Sn^{2+} center. The broad emission suggests that different emission colors can be obtained from the same glass phosphor by changing the excitation light source. **Figure 7** shows a photograph of the $x\text{MnO-2.5SnO-57.5ZnO-40P}_2\text{O}_5$ glass under UV light irradiation ($4.88\ \text{eV}$), and the chromaticity coordinates. It is notable that these glasses shows a high normalized QE value, comparable to that of practical MgWO_4 . This value enables us to confirm the potential application of the

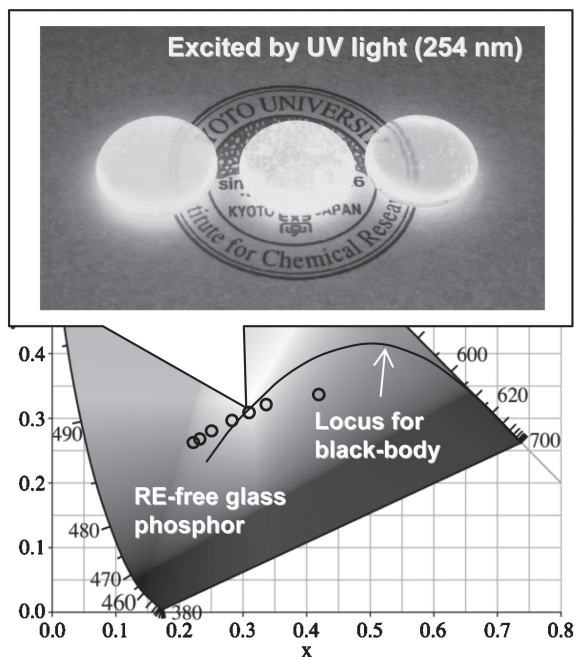


Fig. 7. Chromaticity coordinates of the MnO-doped $2.5\text{SnO}-57.5\text{ZnO}-40\text{P}_2\text{O}_5$ glasses. These glasses were excited by a photon energy of 4.88 eV (254 nm). The glass phosphor can attain color tuning with a wide range of color temperatures by one monolithic transparent glass. Inset shows photograph of the glass phosphors ($x = 0, 0.7, 2.0$) with irradiation of deep UV light (254 nm).

obtained RE-free glass as a phosphor with a high QE. On the other hand, it is also noteworthy that the color coordination positions continuously changes from blue to red with the addition of MnO. In particular, several glasses satisfied the white light emission condition without the RE cation. As shown in Fig. 6(a), the blue color (Sn^{2+}) decreased with increasing amounts of Mn^{2+} .

From the obtained results, we suggest that the basicity of the glass affects both the emission center and the resulting emission color. Since the basicity of oxide glasses can be tailored by a great variety of chemical compositions, the emission color can also be controlled over a wide range. The present results indicate that the Mn-doped $\text{SnO}-\text{ZnO}-\text{P}_2\text{O}_5$ glasses will be novel glass-based materials that possess emission properties. Although the present glass shows white light emission that is similar to the calcium halophosphate crystals, there are several large differences between the two. First, for a greater number of emission centers, Sn^{2+} can be doped in the glass. Second, various kinds of elements can be added to the glass to control the emission properties as well as to improve mechanical or thermal properties. Third, monolithic materials can reduce optical loss due to scattering at the interface. Moreover, transparent emission materials will meet novel industrial needs. Therefore, such materials can be industrially applied as sealing materials for electronic devices such as LEDs, because these glasses also possess low-melting properties.

Here, we have again emphasized the advantage of combining these low-melting glass phosphors with a next-generation deep-UV LED. From the viewpoint of chemical stability, an inorganic low-melting glass is a candidate for a practical sealant in deep-UV LEDs. Since the light conversion is attained by the monolithic amorphous material without an internal interface, the color change of device by time-dependent deterioration of each phosphor or sealant is inherently prevented. Although deep-

UV LEDs are not yet commercially available, recent developments clearly suggest the possibility for their realization in the near future.^{49),50)} The next-generation white LED indicates the realization of Hg-free white fluorescent lamps. The important point of our results is that amorphous oxide glasses possessing random structures demonstrate high QE values comparable to conventional crystalline phosphors. Although the emission of Sn^{2+} can be explained by the conventional ns^2 -type emission mechanism, there may exist a mechanism characteristic of amorphous material. Unlike RE cations, which exhibit high QE values because of the small influence of phonons, the ns^2 -type centers in our glasses have many uncertain points. Although the mechanism of the emissions has not been fully clarified yet, the present RE-free glass phosphors are very fascinating materials from the viewpoint of unique emission mechanisms in a random matrix.

6. Summary and future prospects

The UV-excited light emission of RE-free zinc phosphate glasses has been demonstrated. Notably, a high efficiency, comparable to practical crystalline phosphors, is attained in the amorphous material. The emission, consisting of broad bands, can be tailored by the addition of another emission center such as Mn^{2+} or by changing the local coordination field (i.e., the chemical composition of the mother glass) of Sn^{2+} . These tuning is the forte of oxide glass, and it is characteristic of glass-based device. Recently, our group has reported Sn^{2+} -doped oxide glasses exhibit scintillation property, which is another application of this material.⁵¹⁾ On the other hand, preparation of Sn-doped thin film is also examined for application of transparent plane emission device without RE.⁵²⁾ Therefore, RE-free inorganic amorphous materials possessing emission properties will be required for novel, practical optical devices. Since the emission mechanism as well as the local coordination state of Sn^{2+} in oxide glass has not been clarified yet, further study is needed for understanding the basic science to improve the performance. The author thus believes that ns^{2+} -type cation containing oxide glass will attract much attention from both scientific and industrial viewpoints.

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