Modification of the Network Structure in Multicomponent Oxide Glasses by Metal Ions

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Molecular dynamics simulations based on an ionic potential model are applied to elucidate modification processes in the network structures of representative oxide glasses (B_2O_3, SiO_2, GeO_2) caused by doped sodium oxide. The validity of the simulations is established through extensive comparison with available neutron-scattering data. The present model characterized only by the atomic charges and sizes is successful in differentiating the three glasses as regards the network modification.
Key words: oxide glass, network modification, medium-range order, molecular dynamics, neutron scattering

1. INTRODUCTION

The network structure of typical monolithic oxides such as B_2O_3, SiO_2 and GeO_2 consists of basic building units in which the network-forming cations are threefold or fourfold coordinated by oxygen ions (triangle for B_2O_3; tetrahedron for SiO_2 and GeO_2). The glassy structure is ascribed to disordered connection of those basic units [1]. Medium-range order extending over the nearest-neighbor distances emerges as a result of structural correlations among the units [2]. The first sharp diffraction peak (FSDP) in the static structure factor reflects the medium-range order in the glassy network. A wide variety of complex glassy materials are synthesized, very often with novel physical properties far beyond our expectation, by controlling the medium-range order through doping of metal ions. A slight amount of impurities in the monolithic glasses can drastically change their material characteristics.

A number of experiments on the structural properties of glasses have been carried out by means of various kinds of probes such as x-ray, neutron, and NMR [3]. However one has established no unified point of view on the glassy structures at an atomic level. The purpose of the present study is thereby to elucidate modifications of the network structures of the three representative oxide glasses caused by incorporation of Na_2O through molecular dynamics (MD) simulations on a same footing. To this end interatomic interactions used in the simulations should be as simple as possible. Here we adopt a Born-Huggin-Mayer potential containing only electric charges and steric radii as disposable parameters. Comparison with neutron scattering experiments [4-6] demonstrates essential features of the structural properties of the glasses are reproduced even with such a primitive ionic model.

A doped metal ion has two possible roles as a network modifier in the glassy networks. The one is to promote structural change of the building units to polyhedra with higher coordination number, leading to increase of the network coherence (network-decoration process). The other is to terminate connection of the units associated by formation of non-bridging oxygen (network-termination process). The MD simulations

clarify which role the metal ion plays in a given multicomponent glass.

2. MOLECULAR DYNAMICS SIMULATIONS

The formulae for the glasses studied here are summarized as $(Na_2O)_x(B_2O_3)_{1-x}$, $(Na_2O)_x(SiO_2)_{1-x}$, and $(Na_2O)_x(GeO_2)_{1-x}$. The Born-Mayer-Huggins potential for those glasses consists of an attractive or repulsive Coulomb part and a steep repulsive part:

$$\phi_{ij}(r) = \frac{Z_i Z_j e^2}{r} + \left(1 + \frac{Z_i}{\xi_i} + \frac{Z_j}{\xi_j}\right) b \exp\left(\frac{\sigma_i + \sigma_j - r}{\rho}\right). \quad (1)$$

The repulsive parameters b and ρ, taken as 0.338×10^{-19} J and 0.026 nm respectively, are common for all species of atoms investigated here. The remaining parameters are listed in Table 1; the size of Ge has been newly determined. This model has been extensively used to describe various oxide glasses [7, 8]. More accurate potentials with three-body terms have been worked out for each of the representative glasses; e.g., see Refs. 9 and 10 for SiO_2 and Ref. 11 for B_2O_3. We will see later that the present simple approach is still valuable to understand complicated structural properties of multicomponent oxide glasses in a *systematic* and *unified* way, that is, in terms of the atomic charges and sizes.

Table 1. Potential parameters in Eq. (1)

Atoms	Z_i	ξ_i	σ_i (nm)
B	+3	2	0.074
Si	+4	8	0.113
Ge	+4	18	0.127
O	−2	8	0.142
Na	+1	8	0.117

The size of a cubic MD box were determined from the experimental value of number density n for each glass with a number of MD particles centered around 650. The long-range nature of the Coulomb term in Eq. (1) was treated using the Ewald method in conjunction
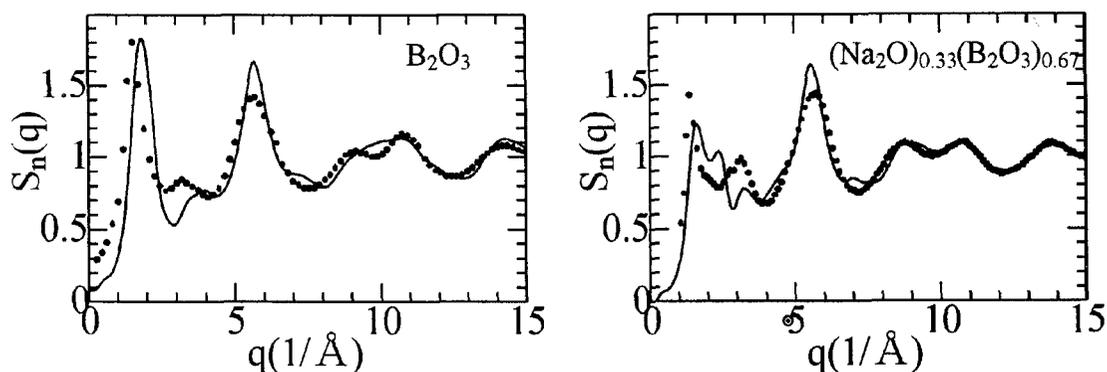
Fig. 1. Neutron static structure factor for monolithic and Na_2O-doped borate glasses at room temperature. The solid lines and dots show the MD and experimental results [6], respectively.
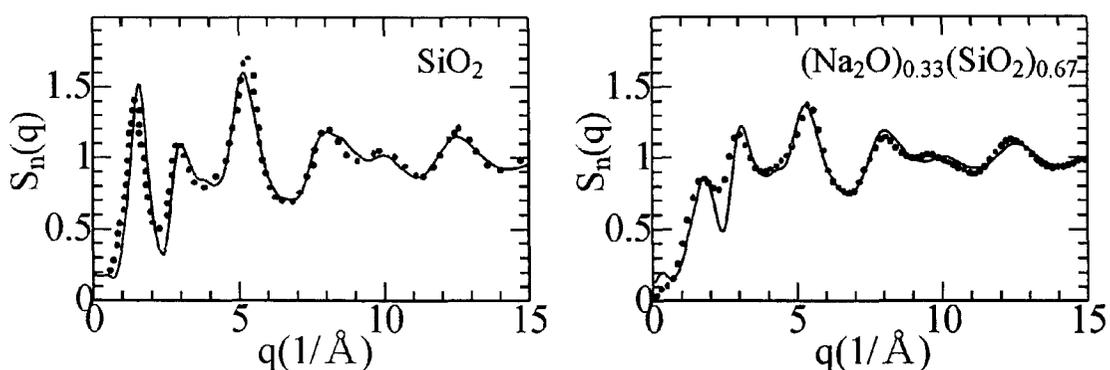
Fig. 2. Same as Fig. 1, but for silicate glasses. The experimental results are cited from Ref. 4.
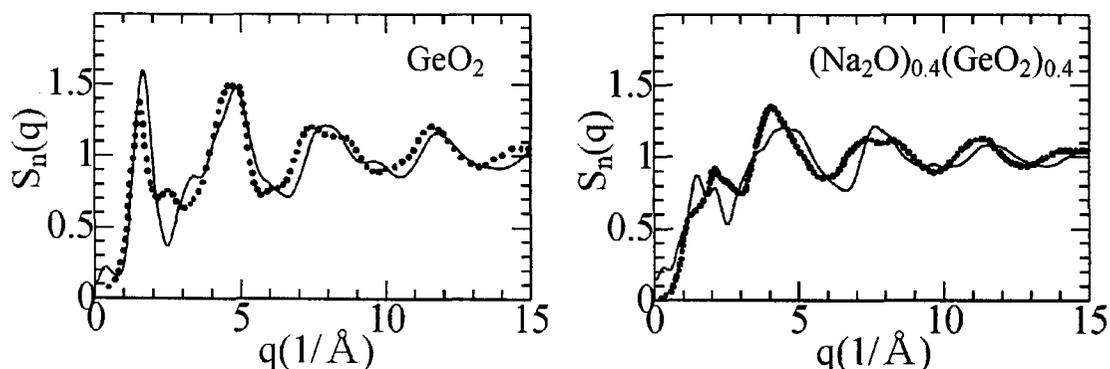
Fig. 3. Same as Fig. 1, but for germanate glasses. The experimental results are cited from Ref. 5.

with periodic boundary conditions. We carefully prepared glasses with varied degrees of the doping rate starting from molten states at high temperatures around 10,000 K; we spent totally over 200,000 time steps with a time interval of 2×10^{-15} s for each glass.

3. RESULTS AND DISCUSSION

Structural information of glasses is obtained by neutron scattering experiments primarily in a form of the static structure factor $S_n(q)$, which is a linear combination of the partial contributions $S_{\mu\nu}(q)$ with appropriate weighting factors:

$$S_n(q) = \frac{\sum_{\mu\nu} b_\mu b_\nu (x_\mu x_\nu)^{1/2} \left[S_{\mu\nu}(q) - \delta_{\mu\nu} + (x_\mu x_\nu)^{1/2} \right]}{(\sum_\mu b_\mu x_\mu)^2}, \quad (2)$$

where $x_\mu = n_\mu/n$ and b_μ are the number fraction and the neutron scattering length for atoms of species μ, respectively. Figures 1, 2 and 3 compare results of the MD simulations for $S_n(q)$ of the monolithic and Na_2O-doped glasses with those of the corresponding neutron experiments. We see the simple ionic model is capable of accounting for essential features in the structural correlation functions including the behavior of the FSDP with respect to the Na_2O doping. We also note
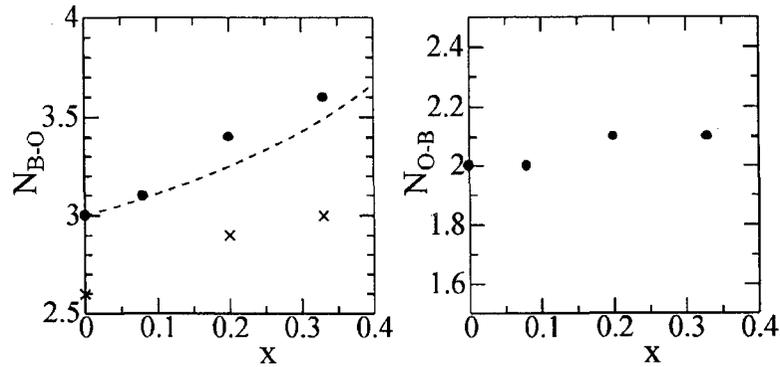
Fig. 4. Coordination number of oxygen atoms around a boron is plotted as a function of the molar fraction x of Na_2O for the borate glasses in the left panel, and the coordination number of B atoms around an O atom in the right panel. MD results (dots) are compared with available neutron data (crosses). The dashed curve in the left panel shows the ideal functional behavior, Eq. (4). The experimental results are cited from Ref. 6.
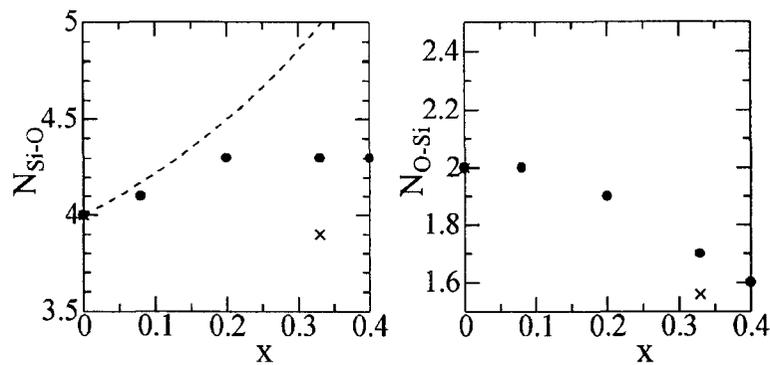
Fig. 5. Same as Fig. 4, but for the silicate glasses. The experimental results are cited from Ref. 4. The dashed curve in the left panel shows the ideal result given by Eq. (5).
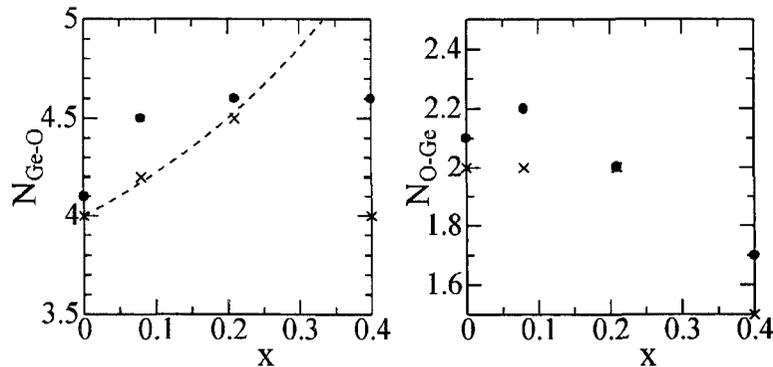
Fig. 6. Same as Fig. 4, but for the germanate glasses. The experimental results are cited from Ref. 5. The dashed curve in the left panel shows the ideal result given by Eq. (5).

that the nearest-neighbor distances of atoms are reproduced within errors of 5 % for the whole set of the glasses. It is well known that the short-range correlations between oxygen atoms are appreciably underestimated in the present model for SiO_2. However, such a deficiency is not so harmful in discussing the network structure of the glass over larger scales.

The coordination number $N_{\mu\nu}$ of atoms of species ν around an atom of species μ is calculated through integration of the partial pair-distribution function $g_{\mu\nu}(r)$ over the first peak:

$$N_{\mu\nu} = 4\pi n_\nu \int_0^{r_c} dr\, r^2 g_{\mu\nu}(r),\qquad(3)$$

where the cutoff distance r_c was chosen to coincide with

the first minimum of $g_{\mu\nu}(r)$ in the present calculations. The results for the coordination numbers related to the framework network are plotted as a function of the molar fraction x of Na_2O for the three representative glasses in Figs. 4-6 and compared with available neutron-scattering results. The functional behavior of the coordination numbers clearly distinguishes those glasses.

In the borate glasses oxygen atoms introduced by the metallic oxide convert the planar triangular units BO_3 into tetrahedral units BO_4. The increase of the O coordination number is in good accordance with the ideal law,

$$N_{B\text{-}O} = 3 + \frac{x}{1-x},\qquad(4)$$

which is derived by assuming that two BO_4 units are formed for each excess oxygen without creation of non-bridging oxygen. This process thus leads to enhancement of the coherence of the glassy network. Two sodium ions accompanying the excess oxygen sit near the BO_4 units just to locally compensate their charge imbalance (the BO_4 unit is negatively charged).

In contrast, the metallic ions terminate the network of the silicate glasses preserving the tetrahedral units SiO_4. Accordingly the number of non-bridging oxygen increases. The coherence of the silicate network is thereby depressed with doping of the network modifiers. In passing we note the ideal increase of the oxygen coordination number without creation of non-bridging oxygen is given as

$$N_{Si-O} = 4 + \frac{2x}{1-x}. \tag{5}$$

This formula is also applicable to the germanate glasses.

The germanate glasses lie between those two types of glasses as regards the network modification. The coordination number N_{Ge-O} increases with introduction of Na_2O as in the borate glasses, but up to about $x = 0.2$. Then the network-termination process, controlling the network modification by metallic dopants in the silicate glasses, takes over the network-decoration process. Figure 7 demonstrates the newly formed units are dominantly GeO_5 polyhedra with a slight amount of GeO_6 polyhedra; GeO_5 units are very rare in the crystalline states of germanates with long-range order. A theoretical study in [12] indicates N_{Ge-O} should be rather sensitive to the choice of Ge size. Experimentally it is
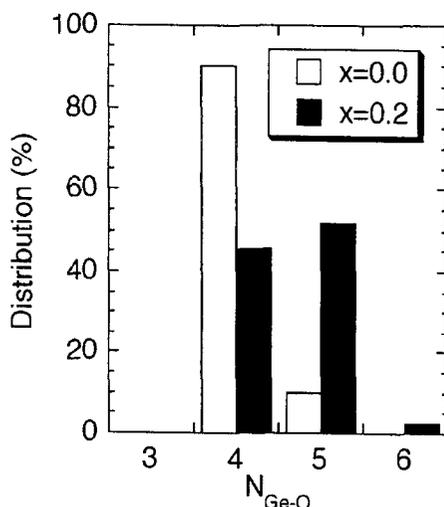
Fig. 7. Distribution of the coordination number N_{Ge-O} for $(Na_2O)_x(GeO_2)_{1-x}$ glasses with $x = 0$ (open bars) and $x = 0.2$ (solid bars).

still difficult to resolve which structural unit is formed in germanate glasses by doped metallic ions [13]. At any rate we like to point out there is no reason to discriminate the GeO_5 polyhedra. The increase of N_{Ge-O} is saturated beyond $x = 0.2$. This functional trend of N_{Ge-O} may contradict the experimental result, while it is consistent with the recent neutron diffraction measurements on rubidium germanate glasses [14].

On doping of sodium oxide into the borate glass the planar feature of BO_3 units enables excess oxygen to easily accommodate between two facing units leading to the structural change of the units themselves. The three-dimensional feature of SiO_4 units however prevents the excess oxygen from connecting to Si centered at the units, so that the dopants enter the silica network by terminating connection between the units along with creation of non-bridging oxygen. The structural change of GeO_4 units in the low doping region of Na_2O is ascribed to the large size of Ge ions as compared with that of Si ions. The basic building unit in the germanate glass is loosely "bonded" and tends to spontaneously fluctuate; in fact Ge takes both fourfold and sixfold O coordination in its crystalline counterparts [15]. Such intrinsic structural fluctuations of the units are enhanced by the doped metallic oxide.

4. CONCLUDING REMARKS

We are now in a position to carry out detailed analyses on the structural properties of the multicomponent oxide glasses, including dependence of the ring structure of the backbone network on the doping rate of network modifiers and their spatial distribution in the glassy matrices.

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