Mn-O bond length in oxide glasses

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1. Introduction

We have investigated the red fluorescence properties of Mn^{2+} ions in the borate, silicate, and phosphate glasses to produce an optimum red phosphor for red and broad LED. As a result, the borate and silicate glasses were opaque with the MnO addition of more than 1 mol% because of absorption of Mn^{2+} ions, and a red fluorescence band due to octahedral Mn^{2+} ions showed maximum intensity with the MnO addition of less than 1 mol%. On the other hand, the phosphate glasses were even transparent with the MnO addition of 20 mol%, and the intensity of the red fluorescence was the strongest with the MnO addition of 10 mol%.

In this study, K-edge XAFS spectra of Mn^{2+} ions in borate, silicate, and phosphate glasses were measured, and the glass composition dependence of the Mn-O bond length obtained by analyzing the XAFS spectra, was investigated.

2. Experimental

To obtain samples for measuring XAFS spectra, $70B_2O_3$-$30M_2O$-10MnO (BM), $70B_2O_3$-30M'O-10MnO (BM'), $60SiO_2$-$40M_2O$-10MnO (SiM), $60SiO_2$-$20M_2O$-20M'O-10MnO (SIMM'), $60P_2O_5$-$35M_2O$-$5Al_2O_3$-10MnO (PMAl), and $60P_2O_5$-35M'O-$5Al_2O_3$-10MnO (PM'Al) glasses (M: Li, Na, and K, M': Ca, Zn, Sr, and Ba) were prepared by melt-quenching method and polished. In addition, a reference sample of MnO powder was put on an adhesive tape. The Mn K-edge XAFS spectra of 6.0-7.6 keV were measured by the fluorescence mode using a XAFS spectrometer of a beam line BL-3 at the SR center of Ritsumeikan University. To obtain the Mn-O bond length, $R_{\mathrm{Mn\text{-}O}}$, Mn K-edge XAFS spectra for the glass and reference samples have been analyzed by using the software of Athena and Artemis.

3. Results and Discussion

For MnO, and Mn^{2+}-doped borate, silicate, and phosphate glasses, radial structure functions, $|F(R)|$s, are shown in Fig. 1. In the MnO, which consists of octahedrally coordinated Mn^{2+}

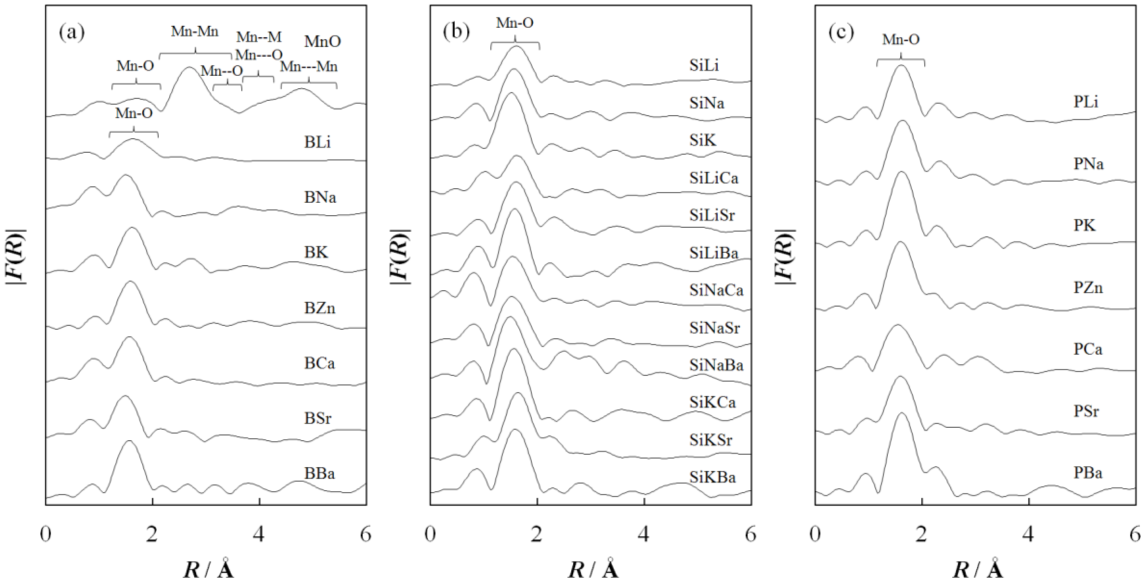

Fig. 1. Radial structure functions, |*F*(*R*)|s, for (a) MnO and Mn^{2+}-doped borate glasses, (b) silicate, glasses and (c) phosphate glasses.

ions to form sodium chloride structure, the interactions of Mn-O, Mn-Mn, Mn--O, Mn--Mn and Mn---O, and Mn---Mn appeared in the *R* regions of 1.29-2.15, 2.15-3.20, 3.20-3.62, 3.62-4.40, and 4.40-5.46 Å, respectively. In the borate, silicate, and phosphate glasses containing octahedrally coordinated Mn^{2+} ions, only the Mn-O interaction appeared in the *R* region of 1.00-2.20 Å. The Mn-O bond lengths, $R_{\text{Mn-O}}$s were obtained by analyzing radial structure functions, |*F*(*R*)|s using the ab-initio multi-scattering calculation cord FEFF, are shown in Table 1. The $R_{\text{Mn-O}}$ value of MnO was 2.23 Å. In the BM, SiM, SiMSr, and SiMBa glasses, the $R_{\text{Mn-O}}$ had the minimum values of 2.02, 2.05, 2.05, and 2.03 Å for M = Na, respectively. The $R_{\text{Mn-O}}$ value in the BM' glasses showed a minimum of 2.02 Å for M' = Sr. In the SiMCa glasses, the $R_{\text{Mn-O}}$ value decreased from 2.11 to 2.04 Å with increasing the size of M^+ ions. In the phosphate glasses, the $R_{\text{Mn-O}}$ value for the PMAl glasses was constant at about 2.12 Å regardless of M^+ ions, and the $R_{\text{Mn-O}}$ value for the PM'Al glasses increased from 2.06 to 2.11 Å with increasing the size of M'^{2+} ions.

Table 1. Mn-O bond length, $R_{\text{Mn-O}}$ of borate, silicate and phosphate glasses.

Sample name	$r_{\text{Mn-O}}$ / Å
MnO	2.23
BLi	2.12
BNa	2.02
BK	2.10
BZn	2.08
BCa	2.07
BSr	2.02
BBa	2.05
SiLi	2.09
SiNa	2.05
SiK	2.14
SiLiCa	2.11
SiNaCa	2.06
SiKCa	2.04
SiLiSr	2.09
SiNaSr	2.05
SiKSr	2.07
SiLiBa	2.06
SiNaBa	2.03
SiKBa	2.06
PLiAl	2.12
PNaAl	2.13
PKAl	2.12
PZnAl	2.06
PCaAl	2.08
PSrAl	2.10
PBaAl	2.11