AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **114**, 083502 (2013); doi: 10.1063/1.4819102
View online: http://dx.doi.org/10.1063/1.4819102
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/114/8?ver=pdfcov
Published by the AIP Publishing

JOURNAL OF APPLIED PHYSICS **114**, 083502 (2013)

Excitation light source dependence of emission in Sn^{2+}-Ce^{3+} codoped ZnO-P_2O_5 glasses

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(Received 3 June 2013; accepted 6 August 2013; published online 22 August 2013)

Correlation between excitation light source and the emission property of Sn^{2+}-Ce^{3+} co-doped zinc phosphate glasses is examined. Although photoluminescence (PL) peaks of both Sn^{2+} and Ce^{3+} shifted with increasing amount of Ce^{3+}, there was little energy resonance between Sn^{2+} and Ce^{3+} emission centers. On the other hand, radioluminescence (RL) spectra excited by X-ray was independent of the Ce concentration, indicating that emission was mainly observed from Sn^{2+} emission center. It is expected that energy relaxation process in a RL preferentially occurs in an ns^2-type emission center that possesses high transition probability of the excited state in the higher energy region. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4819102]

I. INTRODUCTION

The emission of phosphor is generally classified by the excitation lightsource, such as photoluminescence (PL: UV ~ IR excitation) and radioluminescence (RL: X-ray or high energy particle excitation). The former correlates to direct activation of emission center by one photon, whereas the latter excited by higher energy to far exceed the bandgap induces the multi-photoelectron from an inner shell to activate an emission center. Because of the activation of host material in RL process, the energy path to emission center of RL is quite different from that of PL, and the energy dispersion process is complicated. However, RL materials have been actually used as practical components in medical, security, environmental monitoring, and so on, although the mechanism of whole energy relaxation process is not clarified.[1] Therefore, systematic research on the RL process will be needed in the future.

In the case of RL process, both self-activated material and activator, i.e., emission center-containing material have been used.[1,2] Since number of self-activated materials reported so far is limited, recent trend of examination is shifted to preparation of activator-containing material. Considering the transition probability of emission centers, parity-allowed transition is favorable to attain high emission intensity.[3] Two types of emission center can possess the parity allowed transition: ns^2-type emission center possessing ns^2-nsnp transition and rare earth (RE) cations possessing $4f^n$-$4f^{n-1}5d$ transition.

Since the ns^2-type emission centers possess electrons in the outermost shell, the emission is strongly affected by the coordination field. In addition, the transition probability is high enough for practical phosphor, such as Sb^{3+}, Mn^{2+}-doped calcium halophosphate.[4–6] Using this emission center, we reported high quantum efficiency (QE) of SnO-ZnO-P_2O_5 (SZP) bulk glass, which is the highest QE value of RE-free oxide glass (over 80%).[7,8] In addition, we have also demonstrated the UV-excited white light emission property of MnO-doped SZP glasses.[9,10] More recently, it was reported that the SZP glass also showed scintilating property by excitation of ^{241}Am source.[11] Since RL spectrum shape of the glass was different from the PL one, it suggests excitation energy-dependent emission surely exists. On the other hand, several RE cations, such as Ce^{3+} or Pr^{3+}, can show broad emission due to the 4f-5d transition.[12–19] Different from other trivalent RE cations exhibiting $4f^n$–$4f^n$ transition, these emission centers possess high transition probability that is also suitable for practical device applications, such as YAG:Ce. Since decay constant of the emission centers is much faster than that of ns^2-type centers, these emission centers are enthusiastically focused in phosphor applications.

In several phosphor materials, relationship between PL and RL has been reported, for examples, both luminescence properties of YAG:Ce crystal,[15] ceramics,[16] and SZP glass.[7,11] Apart from a phosphor using energy transfer between two different activators, conventional phosphor contains one emission center. Although co-doping of parity allowed emission centers is an unusual approach for industrial application,[20] we expect that this approach is suitable for examining difference of mechanism between PL and RL. Since phosphate glass is thought to be suitable host among conventional oxide glass, correlation between excitation light source and the emission property of Sn^{2+}-Ce^{3+} co-doped zinc phosphate glasses is examined.

II. EXPERIMENTAL

The Ce^{3+}-doped SZP (CeSZP) glasses were prepared by a conventional melt-quenching method using a platinum crucible. The chemical composition of the SZP glass was fixed at 2.5SnO-57.5ZnO-40P_2O_5 (in mol%), which is the chemical composition possessing the highest QE in a previous

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0021-8979/2013/114(8)/083502/6/$30.00

paper.[4] Following the calcination of mixture of ZnO and $(NH_4)_2HPO_4$ at 800 °C for 3 h, the calcined solid was mixed with SnO and CeO_2 at room temperature (r.t.) and then melted at 1100 °C for 30 min in the air.[21] 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 cut to dimensions of 10 mm × 10 mm × ∼1 mm and mechanically polished to obtain mirror surface.

The T_g was determined by differential thermal analysis operated at a heating rate of 10 °C/min using TG8120 (Rigaku). The PL and PL excitation (PLE) spectra were measured at r.t. using F-7000 fluorescence spectrophotometer (Hitachi). Contour plots of PL intensity of the glasses were prepared using dozens of PL spectra measured at different excitation energies. According to a previous paper,[22] PL spectra under vacuum ultraviolet (VUV) excitation were also evaluated in the excitation wavelength from 120 to 200 nm using a deuterium lamp as the light source. The atmosphere of measurements was nitrogen, because oxygen absorbs VUV photons. The absorption spectra were measured at r.t. using U3500 spectrophotometer (Hitachi). The emission decay at r.t. was measured using a Quantaurus-Tau (Hamamatsu Photonics) whose excitation light source was 280 nm LED, which was the highest excitation source in this equipment, operated at a frequency of 10 kHz.

In the X-ray radiation response measurements, samples were coupled to the monochromator equipped charge coupled device (CCD, Andor DU-420-BU2) via 2 m length optical fiber. The emission spectra were measured by irradiation of X-ray supplied with bias voltage of 50 kV and tube current of 4 mA. The spectra whose accumulated numbers were five to reduce the influence from background noise due to environmental radiation (e.g., muon) by the averaging. The detailed description about the geometry can be shown the past work.[19]

III. RESULTS AND DISCUSSION

The obtained glasses, whose T_gs were about 420 °C, were transparent and colorless. Figure 1 shows the optical absorption spectra of xCeO$_\alpha$-2.5SnO-57.5ZnO-40P$_2$O$_5$ (xCeSZP) glasses. Since there is no absorption at near UV region (∼3.1 eV),[23] we consider that most of the Ce valence is trivalent and α value is almost 3/2, although the precise valence of cerium cation was not estimated. Absorption spectra mainly consist of two bands at UV region: a band at 4.3 eV and another band at higher energy about 4.8 eV. Since absorption of Ce^{3+} is due to allowed-transition possessing high transition probability, the lower band peak in the sample $x = 1.00$ is not observed because of limit of sample thickness. Since intensity of the lower band increases with increasing amount of x value, it is suggested that the lower excitation band is due to 4f-5d transition of Ce^{3+} emission center.[12] On the other hand, it was reported that SZP glass possessed the absorption edge over 4.6 eV corresponding to the s-p transition of Sn^{2+} emission center. Since the optical band edge energy of 60ZnO-40P$_2$O$_5$ glass is over 6 eV,[8,24] it ensures that the observed higher band correlates with Sn^{2+} center.[8] It is notable that the optical absorption edge due to Ce^{3+} red-shifts with increasing Ce amount, which is also observed in the SZP glasses containing Sn^{2+} center.[8,21] It is expected that the composition-dependent state governs the optical property of the Ce^{3+} center. From these spectra, it is expected that Ce^{3+} emission is preferentially observed by excitation of lower photon energy, whereas Sn^{2+} emission is observed by higher energy excitation. Figure 2 shows the PL-PLE spectra of the 0.05CeSZP glass with different excitation peak energies. In the case of excitation of 4.64 eV, broad emission at 3.00 eV due to Sn^{2+} center is mainly observed. On the other hand, the excitation of 4.20 eV mainly induces emission of Ce^{3+} center whose emission peak is 3.67 eV. Thus, it is expected that emission of the xCeSZP glass depends on interaction between activator and the excitation photon energy, i.e., energy overlap between excitation energy and the excitation state of different parity-allowed emission centers.

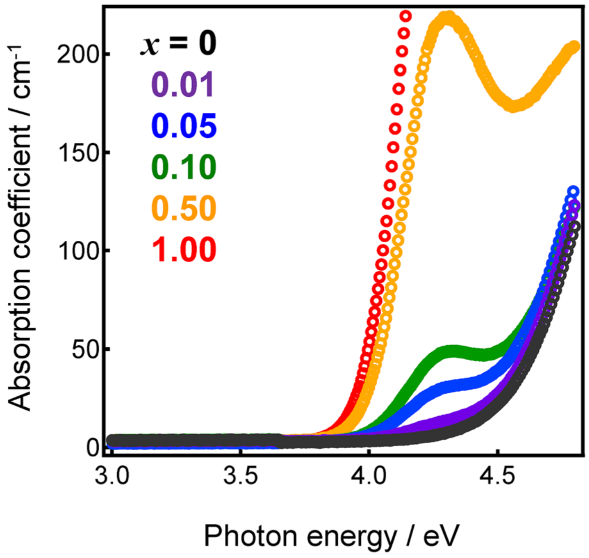

FIG. 1. Optical absorption spectra of the xCeSZP glasses.

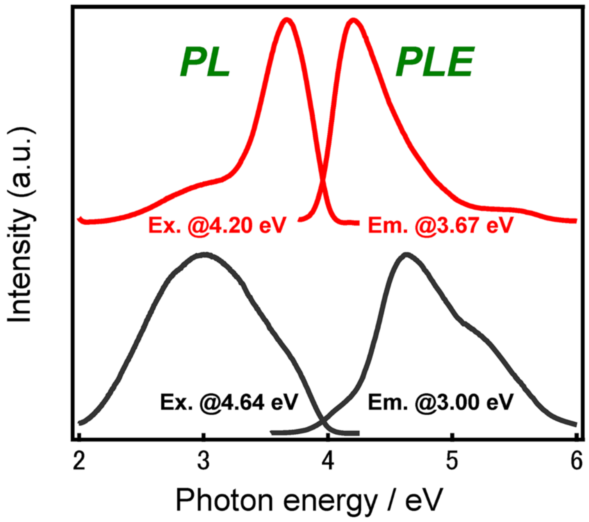

FIG. 2. PL-PLE spectra of the 0.05CeSZP glass at different excitation energies.

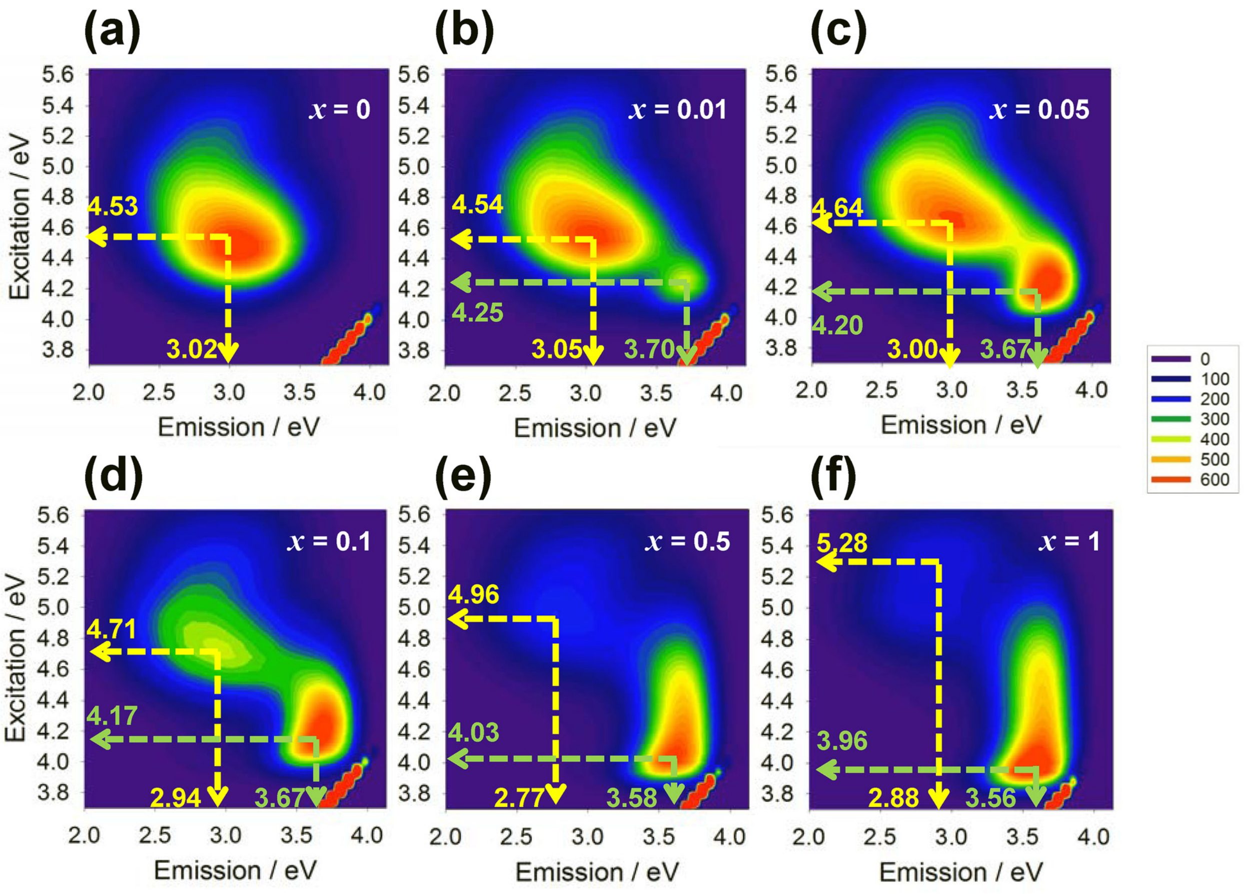

FIG. 3. Contour plots of PL intensity of the *x*CeSZP glasses with different amounts of Ce concentration. (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.5, and (f) 1.0 mol. %. Linear scale is used for the intensity axis.

To understand the site selective emission property of the glasses, contour plots of PL intensity of the *x*CeSZP glasses with different amounts of Ce concentration are shown in Fig. 3: (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.5, and (f) 1.0 mol%. The photon energy of excitation and emission are shown in ordinate and abscissa, respectively, and the intensities are plotted using an intensity axis on a linear scale. Both peak energies of emission and excitation bands are shown: Sn^{2+} (yellow) and Ce^{3+} (green). With increasing x value, emission intensity of Ce^{3+} increases in contrast to Sn^{2+}. From these figures, it is found that each peak energy is changed with addition of CeO_2, and not only emission and excitation peaks of Ce^{3+} but also those of Sn^{2+} are changed. To discuss Ce concentration dependence, peak photon energies of *x*CeSZP glasses are plotted as a function of Ce amount (Fig. 4). With increasing amount of Ce cation, both PLE and PL peaks of Ce^{3+} are red-shifted. Since PLE peak of Sn^{2+} was also red-shifted with increasing amount of SnO in SZP glass,[8] similar tendency of Ce^{3+}, whose 4f5d transition is also affected by the coordination state, is observed. On the other hand, PLE peak energy of Sn^{2+} in the *x*CeSZP glasses blue-shifts, whereas the PL peak energy slightly decreases, which is an opposite peak shift observed in previous SZP glasses.[8] It is suggested that the change in oxidation state and coordination number of tin occurs to change the peak energies of PL and PLE. Since starting material was CeO_2 and the melt condition was air, redox reaction ($Sn^{2+} + Ce^{4+} \leftrightarrows Sn^{4+} + Ce^{3+}$) might be existed between two emission centers during the melting.

Figure 5 shows emission decay curves of the *x*CeSZP glasses at 3.1 eV (emission of Sn^{2+}) with excitation of a 280 nm (4.43 eV) LED. The Ce-free glass shows almost single exponential decay whose lifetime $\tau_{1/e}$ is 4.5 μs whose

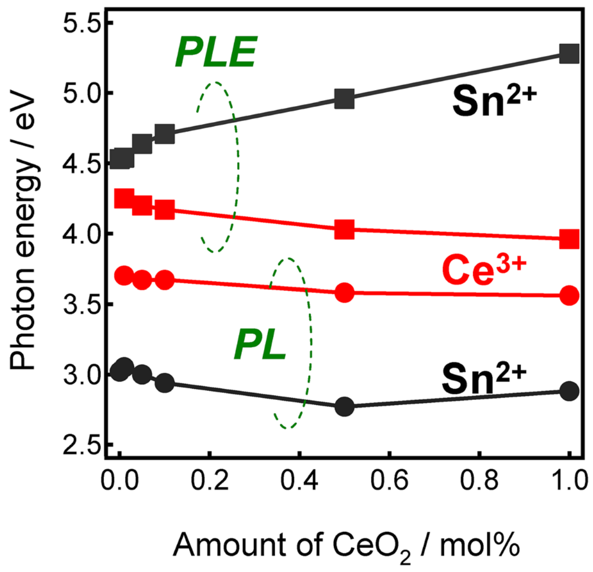

FIG. 4. Peak photon energies of *x*CeSZP glasses as a function of CeO_2 amount.

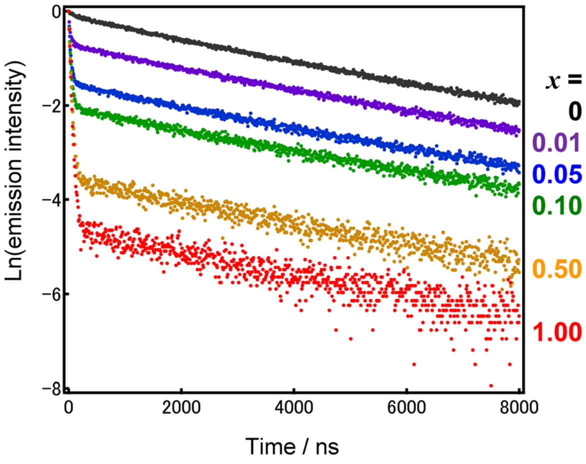

FIG. 5. Emission decay curves at 3.1 eV (Sn^{2+} emission) of the xCeSZP glasses. The decay curves were measured at r.t. using a 280 nm (4.43 eV) LED.

timescale is characteristic of triplet-singlet relaxation in Sn^{2+} emission center.[3,8] On the other hand, Ce-codoped samples possess two decay components: one is a faster decay at nanosecond order, and another is a slower decay comparable to that in the Ce-free glass. With increasing amount of Ce concentration, the faster decay part due to relaxation from Ce^{3+} center increases. On the other hand, slower decays due to Sn^{2+} center are calculated by linear fitting of the decay curves in the 1–7 μs region. These $\tau_{1/e}$ decays are 4.5 μs with the r^2 values of 0.996 ($x = 0$) ~ 0.946 ($x = 1.00$), and independent of the Ce concentration. On the contrary, the $\tau_{1/e}$ values of faster decay components are about 20 ns, which is also independent of the Ce concentration. It is, therefore, expected that there is no energy resonance between Sn^{2+} and Ce^{3+} centers. These results suggest that a parity-allowed emission center only work as an energy donor, not an acceptor.

In contrast to PL spectra, RL spectra show a characteristic phenomenon. Figure 6(a) shows X-ray-induced RL spectra of the xCeSZP glasses. There is no remarkable difference among these spectra despite increasing x value. Since intensity of both PL and RL from zinc phosphate glass without any activator was much lower than that of the xCeSZP glasses,[8,25] we can conclude that the observed emission is due to a doped activator. To demonstrate excitation source dependence, emission spectra of the 0.05CeSZP glass with different excitation energies are shown in Fig. 6(b). In the case of PL spectra, emission spectra are changed depending on the excitation photon energy. At lower excitation energy (4.20 eV), the spectrum mainly consists of emission of Ce^{3+}. In the case of higher energies (4.64, 5.06, and 7.75 eV), the spectra mainly consist of emission of Sn^{2+}, which is also confirmed in Fig. 3(d). When the excitation energy is over the band gap energy, two emission peaks are observed, and the lower emission peak at 2.3 eV is not observed in conventional PL process (see Fig. 3). Since intrinsic emission due to exciton or defects sometimes has the excitation band over the band gap, the emission origin at 2.3 eV is attributed to the host (intrinsic) luminescence of SZP characterized by higher excitation over the band gap. On the other hand, spectrum shape of RL is very similar to that of PL excited by 5.06 eV. It is notable that spectra change at the energy region of 3 ~ 4 eV due to Ce^{3+}, which is clearly observed in PL spectra (see Fig. 2), is not observed. Since the higher excitation band originates from Sn^{2+} center as shown in Fig. 3(c), we can conclude that Ce^{3+} emission was not obtained from the present Sn-Ce codoped glasses by excitation of X-ray, and that RL is only observed from a Sn species. Peak energy of RL spectrum is similar to that of higher band in PL spectrum excited by 7.75 eV, indicating that the observed emission at 2.8 eV also correlates with high energy excitation over the band gap.

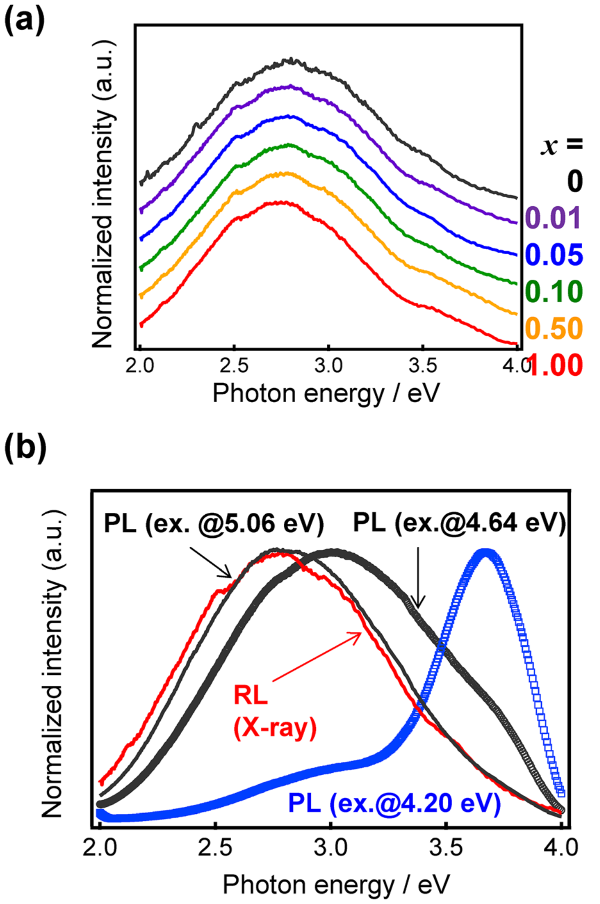

FIG. 6. (a) RL spectra of the xCeSZP glasses. (b) Emission spectra of the 0.05CeSZP glass with different excitation energies.

In order to confirm the existence of Ce^{3+} emission of zinc phosphate glass in the RL process, we have also prepared ySnO-1CeO$_\alpha$-59ZnO-40P$_2$O$_5$ glasses using melt-quenching method. Figure 7 shows RL spectra of several ySnO-1CeO$_\alpha$-59ZnO-40P$_2$O$_5$ glasses containing different amount of SnO. In the figure, emission intensity of 3.5SnO-1CeO$_\alpha$-59ZnO-40P$_2$O$_5$ glass is displayed as one-twentieth for comparison. We can find existence of Ce^{3+} emission whose emission peak energy is similar to that in PL process (see Fig. 2 or 6(b)). Although emission of Ce^{3+} can be observed in the glass with lower-SnO concentration, the observed emission is mainly consisted of Sn^{2+} center in higher SnO-containing glass. Therefore, we expected that the absence of Ce^{3+} emission in RL process by introducing Sn^{2+} center is due to competing energy path between different centers.

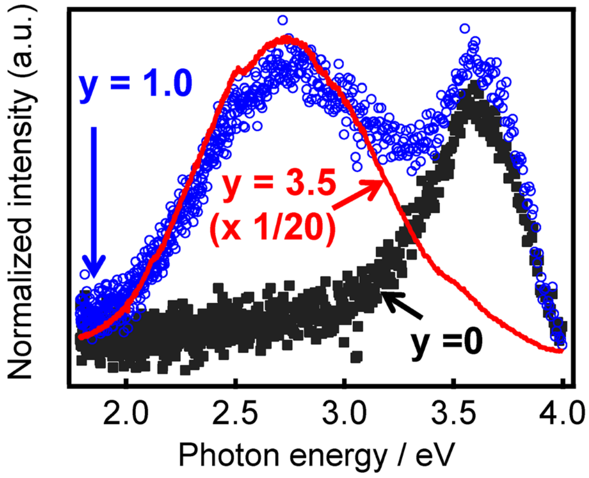

FIG. 7. RL spectra of the ySnO-1CeO$_x$-59ZnO-40P$_2$O$_5$ glasses ($y = 0$: closed squares, $y = 1.0$: open circles, and $y = 3.5$ solid line.) Emission intensity of 3.5SnO-1CeO$_x$-59ZnO-40P$_2$O$_5$ glass is displayed as one-twentieth for comparison.

From the obtained results, we discuss a plausible emission mechanism of the xCeSZP glass as shown in Fig. 8. In the case of PL process, two emission centers are directly and individually excited. The observed emission decay of Sn^{2+} center suggests that no energy resonance between Sn^{2+} and Ce^{3+} centers existed, although local coordination field of each center has changed by increasing Ce amount. On the other hand, only emission from Sn^{2+} was observed in the case of RL excited by X-ray. Since RL of Ce^{3+} has been observed in many reports, and energy-level structure of free Ce^{3+} ion has already reported,[26] it suggests that energy relaxation path of Ce^{3+} is relatively limited because of coexistence of Sn^{2+}. Although we have also observed RL property of Ce^{3+} in ZnO-P$_2$O$_5$ glass, the intensity of emission is much weaker than that of Sn^{2+}. Compared with silicate-based Li-glass, in which Ce^{3+} is used as an emission center, it suggests that there are many killer sites in phosphate glass, and these sites prevent the effective energy transfer from the host matrix to an activation center. We assume that the observed difference of RL process between Sn^{2+} and Ce^{3+} centers is originated from those transition probabilities or these energy levels of excited states. Since the excitation energy is over the band gap, higher excited state of emission center existing at much higher energy than conventional PL process may correlate the energy transfer. From this point of view, Sn^{2+} will be a desirable emission center by more precise compositional tuning although the decay time is on the order of microseconds.

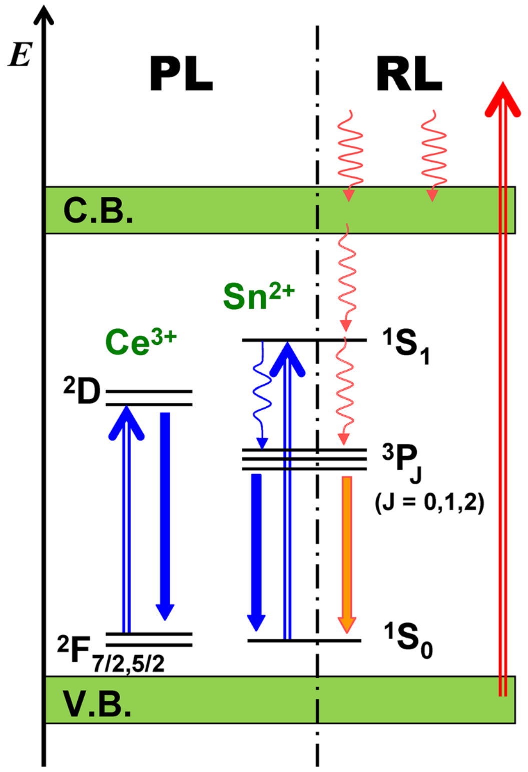

FIG. 8. Plausible emission mechanism of the xCeSZP glass.

The importance of the present study is to demonstrate energy relaxation process depending on the emission center. The present unusual approach using two parity-allowed emission centers in phosphor material suggests that energy path of these emission centers are independent, and that relaxation process of RL preferentially occurs from one center possessing the transition probability. Although the energy relaxation path in RL has not been clarified yet, examination between higher energy region (over the band gap) of matrix and the doped activator has particularly a key for the efficient emission in RL process.

IV. CONCLUSION

We have demonstrated PL and RL properties in CeSZP glasses. Peak positions of PLE and PL band of both Sn^{2+} and Ce^{3+} centers were changed with increasing amount of Ce. The PL emission decay indicates that energy relaxation paths of Ce^{3+} and Sn^{2+} are independent. In contrast to PL spectra, there was no Ce-dependence in RL spectra, and only emission of Sn^{2+} was observed by X-ray excitation. It is expected that Sn^{2+} center is preferentially activated than Ce^{3+} center by high photon energy over the band gap in the zinc phosphate glass system.

ACKNOWLEDGMENTS

This work was partially supported by the Asahi Glass Foundation, and the Kazuchika Okura Memorial Foundation, the Research Institute for Production Development, and the Collaborative Research Program of Institute for Chemical Research, Kyoto University (Grant No. 2013-62).

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