Local Structure around $\text{Mn}^{2+}$ in Phosphate Glasses

Noriyuki Wada¹, Misaki Katayama², Tomoe Sanada², Kazuhiko Ozutsumi², Kazuo Kojima²

1) Department of Materials Science and Engineering, Suzuka National College of Technology, Shiroko, Suzuka, Mie, 510-0294, Japan
2) Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga, 525-8577, Japan

Abstract
Mn K-edge X-ray absorption fine structure (XAFS) spectra of $\text{Mn}^{2+}$-doped phosphate glasses were measured. Assuming that $\text{Mn}^{2+}$ ions were octahedrally coordinated with 6 oxide ions, the Mn-O bond length was obtained by analyzing the XAFS spectra. In 60P₂O₅-35M₂O-5Al₂O₃-10MnO glasses (M: Li, Na, and K), the Mn-O bond length was almost constant, irrespective of M⁺. In 60P₂O₅-35M'₂O-5Al₂O₃-10MnO glasses (M': Ca, Zn, Sr, and Ba), the Mn-O bond length increased with increasing the M'²⁺ ionic radius in the order Zn²⁺, Ca²⁺, Sr²⁺, and Ba²⁺. In (65-x)P₂O₅-35ZnO-xAl₂O₃-10MnO glasses (x = 0-10), the Mn-O bond length for x = 0 (2.13 Å) was much longer than that for x = 1-10 (about 2.07 Å), because Al₂O₃ effects the formation of 3-dimensional phosphate network structure. In (100-y)P₂O₅-yZnO-10MnO (y = 20-60) and 65P₂O₅-35Zn-zMnO (z = 0.5-20) glasses, the Mn-O bond length changed depending on y and z, because the numbers of bridging oxygen (BO) and non-bridging oxygen (NBO) in the PO₄ groups were changed by y and z. The Mn-O bond length was the maximum of 2.13 Å in a 65P₂O₅-35ZnO-10MnO glass (y = 35 and z = 10), which consists of only PO₄ groups with two BOs and two NBOs.
1. Introduction

Recently, high-brightness light-emitting diodes (LEDs) with various colors have been developed and applied in various equipments and fields. However, there has been the problem that persons with red-region color blindness could not see a red-traffic-signal even if the luminescence intensity of a red LED is strong because the red LED with monochromatic output properties was used. In addition, most of the rare earth ions used for phosphors have been imported from China; therefore their long-term stable supply and cost jump are concerned.

Noticing that octahedrally coordinated Mn$^{2+}$ ions show a red and broad fluorescence band due to the 3d-3d ($^{4}T_{1g} \rightarrow ^{6}A_{1g}$) transitions, and that the fluorescence band is broadened by using glass host materials, we have investigated the red fluorescence properties of Mn$^{2+}$ ions in various oxide glasses. As a result, we found that the Mn$^{2+}$ ions only in the phosphate glasses showed the strong; red fluorescence, as has been reported in the metaphosphate glasses [1]. Among $60P_{2}O_{5}-35M_{2}O-5Al_{2}O_{3}-10MnO$ and $60P_{2}O_{5}-35M'O-5Al_{2}O_{3}-10MnO$ glasses (M: Li, Na, and K; M': Ca, Zn, Sr, and Ba), it was found that the Mn$^{2+}$ red fluorescence intensity in the $60P_{2}O_{5}-35ZnO-5Al_{2}O_{3}-10MnO$ glass was strongest. In $(65-x)P_{2}O_{5}-35ZnO-xAl_{2}O_{3}-10MnO$ glasses ($x = 0-10$), it was found that the Mn$^{2+}$ red fluorescence intensity of the glasses without Al$_2$O$_3$ was strong. In $(100-y)P_{2}O_{5-y}ZnO-10MnO$ and $60P_{2}O_{5}-35Zn-zMnO$ glasses ($y = 20-60$, and $z = 0.5-20$), the Mn$^{2+}$ red fluorescence intensity of $65P_{2}O_{5}-35ZnO-10MnO$ glass was strongest.

It is considered that Mn$^{2+}$ red fluorescence properties are directly influenced by the local structure of the Mn$^{2+}$ ions, because the red fluorescence are caused by the transitions of 3d electrons in the outermost shell of Mn$^{2+}$ ions. In addition, it has already been reported that the local structure around Mn$^{2+}$ ions in the borate glasses was investigated by analyzing the XAFS spectra [2]. However, in studying the glass composition dependence of the Mn$^{2+}$ local structure, phosphate glasses have not been investigated.

In this study, to reveal the glass composition dependence of the local structure around Mn$^{2+}$ ions in phosphate glasses, the Mn K-edge X-ray absorption fine structure (XAFS) spectra of various phosphate glasses were measured and the Mn-O bond length was analyzed.

2. Experimental

For measuring the XAFS spectra, $60P_{2}O_{5}-35M_{2}O-5Al_{2}O_{3}-10MnO$ (35M5A110Mn), $60P_{2}O_{5}-35M'O-5Al_{2}O_{3}-10MnO$ (35M'5A110Mn), $(65-x)P_{2}O_{5}-35ZnO-xAl_{2}O_{3}-10MnO$ (35ZnxAl110Mn), $(100-y)P_{2}O_{5-y}ZnO-10MnO$ (yZn10Mn), and $65P_{2}O_{5}-35Zn-zMnO$ (35ZnzMn) glasses (M: Li, Na, and K; M': Ca, Zn, Sr, and Ba, $x = 0-10$; $y = 20-60$; $z = 0.5-20$) were prepared by a melt-quenching method and polished. The Mn K-edge XAFS spectra of 6.0-7.5 keV were measured by the fluorescence mode using a XAFS spectrometer of a beam line BL-3 at the SR center of Ritsumeikan University. In addition, the XAFS
spectra of reference samples, MnO, MnAl₂O₄, and MnFe₂O₄, which were put on an adhesive tape, were measured by the same method. The analysis of Mn K-edge XAFS spectra for the phosphate glasses and the reference samples has been performed by using the software packages, Athena and Artemis of Ifffit, as follows: The XAFS oscillation curve, $\chi(k)$, was obtained after normalization and subtraction of the smooth background, where $k$ is the magnitude of the wave vector of the photoelectron. To obtain the radial structure functions, $|F(R)|s$, the $k^3$ weighted $\chi(k)$, $k^3\chi(k)$, was Fourier transformed over the range from 2 to 9 Å⁻¹ in $k$, where $R$ is the distance from the Mn²⁺ ion. To obtain the Mn-O bond length, $R_{\text{Mn-O}}$, the Mn-O interaction in the radial structure functions, $|F(R)|s$ for the phosphate glasses in the $R$-range of 1-2 Å (in the first shell) was curve-fitted by the nonlinear least square curve-fitting method using the first scattering path of MnO FEFF.

3. Results and discussion

3.1 Analysis of MnO, MnAl₂O₄, and MnF₂O₄

Radial structure functions, $|F(R)|s$, of reference samples, MnO, MnAl₂O₄, and MnFe₂O₄, are shown in Fig. 1. In the MnO (NaCl structure), which consists of octahedrally coordinated Mn²⁺ ions, the Mn-O interaction appeared in the region 1.29-2.15 Å, Mn-Mn interaction appeared in the region 2.15-3.20 Å, Mn-O interaction appeared in the region 3.20-3.62 Å, Mn--Mn and Mn---O interactions appeared overlappingly in the legion 3.62-4.40 Å, Mn---Mn interaction appeared in the region 4.40-5.46 Å. In the MnF₂O₄ (inverse-spinel structure), which consists of octahedrally coordinated Mn²⁺ ions, the Mn-O interaction appeared in the region 0.98-1.96 Å, Mn-Mn (or Fe(2)), Mn-Fe(1), Mn--O and Mn---O interactions appeared overlappingly in the region 2.15-3.70 Å, Mn----O and Mn-----O interactions appeared overlappingly in the region 3.70-4.55 Å, and Mn-Mn (or Fe(2)) interactions appeared overlappingly in the region 4.55-5.50 Å, where Fe(1) and Fe(2) are tetrahedrally and tetrahedrally coordinated Fe³⁺ ions, respectively. In MnAl₂O₄ (normal spinel structure), which consists of tetrahedrally coordinated Mn²⁺ ions, the Mn-O interaction appeared in the region 1.07-2.02 Å, Mn-Al, Mn--O, and Mn-Mn interactions appeared overlappingly in the region 2.30-3.68 Å, Mn---O interaction appeared in the region 3.95-4.66 Å, and Mn----O, Mn--Al, Mn-----O and Mn---Al interactions appeared overlappingly in the region 4.66-5.73 Å. In these reference samples, although the coordination
number of Mn$^{2+}$ ions in MnO and MnFe$_2$O$_4$ differs from that in MnAl$_2$O$_4$, the Mn-O interactions nevertheless appeared at the same distance from the Mn$^{2+}$ ion. Therefore, it is difficult to decide the coordination number of Mn$^{2+}$ by using the Mn-O bond length.

3.2 Mn-O bond length in 35M5Al10Mn and 35M'5Al10Mn glasses

Radial structure functions, $|F(R)|$, of 35M5Al10Mn and 35M'5Al10Mn glasses are shown in Fig. 2. In these samples, only the Mn-O interaction appeared in the region 1.07-2.15 Å. Fluorescence spectra of 35M5Al10Mn and 35M'5Al10Mn glasses are shown in Fig. 3. In these samples, only the red fluorescence band due to the 3d-3d ($^4T_{1g} \rightarrow ^6A_{1g}$) transition of Mn$^{2+}$ ions appeared at about 600 nm, and therefore it is certain that the Mn$^{2+}$ ions are octahedrally coordinated with 6 oxide ions.

Accordingly, assuming that the Mn$^{2+}$ ions are octahedrally coordinated with 6 oxide ions in a phosphate glass, the Mn-O bond length, $R_{\text{Mn-O}}$ is obtained by analyzing the radial structure function using the FEFF of MnO. The values of $R_{\text{Mn-O}}$ for the 35M5Al10Mn and 35M'5Al10Mn glasses are shown in Table 1. The $R_{\text{Mn-O}}$ of MnO is 2.18 Å, which agrees with that of a previous report [3]. In the 35M5Al10Mn glasses, the $R_{\text{Mn-O}}$ is constant to be about 2.12 Å. In the 35M'5Al10Mn glasses, the $R_{\text{Mn-O}}$ increased from 2.06 to 2.11 in the M'2+ order Zn$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$. Therefore, in the 35M5Al10Mn glasses, it is thought that the Mn$^{2+}$ ions are easily dissolved into these host glasses by themselves, because the size of MnO$_6^{10-}$ is not changed. On the other hand, in the 35M'5Al10Mn glasses, the Mn$^{2+}$ ions, of which the valence is equal to that of M'$^{2+}$ ions, are dissolved in the M'$^{2+}$ sites, and therefore the size of MnO$_6^{10-}$ increases with increasing the ionic radius of M'$^{2+}$ in the order...
Zn$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$ [4].

3.3 Mn-O bond length of $35Zn_xA1_{10}Mn$ glasses

Radial structure functions, $|F(R)|$, of $35Zn_xA1_{10}Mn$ glasses are shown in Fig. 4. For $x = 0$, the Mn-O interaction appeared in the region 1.22-2.12 Å, while for $x = 1-8$, the Mn-O interaction appeared in the region 1.07-2.05 Å. As mentioned above, the values of $R_{Mn-O}$, which were obtained by curve-fitting the Mn-O interactions, are shown in Table 2. The $R_{Mn-O}$ was 2.13 Å for $x = 0$, whereas the $R_{Mn-O}$ was about 2.07 Å for $x = 1-8$. In aluminophosphate glasses, the amount of the $Q^n$ units of PO$_4$ groups with lower $n$, where $n$ denotes the number of bridging oxygen, that is, 0, 1, 2, or 3, increases with an increase in Al$_2$O$_3$ content [5, 6]. Therefore, the amount of non-bridging oxygen increases with an increase in Al$_2$O$_3$ content. As mentioned above, the Mn$^{2+}$ ions dissolve in the Zn$^{2+}$ site, and hence the effect of MnO on glass structure is similar to that of ZnO as an intermediate oxide. Therefore, on the basis of the report that the change of $Q^n$ units in $(100-y')$PO$_5$-$y'ZnO$ glasses [7], $35Zn10Mn$ glass consists of only $Q^2$ units. In the $Zn_xA1_{10}Mn$ glasses, with increasing $x$, the amount of $Q^2$ units decreased and the amount of $Q^1$ units increased. However, it is difficult that the significant change of $R_{Mn-O}$ due to the small addition of Al$_2$O$_3$ is explained by the gradual changes in the amount of $Q^2$ and $Q^1$ units. It has been reported that PO$_4$ groups form into the 2-dimensional network structure in a phosphate glass and into the 3-dimensional network structure in an aluminophosphate glass [8]. This is because that Al$_2$O$_3$ effects the formation of 3-dimensional phosphate network structure because of incorporating an AlO$_4$, AlO$_5$, or AlO$_6$ group into a space among the PO$_4$ groups. Consequently, in the $35Zn_xA1_{10}Mn$ glasses, it is thought that the $R_{Mn-O}$ of $35Zn10Mn$ glass ($x = 0$) was much longer than that of $35Zn_xA1_{10}Mn$ glasses ($x = 1-10$) because of the difference in the phosphate network structure.

3.4 Mn-O bond length of $yZn10Mn$ glasses

Radial structure functions, $|F(R)|$, of $yZn10Mn$ glasses are shown in Fig. 5. The Mn-O interaction appeared in the region 1.07-2.18 Å. The glass composition dependence on $R_{Mn-O}$, which was obtained by curve-fitting as mentioned above, is shown in Fig. 6. The $R_{Mn-O}$ values

![Fig. 4. Radial structure functions, $|F(R)|$, of $35Zn_xA1_{10}Mn$ glasses.](image.png)

Table 2. Mn-O bond length, $R_{Mn-O}$ of $35Zn_xA1_{10}Mn$ glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{Mn-O}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>35Zn10Mn</td>
<td>2.13</td>
</tr>
<tr>
<td>35Zn1A10Mn</td>
<td>2.08</td>
</tr>
<tr>
<td>35Zn2A10Mn</td>
<td>2.07</td>
</tr>
<tr>
<td>35Zn4A10Mn</td>
<td>2.08</td>
</tr>
<tr>
<td>35Zn5A10Mn</td>
<td>2.08</td>
</tr>
<tr>
<td>35Zn6A10Mn</td>
<td>2.05</td>
</tr>
<tr>
<td>35Zn8A10Mn</td>
<td>2.08</td>
</tr>
<tr>
<td>35Zn10A10Mn</td>
<td>2.06</td>
</tr>
</tbody>
</table>
for \( y = 35 \) and 60 show the maximum of 2.13 and 2.12 Å, respectively, and the \( R_{\text{Mn-O}} \) for \( y = 55 \) has the minimum of 2.06 Å. In \((100-y')P_2O_5-y'ZnO\) glasses, the Q\(^6\) units of the PO\(_4\) groups have already been analyzed using \(^{31}\text{P}\) MAS NMR as follows [7]: For \( 35 \leq y' < 40 \), the PO\(_4\) groups are composed of Q\(^2\) and Q\(^3\) units. In addition, with increasing \( y' \), the amount of Q\(^2\) units increases and that of Q\(^3\) units decreases. For \( y' = 40 \), all the PO\(_4\) groups have Q\(^2\) units. For \( 40 < y' < 65 \), the PO\(_4\) groups consist of both Q\(^1\) and Q\(^2\) units, and the amount of Q\(^1\) units nearly equals to that of Q\(^2\) units at \( y' \) of 60. All the PO\(_4\) groups have Q\(^1\) units for \( y' = 65 \). For \( 65 < y' \leq 70 \), the PO\(_4\) groups consist of Q\(^0\) units. With increasing \( y' \), the amount of Q\(^0\) units increases and that of Q\(^1\) units decreases. As mentioned above, the effect of MnO on glass structure is similar to that of ZnO, because the Mn\(^{2+}\) ions dissolve in the Zn\(^{2+}\) site in the \( yZn10Mn \) glasses. Therefore, it is supposed that the structures of the \( yZn10Mn \) glasses for \( y = 35, 55, \) and 60 are similar to those of the \((100-y')P_2O_5-y'ZnO\) glasses for \( y' = 41, 59, \) and 64, respectively. Consequently, it is found that the \( R_{\text{Mn-O}} \) is the maximum in the phosphate glass consisting of either Q\(^1\) or Q\(^2\) units, and that the \( R_{\text{Mn-O}} \) is the minimum in the phosphate glass consisting of the same amount of Q\(^1\) and Q\(^2\) units.

### 3.5 Mn-O bond length of 35Zn\(_z\)Mn glasses

Radial structure functions, \( |F(R)|s \), of 35Zn\(_z\)Mn glasses are shown in Fig. 7. The Mn-O interaction appeared in the region 0.98-2.18 Å. The MnO addition dependence on \( R_{\text{Mn-O}} \), which was obtained by curve-fitting as mentioned above, is shown in Fig. 8. The \( R_{\text{Mn-O}} \) increases with increasing \( z \) from 0.1 to 10, and has the maximum at \( z = 10 \), and the decreases with the increasing \( z \) from 10 to 20. As mentioned above, the effect of MnO on glass structure is similar to that of ZnO, and therefore the structures of the 35Zn\(_z\)Mn glasses (0.1 \( \leq z < 10 \)) are corresponding to those of the \((100-y')P_2O_5-y'\)ZnO glasses (35 \( \leq y' < 41 \)) [7]. The PO\(_4\)
groups form $Q^2$ and $Q^3$ units, and with increasing $z$, the amount of $Q^2$ units increases and that of $Q^3$ units decreases. The structure of 35Zn10Mn glass is similar to that of 59P$_2$O$_5$-41ZnO glass, and hence the PO$_4$ groups consist of $Q^2$ units. The structures of the 35Zn$z$Mn glasses ($10 < z \leq 20$) are corresponding to those of the $(100-\gamma')P_2O_5\gamma'ZnO$ glasses ($35 \leq \gamma' < 41$), and the PO$_4$ groups consist of $Q^1$ and $Q^2$ units, and with increasing $z$, the amount of $Q^1$ units increases and that of $Q^2$ units decreases. Consequently, the $R_{Mn-O}$ has the maximum in 35Zn10Mn, where the PO$_4$ groups form only $Q^2$ units.

4. Conclusion
In the 60P$_2$O$_5$-35M$_2$O-5Al$_2$O$_3$ glasses, where the Mn$^{2+}$ ions are easily dissolved by themselves, and therefore, the Mn-O bond length of the MnO$_{6}^{10-}$ groups was constant to be about 2.12 Å. On the other hand, in the 60P$_2$O$_5$-35M$'$_O-5Al$_2$O$_3$-10MnO glasses, the Mn-O bond length of MnO$_{6}^{10-}$ increased with increasing the ionic radius of M$^{2+}$ in the order Zn$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, and Ba$^{2+}$, since the Mn$^{2+}$ ions, of which the valence was equal to that of M$^{2+}$ ions, were dissolved in the M$^{2+}$ sites. In the 60P$_2$O$_5$-35ZnO-xAl$_2$O$_3$-10MnO glasses, Al$_2$O$_3$ effects the formation of 3-dimensional phosphate network structure; the Mn-O bond lengths of MnO$_{6}^{10-}$ groups were 2.13 and 2.07 Å without and with addition of Al$_2$O$_3$, respectively. In the $(100-\gamma)P_2O_5\gammaZnO$-10MnO and 65P$_2$O$_5$-35ZnO-zMnO glasses, the effect of MnO on glass structure is similar to that of ZnO, because the Mn$^{2+}$ ions dissolve in the Zn$^{2+}$ site in the $yZn10Mn$ glasses as mentioned above, and therefore it was found that the Mn-O bond length was changed, because the $Q^n$ unit ratio of the PO$_4$ groups was changed by mole fractions of $y$ and $z$. That is to say, for $y = 35$ and $z = 10$, the $Q^n$ units of the PO$_4$ groups were only $Q^2$ units, and the Mn-O bond length of the MnO$_{6}^{10-}$ groups was the maximum of 2.13 Å. For $y = 60$, the PO$_4$ groups consisted of only $Q^1$ units, and the Mn-O bond length was the maximum of 2.12 Å. For $y = 55$, the amount of $Q^1$ units was nearly equal to that of $Q^2$, and the Mn-O bond
length was the minimum of 2.06 Å.

References