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

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Abstract

Mn K-edge X-ray absorption fine structure (XAFS) spectra of Mn^{2+}-doped phosphate glasses were measured. Assuming that Mn^{2+} ions were octahedrally coordinated with 6 oxide ions, the Mn-O bond length was obtained by analyzing the XAFS spectra. In $60P_2O_5$-$35M_2O$-$5Al_2O_3$-10MnO glasses (M: Li, Na, and K), the Mn-O bond length was almost constant, irrespective of M^+. In $60P_2O_5$-35M'O-$5Al_2O_3$-10MnO glasses (M': Ca, Zn, Sr, and Ba), the Mn-O bond length increased with increasing the M'^{2+} ionic radius in the order Zn^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}. In (65-*x*)P_2O_5-35ZnO-*x*Al_2O_3-10MnO 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 Al_2O_3 effects the formation of 3-dimensional phosphate network structure. In (100-*y*)P_2O_5-*y*ZnO-10MnO (*y* = 20-60) and $65P_2O_5$-35Zn-*z*MnO (*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 PO_4 groups were changed by *y* and *z*. The Mn-O bond length was the maximum of 2.13 Å in a $65P_2O_5$-35ZnO-10MnO glass (*y* = 35 and *z* = 10), which consists of only PO_4 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 ($^4T_{1g} \rightarrow {}^6A_{1g}$) 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 $60P_2O_5$-$35M_2O$-$5Al_2O_3$-10MnO and $60P_2O_5$-35M'O-$5Al_2O_3$-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 $60P_2O_5$-35ZnO-$5Al_2O_3$-10MnO glass was strongest. In (65-*x*)P_2O_5-35ZnO-*x*Al_2O_3-10MnO glasses (*x* = 0-10), it was found that the Mn^{2+} red fluorescence intensity of the glasses without Al_2O_3 was strong. In (100-*y*)P_2O_5-*y*ZnO-10MnO and $60P_2O_5$-35Zn-*z*MnO glasses (*y* = 20-60, and *z* = 0.5-20), the Mn^{2+} red fluorescence intensity of $65P_2O_5$-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, $60P_2O_5$-$35M_2O$-$5Al_2O_3$-10MnO (35M5Al10Mn), $60P_2O_5$-35M'O-$5Al_2O_3$-10MnO (35M'5Al10Mn), (65-*x*)P_2O_5-35ZnO-*x*Al_2O_3-10MnO (35Zn*x*Al10Mn), (100-*y*)P_2O_5-*y*ZnO-10MnO (*y*Zn10Mn), and $65P_2O_5$-35Zn-*z*MnO (35Zn*z*Mn) 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, $MnAl_2O_4$, and $MnFe_2O_4$, 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 Ifeffit, 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 Mn^{2+} ion. To obtain the Mn-O bond length, $R_{Mn\text{-}O}$, 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, $MnAl_2O_4$, and MnF_2O_4

Radial structure functions, $|F(R)|$s, of reference samples, MnO, $MnAl_2O_4$, and $MnFe_2O_4$, are shown in Fig. 1. In the MnO (NaCl structure), which consists of octahedrally coordinated Mn^{2+} 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 MnF_2O_4 (inverse-spinel structure), which consists of octahedrally coordinated Mn^{2+} 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 Fe^{3+} ions, respectively. In $MnAl_2O_4$ (normal spinel structure), which consists of tetrahedrally coordinated Mn^{2+} 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

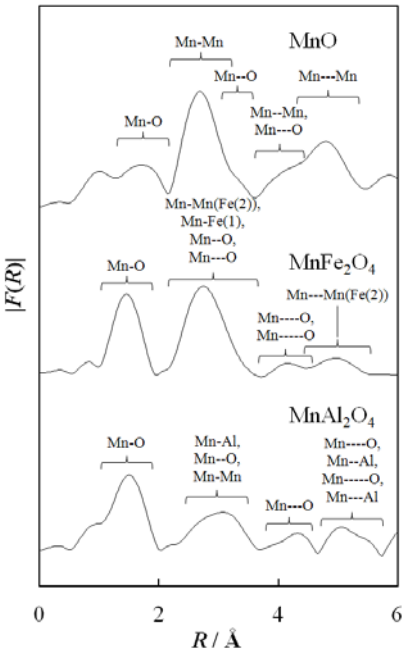

Fig. 1. Radial structure functions, $|F(R)|$s, for the reference samples, MnO, $MnAl_2O_4$, and $MnFe_2O_4$.

number of Mn^{2+} ions in MnO and $MnFe_2O_4$ differs from that in $MnAl_2O_4$, 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, $|F(R)|$s, 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, $R_{Mn\text{-}O}$ is obtained by analyzing the radial structure function using the FEFF of MnO. The values of $R_{Mn\text{-}O}$ for the 35M5Al10Mn and 35M'5Al10Mn glasses are shown in Table 1. The $R_{Mn\text{-}O}$ of MnO is 2.18 Å, which agrees with that of a previous report [3]. In the 35M5Al10Mn glasses, the $R_{Mn\text{-}O}$ is constant to be about 2.12 Å. In the 35M'5Al10Mn glasses, the $R_{Mn\text{-}O}$ 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

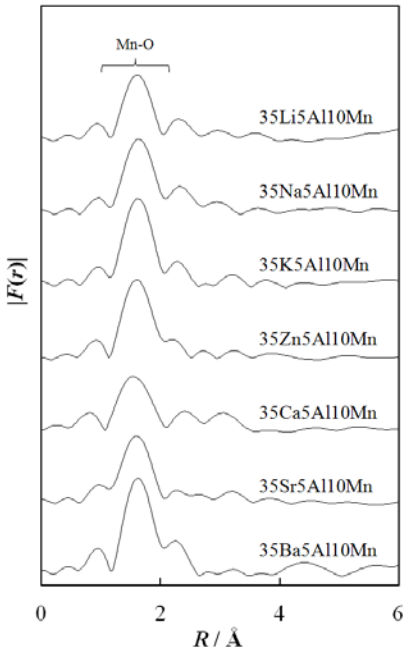

Fig. 2. Radial structure functions, $|F(R)|$s, of 35M5Al10Mn and 35M'5Al10Mn glasses.

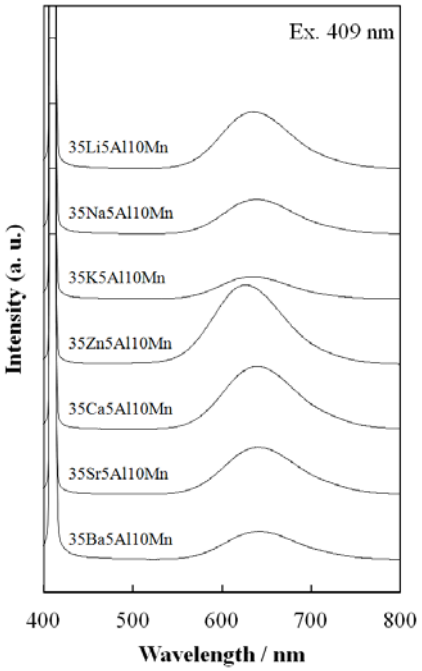

Fig. 3. Fluorescence spectra of 35M10Al10Mn and 35M'10Al10Mn glasses under excitation of 409 nm.

Table 1. Mn-O bond length, $R_{Mn\text{-}O}$ of 35M10Al10Mn and 35M'10Al10Mn glasses.

Sample	$R_{Mn\text{-}O}$ / Å
35Li5Al10Mn	2.12
35Na5Al10Mn	2.13
35K5Al10Mn	2.11
35Zn5Al10Mn	2.06
35Ca5Al10Mn	2.08
35Sr5Al10Mn	2.10
35Ba5Al10Mn	2.11

Zn^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+} [4].

3.3 Mn-O bond length of 35Zn*x*Al10Mn glasses

Radial structure functions, |*F*(*R*)|s, of 35Zn*x*Al10Mn 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 $R_{Mn\text{-}O}$, which were obtained by curve-fitting the Mn-O interactions, are shown in Table 2. The $R_{Mn\text{-}O}$ was 2.13 Å for *x* = 0, whereas the $R_{Mn\text{-}O}$ 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_2O_3 content [5, 6]. Therefore, the amount of non-bridging oxygen increases with an increase in Al_2O_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*')P_2O_5-*y*'ZnO glasses [7], 35Zn10Mn glass consists of only Q^2 units. In the Zn*x*Al10Mn 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 $R_{Mn\text{-}O}$ due to the small addition of Al_2O_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_2O_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*x*Al10Mn glasses, it is thought that the $R_{Mn\text{-}O}$ of 35Zn10Mn glass (*x* = 0) was much longer than that of 35Zn*x*Al10Mn glasses (*x* = 1-10) because of the difference in the phosphate network structure.

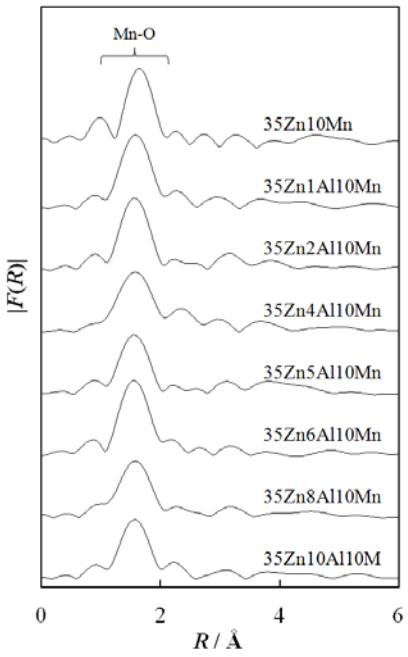

Fig. 4. Radial structure functions, |*F*(*R*)|s, of 35Zn*x*Al10Mn glasses.

Table 2. Mn-O bond length, $R_{Mn\text{-}O}$ of 35Zn*x*Al10Mn glasses.

Sample	$R_{Mn\text{-}O}$ / Å
35Zn10Mn	2.13
35Zn1Al10Mn	2.08
35Zn2Al10Mn	2.07
35Zn4Al10Mn	2.08
35Zn5Al10Mn	2.08
35Zn6Al10Mn	2.05
35Zn8Al10Mn	2.08
35Zn10Al10Mn	2.06

3.4 Mn-O bond length of *y*Zn10Mn glasses

Radial structure functions, |*F*(*R*)|s, of *y*Zn10Mn glasses are shown in Fig. 5. The Mn-O interaction appeared in the region 1.07-2.18 Å. The glass composition dependence on $R_{Mn\text{-}O}$, which was obtained by curve-fitting as mentioned above, is shown in Fig. 6. The $R_{Mn\text{-}O}$ values

for y = 35 and 60 show the maximum of 2.13 and 2.12 Å, respectively, and the $R_{Mn\text{-}O}$ for y = 55 has the minimum of 2.06 Å. In (100-y')P_2O_5-y' ZnO glasses, the Q^n units of the PO_4 groups have already been analyzed using ^{31}P MAS NMR as follows [7]: For 35 ≦ y' < 40, the PO_4 groups are composed of Q^2 and Q^3 units. In addition, with increasing of 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' ≦ 70, the PO_4 groups form Q^1 and 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 $R_{Mn\text{-}O}$ is the maximum in the phosphate glass consisting of either Q^1 or Q^2 units, and that the $R_{Mn\text{-}O}$ is the minimum in the phosphate glass consisting of the same amount of Q^1 and Q^2 units.

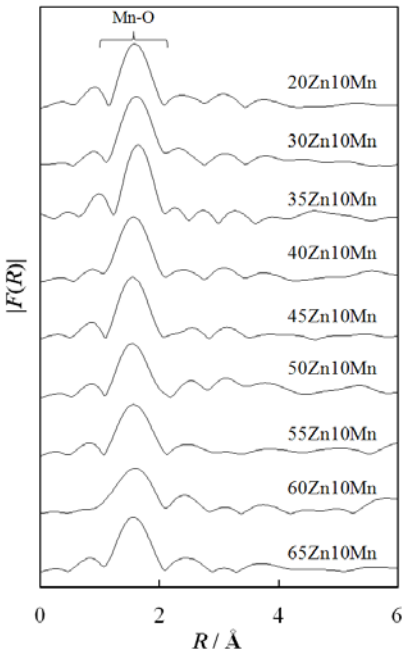

Fig. 5. Radial structure functions, |F(R)|s, of yZn10Mn glasses.

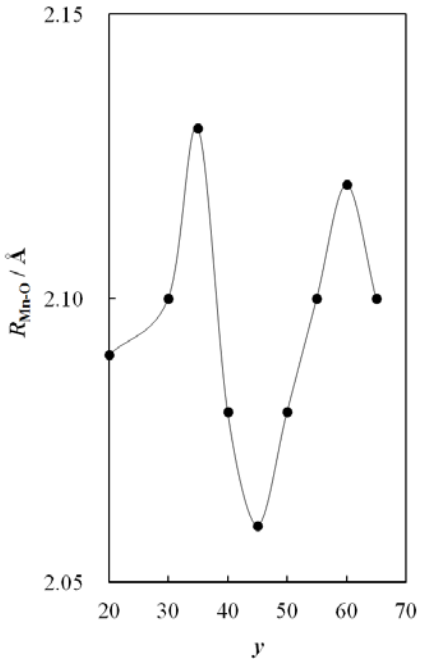

Fig. 6. Glass composition dependence on $R_{Mn\text{-}O}$ in yZn10Mn glasses.

3.5 Mn-O bond length of 35ZnzMn glasses

Radial structure functions, |F(R)|s, of 35ZnzMn glasses are shown in Fig. 7. The Mn-O interaction appeared in the region 0.98-2.18 Å. The MnO addition dependence on $R_{Mn\text{-}O}$, which was obtained by curve-fitting as mentioned above, is shown in Fig. 8. The $R_{Mn\text{-}O}$ 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 35ZnzMn glasses (0.1 ≦ z < 10) are corresponding to those of the (100-y')P_2O_5-y'ZnO glasses (35 ≦ 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 $59P_2O_5$-41ZnO glass, and hence the PO_4 groups consist of Q^2 units. The structures of the 35ZnzMn glasses ($10 < z \leqq 20$) are corresponding to those of the (100-*y'*)P_2O_5-*y'*ZnO glasses ($35 \leqq y' < 41$), 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 $R_{Mn\text{-}O}$ has the maximum in 35Zn10Mn, where the PO_4 groups form only Q^2 units.

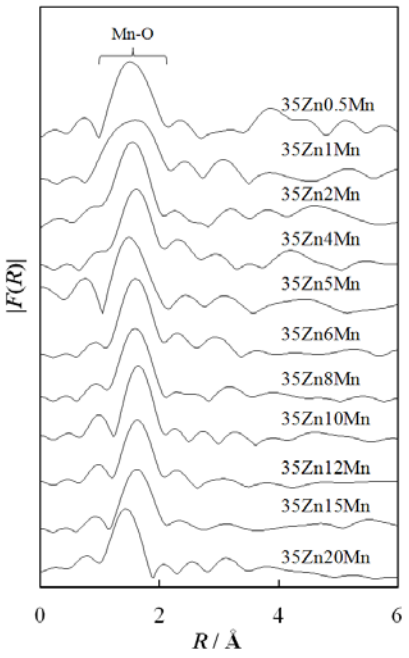

Fig. 7. Radial structure functions, $|F(R)|$s, of 35ZnzMn glasses.

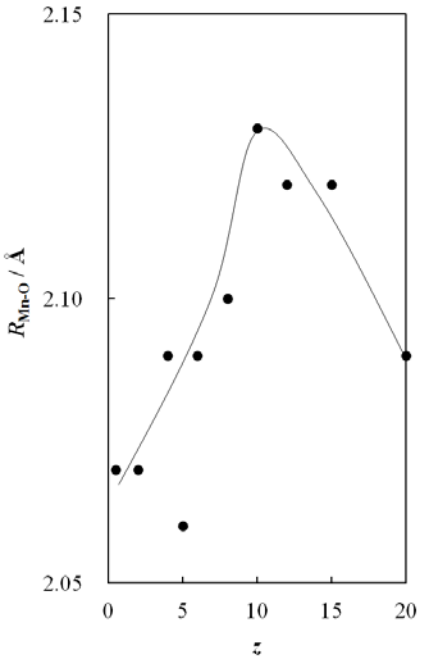

Fig. 8. MnO addition dependence on $R_{Mn\text{-}O}$ in 35ZnzMn glasses.

4. Conclusion

In the $60P_2O_5$-$35M_2O$-$5Al_2O_3$ 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 $60P_2O_5$-35M'O-$5Al_2O_3$-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 $60P_2O_5$-35ZnO-*x*Al_2O_3-10MnO glasses, Al_2O_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_2O_3. respectively. In the (100-*y*)P_2O_5-*y*ZnO-10MnO and $65P_2O_5$-35ZnO-*z*MnO 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 *y*Zn10Mn 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.

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