Correlation between the emission properties of Sn\(^{2+}\) center and the chemical composition of ZnO–P\(_2\)O\(_5\) glasses

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Photoluminescence (PL) properties of Sn-doped zine phosphate (Sn\(_{x}\)ZP) glasses with different chemical compositions are investigated. Sn exists only in the form of Sn\(^{2+}\) in Sn\(_{x}\)ZP glasses, which were prepared by a conventional melt-quenching method in Ar atmosphere. The glass-transition temperatures, \(T_g\), of the Sn-doped glasses are lower than that of Sn-free glasses, and the change in the \(T_g\) values of Sn-doped glasses increases with increasing ZnO amount. Since the relative ratio of 4-fold coordinated Sn\(^{2+}\) becomes higher with increasing ZnO amount, the coordination state is found to depend significantly on the network structure and not on the optical basicity of the Sn\(_{x}\)ZP glasses. The PL bandwidth, indicating the site distribution, becomes narrower as the ZnO amount increases. In addition, the PL decay lifetime in the Zn-rich glass is shorter compared to that of the P\(_2\)O\(_5\)-rich glasses, implying that the distribution of Sn\(^{2+}\) is also associated with the network structure. Thus, the network structure of the host matrix rather than the average optical basicity significantly influences the local structure of Sn\(^{2+}\) emission center.

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1. Introduction

Sn\(^{2+}\) emission center, belonging to the ns\(^2\) type emission center,\(^{1}\) is one of the fascinating activators in solid state matter, especially in oxide glasses. This is because the ns\(^2\)-type center \((n \geq 4)\) exhibits s-p parity allowed transition and these species, such as Sn\(^{2+}\), Sn\(^{3+}\), H\(_2\)O\(^6\), Ti\(^{4+}\), Pb\(^{2+}\), and Bi\(^{3+}\), have metastable valence states.\(^{1-7}\) Recently, other metastable cations such as In\(^{3+}\) and Te\(^{4+}\) have also been reported to exhibit photoluminescence (PL) properties characteristic of the ns\(^2\)-type emission center in oxide glasses.\(^{8,9}\) It is of particular importance to study the optical properties of such metastable species in amorphous materials such as random oxide networks, in order to understand their local environment. Since the ns\(^2\) type emission centers possess electrons in the outermost shell in the ground (ns\(^2\)) and excited states (ns\(^n\)p\(^l\)),\(^{1}\) the emission is strongly affected by the coordination field. Therefore, it is worthwhile to examine ns\(^2\) center-doped oxide glasses for understanding the correlation between the luminescence property and the chemical composition of the glass.

On the other hand, Sn\(^{2+}\) glasses have been also considered as an intermediate glass forming group that can act as either a network former or a network modifier.\(^{10}\) Morena reported the glass forming region of the ternary SnO–ZnO–P\(_2\)O\(_5\) glass\(^{11}\) and suggested that both SnO and ZnO act as network formers of oxide glasses. Recently, our group examined Sn\(^{2+}\)-doped oxide glasses\(^{12-17}\) and amorphous film\(^{18}\) for phosphor applications, in which Sn concentration was much smaller compared to that of the conventional SnO-containing low-melting glass. Transparent oxide glasses containing Sn\(^{2+}\) center exhibit photo-\(^{12,13,17}\) and radio-luminescences.\(^{16,17}\) Several oxide glasses are known to exhibit intense UV-excited emission comparable to crystal phosphor such as MgWO\(_4\). Several researchers have investigated the emission properties of Sn-doped oxide glasses.\(^{19-23}\) An oxidation from Sn\(^{2+}\) to Sn\(^{4+}\) was reported to occur during melting in air even in the presence of added reducing agents.\(^{12,13,15,19,20}\) This indicates that the real mechanism of luminescence is obscure in the absence of control of the atmospheric condition and/or valence states. The emission properties of the glass, especially the correlation between the emission properties and the chemical composition of the host glass, have not yet been fully understood.

The network structure of ZnO–P\(_2\)O\(_5\) glasses changes depending on the chemical composition and the main glass network forming oxide changes around the zine pyrophosphate chemical composition, according to a previous study.\(^{24}\) Since the Sn\(^{2+}\) center is affected by the local coordination state, the emission is also expected to be affected by the network structure. Moreover, the average optical basicity of the host materials might affect the emission properties of Sn\(^{2+}\) in the glass. Optical basicity is a parameter related to electron-donating capacity of oxide ions. Host matrix with a higher optical basicity can compensate positive charges with a small number of oxide ions, resulting in a low coordination number of the cations.\(^{25}\) According to previously reported values for individual compounds (P\(_2\)O\(_5\): 0.33, ZnO: 0.95),\(^{26}\) optical basicity of the host matrix increases with increase in the ZnO concentration. In the present study, we have prepared several Sn-doped ZnO–P\(_2\)O\(_5\) glasses in Ar atmosphere to examine the relationship between the luminescence properties (the local coordination state of Sn\(^{2+}\)) and the network structure.
2. Experimental

2.1 Sample preparation

The chemical composition (in mol %) of the prepared glass was 1.0SnO–xZnO–(100–x)P2O5 (Sn:xZP), with excess amounts of Sn2+ added. Following a previous method, a mixture of ZnO (99.99%) and (NH4)2HPO4 (99.0%) was initially calcined in an electric furnace at 800°C for 3 h in air. The calcined solid was then mixed with SnO (99.5%) at room temperature (r.t.) and the mixture was melted at 1100°C for 30 min in Ar atmosphere using a tubular electric furnace (Motoyama). The glass melt was quenched on a stainless steel plate at 200°C followed by annealing at the glass transition temperature (Tg) for 1 h, which was measured by differential thermal analysis (DTA). The samples were mechanically polished to obtain a mirror surface. In addition, Sn-free xZP glasses were prepared by melt quenching in air after the calcination process.

2.2 Analysis

Tg was determined with a TG8120 DTA system (Rigaku) operating at a heating rate of 10°C/min. 119Sn Mössbauer spectra were measured in conventional transmission geometry using a Ca119mSnO3 source at r.t. The valence states of the Sn atoms, reflected as peaks in the 119Sn Mössbauer spectra, were deduced by fitting the measured spectra using a standard software Normos (developed by R. A. Brand and commercially available from WissEl GmbH). 31P MAS NMR spectra were measured using an integrating sphere Quantaurus-QY (Hamamatsu Photonics) with a 280 nm LED source.

The PL and PL excitation (PLE) spectra were recorded at r.t. using a F7000 fluorescence spectrophotometer (Hitachi High-Tech.). Slits for achieving an optical resolution of 2.5 nm were used for the excitation and emission measurements. The absolute quantum efficiency (QE) of emission of the glass at r.t. was measured using an integrating sphere Quantaurus-QY (Hamamatsu Photonics). The emission decay at r.t. was measured using a Quantaurus-Tau (Hamamatsu Photonics) with a 280 nm LED source.

3. Results and discussion

3.1 Physical properties of the Sn:xZP glasses

The obtained Sn:xZP glasses were transparent in nature. Even though the obtained Sn:65ZP and Sn:70ZP glass was partially composed of crystalline Zn2P2O7, we only characterized the amorphous region in the sample. The valence state of Sn in the Sn:xZP glasses was examined, which could be the most important information in understanding our results. Figure 1 shows the 119Sn Mössbauer spectra of Sn:60ZP and 1SnO–68ZnO–31P2O5 glasses prepared in Ar atmosphere. The peaks around 2 and 4 mm s−1 correspond to Sn2+ species. The peaks for Sn4+ species are observed, indicating the absence of Sn4+ species in the glass matrix. Considering the compositional similarity between the Sn:70ZP and 1SnO–68ZnO–31P2O5 glasses, we assume that only Sn2+ species exist in our glasses prepared by melting in Ar atmosphere. Although isomer shifts of Sn2+ from these non-symmetric peaks can be calculated, no significant differences between the two spectra are observed owing to the low S/N ratio. Based on these results, we assume that the thermal, optical, and emission properties of these glasses (discussed below) depend on the local coordination state of Sn2+ species, although a clear difference in the isomer shift of Sn2+ is not observed.

Figure 2 shows the Tg of 1.0SnO–xZnO–(100–x)P2O5 (Sn:xZP) glasses. The Tg values of Sn-free glasses are also given for comparison. With an increase in the ZnO amount, the Tg of Sn:ZP glasses increases, as observed in the case of Sn-free glasses. The differences in the Tg of Sn-doped glasses and Sn-free glasses are plotted at the right side of the right axis. The difference in Tg increases with increase in the amount of ZnO, suggesting that the doped SnO significantly affects the network structure in Zn-rich glasses. The main glass network of Zn-rich glass consists of Zn–O covalent bonding, whereas that of P2O5-rich glass consists of PO4 chain network, according to a previous report. On the other hand, Morena examined the glass-forming ability of SnO is assumed to be higher than that of ZnO. Thus, SnO could substitute the ZnO units if ZnO forms the glass network structure. SnO could substitute the ZnO units if ZnO forms the main glass network. The changes in Tg with the ZnO amount suggest that SnO could be used as a probe of the glass network forming ability and a drastic decrease is observed in SnO-substituted glasses if some of SnO substitutes the main glass network. Although 31P MAS NMR spectra of Sn:xZP glasses were measured, the spectra of Sn-free and Sn-doped glasses were found to be very similar. Therefore, significant changes cannot be detected by the 31P MAS NMR analysis owing to the small compositional change, even though the PO4 network structure is changed.

Figure 3(a) shows the optical absorption spectra of Sn:xZP glasses containing various amounts of ZnO. As the absorption bands originate from the s–p transition of Sn2+ center, the values of (hν)2 plotted as a function of photon energy. Here, h, ν,
and $\alpha$ are the Planck’s constant, frequency of light, and optical absorption coefficient, respectively. We evaluated the optical absorption edge, $E_{\text{opt}}$, by extrapolating the linear portion of the $(h\nu)^{2}$ curve. Figure 3(b) gives the $E_{\text{opt}}$ of the Sn$_{x}$ZP and Sn-free xZP glasses. As shown in the figure, the optical absorption edge is red-shifted with increase in the ZnO amount and the extend of red-shifting on Sn addition is affected by the chemical composition. This suggests that the chemical composition of the ZP glass, i.e., the ratio between ZnO and P$_2$O$_5$, strongly affects the optical absorption edge. Although the energy shift in the absorption edge could depend on the average optical basicity of the Sn$_{x}$ZP glasses, this would contradict a previous report in which the substitution of alkali earth oxide (RO) for ZnO induces little changes in the optical absorption edge. Considering the previous results, we assume that the changes in the optical absorption edge could be due to a change in the glass network by SnO addition or substitution. Sn$_{x}$ZP glasses exhibit detectable differences in the optical absorption spectra, although no significant difference in the $^{31}$P NMR spectra is observed. It is possible that the sensitivity of NMR measurements is not enough for detecting these small differences. As the absorption spectra effectively reflect the local structure of the Sn$^{2+}$ center, the structural change is found to be more pronounced even with a small amount of SnO added. On the other hand, the substitution of ZnO by RO does not significantly affect the main glass network in 2.5SnO–57.5ZnO–P$_2$O$_5$ glass, whose main network consists of PO$_4$ chains. However, the glass network of Zn-rich glass, with ZnO units as the main constituent, is affected by the amount of ZnO, thereby affecting the local coordination state of the Sn$^{2+}$ center. Thus, we can conclude that the most important factor affecting the emission properties of Sn$^{2+}$ center is the local structure of Sn$^{2+}$ and not the average basicity of the glass.

3.2 Photoluminescence by UV irradiation

Figure 4 shows the PL-PLE contour mappings of the Sn$_{x}$ZP glasses. The vertical and horizontal axes represent the excitation and emission energies, respectively. The redshift of the excitation energy and a peak narrowing of the excitation and emission bands are observed, different from that of the RO-substituted SnO–ZnO–P$_2$O$_5$ glasses. Considering the previous results, we assume that the changes in the optical absorption edge could be due to a change in the glass network by SnO addition or substitution. Sn$_{x}$ZP glasses exhibit detectable differences in the optical absorption spectra, although no significant difference in the $^{31}$P NMR spectra is observed. It is possible that the sensitivity of NMR measurements is not enough for detecting these small differences. As the absorption spectra effectively reflect the local structure of the Sn$^{2+}$ center, the structural change is found to be more pronounced even with a small amount of SnO added. On the other hand, the substitution of ZnO by RO does not significantly affect the main glass network in 2.5SnO–57.5ZnO–P$_2$O$_5$ glass, whose main network consists of PO$_4$ chains. However, the glass network of Zn-rich glass, with ZnO units as the main constituent, is affected by the amount of ZnO, thereby affecting the local coordination state of the Sn$^{2+}$ center. Thus, we can conclude that the most important factor affecting the emission properties of Sn$^{2+}$ center is the local structure of Sn$^{2+}$ and not the average basicity of the glass.

Figure 5(a) shows normalized PL-PLE spectra of Sn$_{x}$ZP glasses. The shape of the excitation and emission spectral bands changes depending on the chemical composition of the glass. Figure 5(b) shows the peak energy of PL and PLE of the Sn$_{x}$ZP glasses as a function of ZnO amount. Stokes shift of the emission is also shown. With an increase in the ZnO amount, the Stokes shift decreases. It has been previously reported that the substitution of RO for ZnO does not decrease the Stokes shift. In other words, the Stokes shift cannot be attributed to the optical basicity. Thus, as long as the main phosphate network structure remains intact, the chemical composition of the glasses (i.e., concentration of doped ion and host matrix) does not affect the Stokes shift. However, as the amount of ZnO increases, the main network structure transforms from phosphate to zinc oxide. This
transition composition is known as the pyrophosphate composition (ZnO:P2O5 = 1:2).\textsuperscript{31} The main network structure component gradually changes from P2O5 to ZnO with the increase in the ZnO amount, which could be attributed to the Stokes shift and the main network structure of the glasses in our glass samples.

PLE spectra consist of minimum two excitation bands, indicating the existence of different kinds of Sn$^{2+}$ coordination states. According to a previous study, the PLE band at the higher energy could be attributed to the excitation of 2-fold Sn$^{2+}$ species\textsuperscript{30} and that at the lower energy to the 4-fold Sn$^{2+}$ species, similar to SnO. Figure 5(c) shows the ratio of the two PLE peak band areas, deconvoluted using Gaussian function, as a function of ZnO amount. The relative intensity of the 4-fold Sn$^{2+}$ increases as the ZnO amount increases. Considering the optical basicity of the glass matrix, which reflects the delocalization degree of electron at the oxygen atoms, the present result contradicts the general trend by which the host matrix possessing higher optical basicity has cations with low coordination numbers.\textsuperscript{25} On the contrary, it would be reasonable to assume that the coordination state of Sn$^{2+}$ emission center does not depend on the average optical basicity, but on the network structure, as previously suggested in the case of substituted SnO–ZnO–P2O5 glasses.\textsuperscript{30} Thus, Sn is more likely to replace the tetrahedral Zn site. Since the coordination number of Zn in zinc phosphate glass is about 4, the relative ratio of the 4-fold Sn$^{2+}$ might increase by the substitution of Zn, which is consistent with the $T_\text{g}$ results, in which the effect of SnO addition is more pronounced in Zn-rich glasses. As shown in Figs. 4 and 5(a), the width of the PL bands differs depending on the chemical composition of the host glass. In order to understand this difference quantitatively, the half width at half maximums (HWHM) values of the PL bands are plotted as a function of ZnO amount [Fig. 5(c)]. HWHM decreases with increasing the ZnO amount. A small HWHM indicates a narrow distribution of the excitation state of Sn$^{2+}$.

Figure 6(a) shows the PL decay curves of the Sn:xZP glasses. The excitation wavelength of 280 nm corresponds to 4.4 eV, which is almost the same as the observed PLE peak of Sn$^{2+}$ center. Since only Sn$^{2+}$ species exist in the glass matrix as shown in Fig. 1, the decay constant, in the order of microseconds, corresponds to the relaxation from $T_1$ to $S_0$ state of Sn$^{2+}$.\textsuperscript{11} Considering the linearity of the decay curves, the emission decay is assumed to consist of a single component. However, the slopes depend on the ZnO amount; the decay constant decreases with increase in the ZnO amount. In general, homogeneous distribution of emission center results in longer decay constants. On the contrary, if the distance among the emission centers is small, energy migration would occur among them, resulting in concentration quenching. The decrease in the decay constant suggests that the concentration quenching is locally induced in the Zn-rich glass. We assume that the Sn$^{2+}$ centers are spatially located close to the P$_4$O$_{10}$ units compared with the ZnO units owing to the electron distribution of P$_4$O$_{10}$ and ZnO units. If ZnO network is formed in the Zn-rich glass, the electronically delocalized P$_4$O$_{10}$ units (i.e., PO$_4$ or PO$_2$) could be spatially localized. The reduction in the variation of Sn$^{2+}$ site could be attributed to an increase of such independent phosphate units. In other words, the local structure of Sn$^{2+}$, i.e., the Sn$^{2+}$ site variation, varies depending on the chemical composition, in agreement with the changes in the PL band. If emission efficiency of 2-fold Sn$^{2+}$ is the same as that of the 4-fold Sn$^{2+}$ center (which has not been experimentally clarified yet), the narrowing of the emission band of Sn$^{2+}$ in ZnO-rich glasses could be attributed to the higher fraction of 4-fold Sn$^{2+}$ in the glass, which practically decreases the variation in the Sn$^{2+}$ site. In addition, the quantum efficiency of these glasses exhibit similar trends; Zn-rich glass exhibit a lower QE than that of P$_2$O$_5$-rich glass as shown in Fig. 6(b). The present results clearly indicate that the PL efficiency of Sn$^{2+}$ center depends on the local coordination state, even though all of the Sn species exist in the divalent state.

4. Summary

Sn-doped ZnO–P$_2$O$_5$ glasses were prepared by a conventional melt-quenching method and their physical and optical properties were evaluated. The network structure of host matrix depends on the local structure of Sn$^{2+}$ emission center such as the coordination state and variation of Sn$^{2+}$ sites. Sn is assumed to replace the tetrahedral Zn site. On the other hand, Sn$^{2+}$ emission center does not seem to depend significantly on the optical basicity of the host matrix.

The variation in the Sn site in the Zn-rich glass is lower compared with that in the P$_2$O$_5$-rich glass based on the PL spectra. Differences in the local structure of Sn$^{2+}$ emission center have also been suggested by the decay constant measurements. A kind of concentration quenching might be induced by a more localized distribution of Sn$^{2+}$. This could be attributed to the existence of the Sn$^{2+}$ center at the vicinity of the electronically delocalized P$_4$O$_{10}$ units, which could be spatially localized in the Zn-rich glass. Moreover, not only the valence state of Sn but also the local coordination state should be tailored for achieving high PL efficiency.

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