

Relationship between Physical Properties and Preparation Atmosphere of Manganese-doped ZnO–P₂O₅ Glasses

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Manganese-doped zinc phosphate (MnZP) glasses were prepared in Ar and air to examine the relationship between the physical properties and preparation atmosphere. The glass transition temperatures of these MnZP glasses were almost the same regardless of the preparation atmosphere. Although the absorption spectra of the 15 mol%-doped MnZP glasses prepared in different atmospheres exhibited significant differences, only small differences in the absorption tail were observed in the other MnZP glasses with lower Mn concentrations. It was found that the Mn K-edge X-ray absorption fine structure (XAFS) spectra of these glasses were also the same, indicating that the average local coordination states of Mn cations were similar in the concentration range considered. The quantum efficiency of the 15 mol%-doped MnZP glass prepared in air was lower than that of the glass prepared in Ar owing to the high absorption in the visible region of the former. It is expected that (NH₄)₂HPO₄, which is the starting material for P₂O₅, prevents the oxidation reaction of Mn²⁺ during melting in air.

1. Introduction

The physical properties of glass are affected by several factors. In glasses obtained by quenching of the supercooled liquid state, various metastable structures exist to form non-periodic network structures. The non-periodic structures are the origin of the good formability of glass, which is a major advantage for large-scale industrial production. On the other hand, the redox state of the glass melt is important for tailoring the physical properties of glasses. Since glass melted in air is inherently affected by the oxygen partial pressure, the physical properties sometimes differ from those prepared in an inert atmosphere.^(1,2) The redox state affects not only the main glass components but also the tiny amount of dopants, such as activators. Our group has reported the relationship between the valence state of tin in phosphate and borate glasses and the preparation atmosphere.^(3–5) It has also been clarified that Ce cations doped in borosilicate glasses are strongly affected by the preparation conditions.^(6–8)

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From the viewpoint of large-scale fabrication, examination of the effect of the preparation conditions on the physical properties is important, particularly for transition-metal-doped glasses, whose optical properties are markedly changed by a small amount of color centers. In this study, manganese (Mn) was selected as a transition metal element whose valence changes with the oxygen partial pressure during melting. Mn is one of the non-rare-earth luminescent centers used in phosphor applications.⁽⁹⁾ Mn cations can exist as Mn^{4+} ,^(9–12) Mn^{3+} ,⁽¹³⁾ and Mn^{2+} in crystals.^(9,10,14,15) The number of Mn^{2+} -doped materials is much larger than that of materials doped with the other species, and most papers on doped glasses have reported Mn^{2+} -doped glasses.^(16–21) So far, our group has reported on the luminescence characteristics obtained by co-doping $\text{ZnO-P}_2\text{O}_5$ glass with Sn^{2+} and Mn^{2+} .^(20,21) In the Sn^{2+} - Mn^{2+} co-doped glasses, energy transfer from the donor (Sn^{2+}) to the acceptor (Mn^{2+}) occurred with a high energy transfer rate. However, the effects of the preparation atmosphere on the optical and luminescence properties of Mn^{2+} -doped phosphate glasses without the co-doping of other donor cations have not been reported. On the other hand, although Mn cations can be doped with a higher concentration than other activators, such a highly doped system has not been studied. In this study, we evaluated the thermal, optical, and luminescence properties of Mn-doped $\text{ZnO-P}_2\text{O}_5$ glass prepared in air and Ar atmospheres. We also evaluated the valence state of Mn cations by Mn K-edge X-ray absorption fine structure (XAFS) measurement. On the basis of the obtained results, we discuss the effect of the preparation atmosphere on the optical and luminescent properties of Mn-doped phosphate glasses.

2. Materials and Methods

The manganese-doped $\text{ZnO-P}_2\text{O}_5$ (MnZP) glasses were prepared by a conventional melt-quenching method. The starting materials were ZnO , $\text{NH}_4\text{H}_2\text{PO}_4$, and MnO . The molar ratio of $\text{ZnO:P}_2\text{O}_5:\text{MnO}$ was fixed as 60:40: x , and we denote the glass composition as $x\text{MnZP}$ for a Mn concentration of x mol%. These chemicals were mixed and calcined using a Pt crucible.⁽²²⁾ The calcined sample was then melted in an electric furnace in Ar or air. The temperature and duration of glass melting were 1100 °C and 30 min, respectively. The glass melt was poured onto a stainless-steel plate to quench it, and the obtained glass was annealed at the glass transition temperature, T_g , for 1 h. The glasses were cut to $\sim 10 \times 10 \times 1$ mm³ and mechanically polished to obtain a mirror surface.

T_g of these glasses was measured by differential thermal analysis using a TG8120 thermal analyzer (Rigaku). The Mn K-edge XAFS spectra were measured at the BL01B1 beamline of SPring-8 (Hyogo, Japan). The storage ring energy was operated at 8 GeV with a typical current of 100 mA. The measurements were performed using a Si (111) double-crystal monochromator in the transmittance or fluorescence mode using a 19-SSD detector at room temperature (RT). Pellet samples for the transmittance measurements were prepared by mixing the granular sample with boron nitride. XAFS data for MnO , Mn_2O_3 , and MnO_2 were collected using the same conditions for reference. The corresponding analyses were performed using Athena software.⁽²³⁾ The PL and PL excitation (PLE) spectra were recorded at RT using an F7000 fluorescence spectrophotometer (Hitachi High-Tech, Japan). The optical absorption spectra at RT were

recorded using a U4150 UV–vis–NIR spectrometer (Hitachi High-Tech, Japan). The absolute quantum yields (QY s) of the glasses were measured using a Quantaaurus-QY integrating sphere (Hamamatsu Photonics, Japan). The error bars were ± 2 , which mainly originated from the samples. The emission decay at RT was measured using a Quantaaurus-Tau system (Hamamatsu Photonics, Japan) using white light with a band pass filter.

3. Results and Discussion

First, we measured the thermal properties of the MnZP glasses prepared in air and Ar. MnO is conventionally categorized as a network-modifying oxide (NMO) according to the classification by Sun.⁽²⁴⁾ Therefore, if the role of MnO is the same as that of other NMOs,^(25,26) T_g should decrease monotonically with increasing Mn concentration. Figure 1 shows T_g of the x MnZP glasses melted in air or Ar as a function of Mn concentration. In the MnZP glasses containing a small amount of Mn cations, T_g decreased with increasing Mn concentration up to 2 mol%. However, after 5 mol% addition, T_g increased, suggesting that the network formation in these glasses was changed. If the MnO only acts as a network modifier without changing the network formation, T_g will monotonically decrease.⁽²⁶⁾ On the other hand, with increasing MnO fraction, i.e., decreasing P_2O_5 fraction, intermediate ZnO will play a role in network formation. Although it is not clear whether MnO can act as an intermediate group⁽²⁴⁾ similarly to ZnO,⁽²⁷⁾ it is expected that the increase in T_g originated from the network change caused by MnO addition. It is notable that the effect of the preparation atmosphere on T_g was not clear. This might be due to the valence state of the Mn cation not changing significantly. To examine this hypothesis, we next measured the Mn K-edge XANES spectra.

The preparation conditions often affect the valence state of activators in glasses. Valence changes of activators in glass, which were evaluated by XANES analysis, have been reported for several luminescent glasses.^(3–8) Figures 2(a) and 2(b) depict Mn K-edge XANES spectra of the x MnZP glasses melted in Ar and air, respectively. The XANES spectra of three references, MnO, Mn_2O_3 , and MnO_2 , are also shown for comparison. The shapes of the spectra are almost the same regardless of the Mn concentration and preparation temperature. If the absorption edge energy E_0 of Mn in glasses is defined as the zero of the second derivative of the absorption edge,

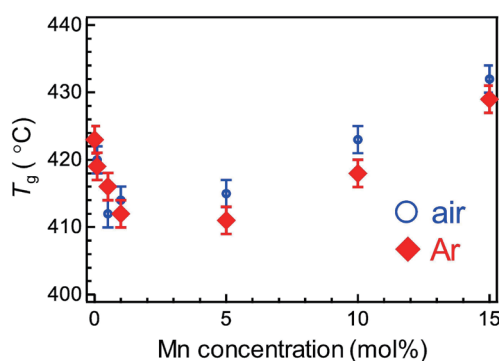


Fig. 1. (Color online) T_g of x MnZP glasses prepared in air and Ar as a function of MnO concentration.

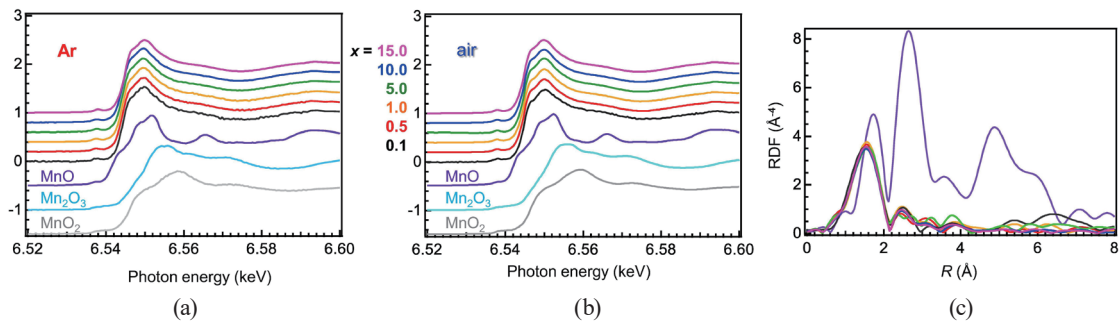


Fig. 2. (Color online) Mn K-edge XANES spectra of x Mn:ZP glasses prepared in (a) Ar and (b) air. (c) FTs of EXAFS spectra of x Mn:ZP glasses along with that of MnO.

we can conclude that most of the Mn species exist as Mn^{2+} and that marked oxidation of Mn^{2+} to higher valence states did not occur. It has been reported that ammonium phosphate, which was the starting material used to obtain P_2O_5 , affects the redox state of a glass melt, and that the reduction of the activator is preferentially induced by the residual ammonium species.⁽⁵⁾ In other words, the oxidation of Mn^{2+} in the preparation of the glass melts in air was prevented by using $(\text{NH}_4)_2\text{HPO}_4$. This suggests that there is no significant difference in the XAFS spectra between the glass melted in Ar and the one melted in air, and that almost all the Mn species exist as Mn^{2+} valence states in ZnO– P_2O_5 glasses melted in both air and Ar. This suggestion based on Mn K-edge XANES analysis is consistent with the above hypothesis based on the T_g data of these glasses. Figure 2(c) shows the Fourier transforms (FTs) of the XAFS spectra in the extended XAFS (EXAFS) region. Both the Mn–O distance and the coordination are similar regardless of the concentration and the preparation atmosphere. The structural change suggested by the T_g measurement was not observed. Thus, we assumed that the difference in T_g originated from the zinc phosphate network. Considering the octahedral coordination of Mn cations in MnO crystal, it is expected that the Mn^{2+} sites in these glasses will be octahedral.

Although the obtained x MnZP glasses were transparent, the coloration increased with increasing MnO concentration. Figure 3 shows optical absorption spectra of the x MnZP glasses melted in air (dashed lines with circles) and Ar (solid lines). The coloration of the glasses is mainly due to the absorption corresponding to the ${}^6\text{A}_1$ to ${}^4\text{A}_{1g}$ transition.^(28,29) In the case of the 0.1MnZP glass, although a small deviation of the absorption coefficient was observed at the onset of the absorption edge, the optical absorption coefficient of the MnZP glasses prepared in air was almost the same as those of the glasses prepared in Ar. On the other hand, a significant redshift of the absorption edge was observed in the 15MnZP glass prepared in air. Since the shape of the XAFS spectrum of the 15MnZP glass melted in Ar is almost the same as that of the 15MnZP glass melted in air, this drastic change owing to the Mn species was unexpected. It has been reported that manganese oxide colloids possess a broad absorption tail in the visible region.⁽³⁰⁾ We assume that the origin of the strong absorption in the near-UV region is a type of Mn cluster whose relative concentration was too low to be detected in the K-edge Mn XANES spectrum.

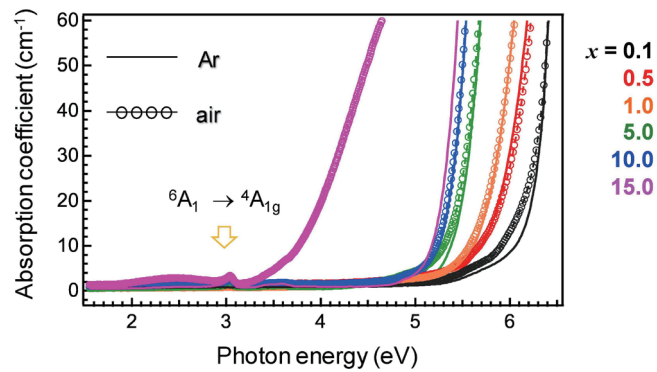


Fig. 3. (Color online) Optical absorption spectra of x MnZP glasses prepared in air and Ar.

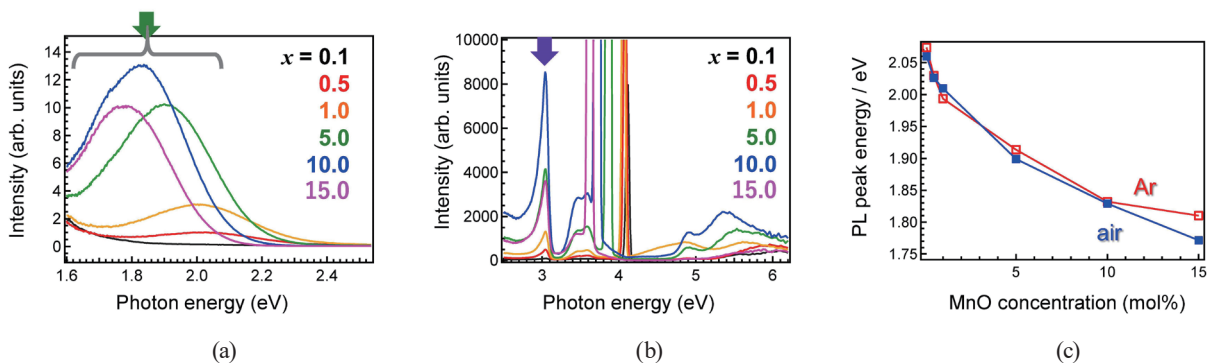


Fig. 4. (Color online) (a) PL and (b) PLE spectra of x MnZP glasses prepared in air. (c) PL peak energies of x MnZP glasses prepared in air and Ar.

For all chemical compositions, the emission intensity of the PL-PLE spectra of the x MnZP glass melted in Ar was higher than that of the glass melted in air. Figures 4(a) and 4(b) show the PL and PLE spectra of the x MnZP glasses prepared in air, respectively. The PL spectra were obtained by excitation of 3.05 eV (407 nm), whereas the PLE spectra were obtained by scanning of the peak energy of the PL spectra. In the PL spectra, the emission peak energy underwent a redshift with increasing Mn concentration. Since the absorption band of the ${}^6A_1 \rightarrow {}^4A_{1g}$ transition exists in the visible region (see Fig. 3), it is assumed that the redshift of the PL spectra was mainly due to the increase in absorption, i.e., band overlap between PL and PLE. Although the PL intensity takes a maximum at a concentration of 10 mol%, the intensity differences between the 5MnZP and 10MnZP glasses are not so large. Therefore, we conclude that concentration quenching occurred at 10 mol% and above. To compare the dependence of the PL properties on the preparation atmosphere, the PL peaks of the MnZP glasses prepared in air and Ar as a function of MnO concentration are compared in Fig. 4(c). The red emission observed from these Mn-doped glasses originated from octahedral-coordinated Mn^{2+} ,⁽⁹⁾ which was also suggested by the XAFS analysis.

To investigate the emission from Mn^{2+} centers, we measured the PL decay curves of the glasses. Figure 5(a) shows PL decay curves of the $x\text{MnZP}$ glasses melted in Ar (solid lines) and air (open circles). The excitation energy was ~ 400 nm and was filtered by a band pass filter. For all MnZP glasses, the decay curves consist of two components: a faster component (lifetime, $\tau'_{1/e}$, of microseconds) and a slower component ($\tau''_{1/e}$ of milliseconds). Considering the previous decay constants of Mn^{2+} centers in oxide crystals or oxide glasses, the decay with ms-order lifetime was due to the ${}^4\text{T}_2 \rightarrow {}^6\text{A}_1$ radiative transition, whose decay constant decreases with increasing MnO concentration. The decay constant is comparable to that previously reported in Refs. 9 and 31. However, a considerable difference between the decay curves of the Ar-prepared and air-prepared samples was observed for the 15MnZP glasses. It is expected that this difference was due to strong absorption in the visible region for the 15MnZP glass prepared in air.

Figure 5(b) shows QE values of the $x\text{MnZP}$ glasses prepared in air and Ar as a function of Mn concentration. For the MnZP glasses with Mn concentration below 10 mol%, the QE values of the MnZP glasses prepared in air are comparable to those of the glasses prepared in Ar. The QE values of these glasses are approximately 60%. It is notable that the maximum QE values of the MnZP glasses are the same for both preparation atmospheres. It is expected that residual ammonium groups after calcination affected the redox state of the glass melt to induce a reducing condition. The reducing condition is the main factor preventing the oxidation reaction of Mn^{2+} . This reducing condition resulting from the ammonium phosphate used as a starting material has also been reported for Sn-doped phosphate glass.⁽³²⁾ In the case of Sn^{2+} , it has been found that most of the Sn^{2+} was oxidized during melting even when using ammonium phosphate. Therefore, as suggested from the redox reaction, Mn oxidation is more greatly inhibited by ammonium phosphate than Sn oxidation during melting. In contrast, large degradation of the QE value was observed in the 15MnZP glass melted in air. We assume that the origin of this decrease was the strong absorption of Mn^{2+} in the visible region, which was also the origin of the faster decay shown in Fig. 5(a).

Here, we consider the optical basicity proposed by Duffy and Ingram.⁽³³⁾ Since MnO was added as an additive, the basicity was changed, especially in the more highly MnO-doped samples. Using the optical basicity of each metal oxide,⁽³⁴⁾ we calculated the Λ value of 10MnZP

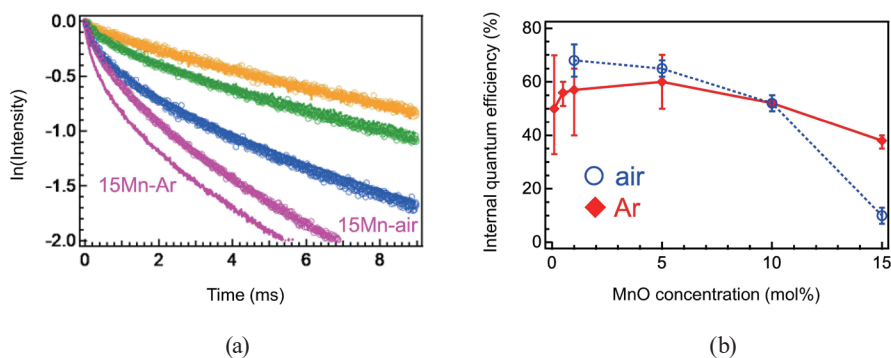


Fig. 5. (Color online) (a) PL decay curves of $x\text{MnZP}$ glasses prepared in Ar and air. (b) Internal QE values of $x\text{MnZP}$ glasses as a function of MnO concentration.

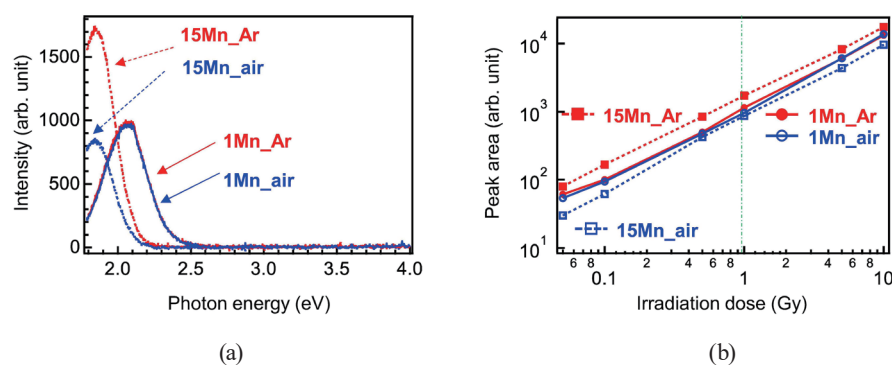


Fig. 6. (Color online) (a) X-ray-induced scintillation spectra of 1MnZP and 15MnZP glasses prepared in air and Ar. These spectra were obtained after X-ray irradiation of 1 Gy. (b) Scintillation peak areas of 1MnZP and 15MnZP glasses prepared in air and Ar. These data are plotted as a function of MnO concentration.

glass as 0.802, which is approximately 14% higher than that of the Mn-free ZP glass (0.702). Thus, the Λ value suggests that a higher valence state of Mn is more preferentially formed upon the addition of MnO.

Finally, we measured the X-ray-induced scintillation spectra of the MnZP glasses. Figure 6(a) shows the X-ray-induced scintillation spectra of the 1MnZP and 15MnZP glasses prepared in air and Ar, whose spectra were obtained after X-ray irradiation of 1 Gy. In the case of the MnZP glasses with low Mn concentrations, the scintillation intensities were almost the same regardless of the preparation atmosphere. In contrast, a significant difference was observed between the 15MnZP glasses. Although the maximum scintillation intensity was observed in both 10MnZP glasses, a large decrease in the scintillation intensity was observed in the 15MnZP glass prepared in air. These tendencies are similar to the various PL properties.

Figure 6(b) shows the scintillation peak areas of the 1MnZP and 15MnZP glasses prepared in air and Ar as a function of MnO concentration. In the case of 1MnZP glass, there is no marked difference between the peak areas of the air- and Ar-prepared samples. These scintillation data are consistent with the PL data, which confirms that the absorption property of these glasses in the visible region governs all their luminescence properties.

4. Conclusions

We have examined the optical and luminescence properties of MnZP zinc phosphate glasses prepared in air and Ar. The Mn-K edge XANES spectra of the glasses suggest that most of the Mn species exist as Mn^{2+} states regardless of the preparation atmosphere. The luminescence and absorption properties appeared to be similar in the MnZP glasses with a Mn^{2+} concentration of 10 mol% or below. In contrast, marked differences in the absorption spectrum, decay constant, and quantum efficiency were observed in the 15 mol%-doped Mn^{2+} ZP glasses. Considering the optical basicity of the host glass, it is expected that Mn cations with the valence state higher than divalent preferentially exist in Mn-rich glasses, which is one of the reasons for the coloration in the glasses doped with higher concentrations of Mn.

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