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Molecular Dynamics Simulation of Lead Borate and Related Glasses in Multicomponent Systems for Low Melting Vitrification of Nuclear Wastes

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Abstract. Glasses based on lead oxide have excellent properties in general such as low melting point, high chemical durability and high stability of glassy form, which are suitable for the preservation of volatile nuclear wastes in a permanent vitrified form. In order to confirm the long-term performance of lead borate based glasses it is necessary to establish dissolution and diffusion processes based on a reliable model of the glass structure. In the present study molecular dynamics (MD) simulation of lead borate based glasses was carried out introducing a dummy negative point charge to reproduce asymmetric PbO_n units. Parameters for the dummy charge were optimized based on the comparison between calculated radial distribution function and experimental one. Asymmetric coordination around Pb, for example trigonal bipyramid, was successfully reproduced in the MD simulated binary and ternary glass models. The simple model using the dummy charge was confirmed to be valid for further simulations of multicomponent glasses containing nuclear wastes and heavy elements.

1. Introduction

Low melting glasses based on lead oxide have attracted our attention because they also show high durability against various chemical attacks and resulting high stability of glassy form. As for lead borate glasses the thermal stability against crystallization is also distinguished, and the glass formation allows the incorporation of additives to form stable multicomponent glasses. These properties are suitable for the long-term preservation of nuclear wastes in a permanent vitrified form. Structural analysis of these glasses has been performed in simple systems so far, but it is necessary to investigate further on the structural modeling of complicated practical compositions in order to evaluate and enhance the long-term stability and reliability of these glasses.

In this study, molecular dynamics (MD) simulations for $66.7PbO\text{-}33.3B_2O_3$ and $65PbO\text{-}5ZnO\text{-}30B_2O_3$ glasses were carried out in order to investigate the structural details in atomic scale, where dummy negative charge was introduced to reproduce asymmetric PbO_n units. Pb^{2+} ion has a $6s^2$ lone pair, and hence PbO_n units are distorted. In the glasses with low PbO content, Pb acts as network modifier with high coordination numbers such as 6. At high PbO content, Pb plays a role of network former, where Pb takes PbO_3 trigonal pyramid or PbO_4 trigonal bipyramid [1]. Difficulty was expected

to reproduce such the asymmetric coordination structure based on the simple ionic pair potential. Then, dummy charge was introduced to simulate the lone pair Pb $6s^2$ electrons. We focused on the effect of the distance from lead atom to the dummy charge on the coordination structure of PbO_n units.

2. Experimental

In this paper, the total potential energy acting on each atom in the system was composed of two-body interaction, given as:

$$\phi_{ij}(r_{ij}) = \frac{Z_i Z_j e^2}{r_{ij}} + A_{ij}\exp(-B_{ij}r_{ij}) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

where Z is the ionic charge ($Z_{Pb + dummy\ negative\ charge} = +1.2$, $Z_B = -1.8$, $Z_O = -1.2$, $Z_{Zn} = +1.2$), e is the unit charge. The potential parameters A_{ij}, B_{ij} and C_{ij} were optimized to obtain good agreement between the calculated and experimental radial distribution functions (RDFs). The best parameter set is given in Table 1, and the number of atoms in an MD cell is shown in Table 2. The dummy charge Q_{DC} and the distance from lead atom to the dummy charge d_{DC} were also optimized. During the MD simulations, d_{DC} was fixed at a given value.

The MD simulations were performed using Materials Explorer 5 by FUJITSU. NVT ensemble (constant cell size and temperature) is used for all simulations. The long range Coulombic interactions were calculated by the Ewald method. The cut-off distance used for interaction was 15.5 Å for $66.7PbO\text{-}33.3B_2O_3$ or 15.0 Å for $65PbO\text{-}5ZnO\text{-}30B_2O_3$ about half length of a unit cell. Periodic boundary condition was used for all simulations. Initial configurations ware randomly generated with a shortest distance constraint between each atom. Structural relaxation was performed for all simulations before rapid-quenching simulation. The glasses were melted at 3000 K for 80 ps and quenched to 300K continuously in 270 ps with a cooling rate of 10 K/ps, and then equilibrium was performed for 80 ps. This rapid-quenching simulation was performed with a time step of 1 fs. Configurations used to calculate pair-distribution function and accumulated coordination number were obtained from the latter half of equilibrium simulation.

3. Results and discussion

As a first step, the potential parameters A_{ij}, B_{ij} and C_{ij} were tentatively optimized for $66.7PbO\text{-}33.3B_2O_3$ glass without using the dummy charge, and as a second step, the parameters Q_{DC} and d_{DC} were also optimized. Table 3 and Fig. 1 show the effect of Q_{DC} and d_{DC} on the coordination number of Pb atom ($N_{Pb\text{-}O}$) and RDF, respectively. When using the dummy charge (non-spherical model), $N_{Pb\text{-}O}$ becomes smaller than spherical model (no dummy charge) and closer to the experimental value [2]. When fixing Q_{DC} at −0.5, optimal $N_{Pb\text{-}O}$ was obtained at d_{DC} = 1.2 Å. The RDFs calculated with dummy charge are in good agreement with the experimental RDF [2]. The peaks near 2.35 Å and 3.80 Å are derived from Pb - O and Pb - Pb pairs, respectively. In X-ray weighted RDF, it is difficult to recognize the change of Pb - O peak, but the change of Pb - Pb peak is clearly seen. After introducing the dummy charge, Pb - Pb peak shifts to shorter side and decreases in peak area.

Then, d_{DC} was fixed at 1.2 Å, and optimal Q_{DC} was explored. However, improvement in $N_{Pb\text{-}O}$ was not achieved at Q_{DC} other than −0.5 (Table 3). Finally, some potential parameters were modified, obtaining the best parameter set (Table 1). Fig. 2 shows the MD model reproduced from the best parameter set, and Fig. 3 shows the X-ray weighted RDF calculated from the MD model shown in Fig. 2. The RDF calculated is in good agreement with the experimental one. $N_{Pb\text{-}O}$ (r < 2.85 Å) in the MD model is 4.17, which is in good agreement with the experimental one, 4.18 (r < 2.82 Å). In the MD model, trigonal bipyramids given in Fig. 2 are successfully reproduced. Fig. 4 shows the accumulated coordination number of boron atoms ($N_{B\text{-}O}$) in the optimal MD model. A plateau is found at around r = 2 Å, indicating that local structure around boron is successfully reproduced. $N_{B\text{-}O}$ (r < 1.75 Å) in the

MD model is 3.28, which is in good agreement with the experimental one, 3.32 estimated from ^{11}B MAS NMR [2].

Next, the MD model for the ternary 65PbO-5ZnO-30B_2O_3 glass was also produced based on the best parameter set. The X-ray weighted RDFs of the ternary glass are shown in Fig. 5. The composition of the ternary glass is not so different from the binary glass, and hence significant difference in RDF is hardly seen between the binary and ternary glasses. $N_{Pb\text{-}O}$ (r < 2.85 Å) is 4.05 in the MD model for the ternary glass, which is somewhat larger than experimental one, 3.93 [2] (r < 2.82 Å).

4. Conclusions

The structural models for the binary 66.7PbO-33.3B_2O_3 and ternary 65PbO-5ZnO-30B_2O_3 glasses were constructed by MD simulations. With introducing the dummy charge, asymmetric PbO_n units were successfully reproduced in the MD models. The RDFs for the MD models showed good agreement with the experimental ones. It was finally concluded that the dummy charge was effective in reproducing not only the local structure around Pb atoms but also the middle range structure of PbO-containing glasses.

References

[1] Takaishi T, Jin J, Uchino T and Yoko T 2000 *J. Am. Ceram. Soc.* **83** 2543-48
[2] Ida K 2010 *Master thesis* (Okayama University)

Table 1. The parameters used in the MD simulations

pairs	A_{ij}(10^7J)	B_{ij}(Å^{-1})	C_{ij}(10^7J*Å^6)
dummy - dummy	0.864E-20	0.588E+01	0.100E-24
dummy - B	0.617E-22	0.606E+01	0.000E+00
dummy - O	0.864E-20	0.588E+01	0.100E-24
dummy - Pb	0.155E-19	0.606E+01	0.750E-25
dummy - Zn	0.894E-21	0.606E+01	0.100E-25
B - B	0.324E-24	0.625E+01	0.000E+00
B - O	0.807E-22	0.606E+01	0.000E+00
B - Pb	0.169E-21	0.345E+01	0.000E+00
O - O	0.864E-20	0.588E+01	0.100E-24
O - Pb	0.925E-20	0.606E+01	0.750E-25
Pb - Pb	0.560E-21	0.303E+01	0.563E-25
B - Zn	0.510E-23	0.625E+01	0.000E+00
O - Zn	0.894E-21	0.526E+01	0.100E-25
Zn - Pb	0.153E-20	0.313E+01	0.750E-26
Zn - Zn	0.803E-21	0.303E+01	0.100E-26

Table 2. Simulation conditions

Glass	Number of atoms in a simulation cell					Cell size (Å)	Density (g/cm^3)
	Pb	B	O	Zn	Total		
binary glass	480	480	1200	0	2160	31.4	6.65
ternary glass	455	420	1120	35	2030	31.0	6.65

Table 3. Change in coordination number of Pb ($N_{Pb\text{-}O}$) by varying Q_{DC} and d_{DC}. for 66.7PbO-33.3B_2O_3 glass

d_{DC}	Q_{DC}	$N_{Pb\text{-}O}$ (r < 2.85Å)
No dummy charge		4.66
2.0	–0.5	4.55
1.6	–0.5	4.40
1.2	–0.5	4.29
0.8	–0.5	4.32
0.4	–0.5	4.54
1.2	–0.7	4.34
1.2	–0.9	4.32

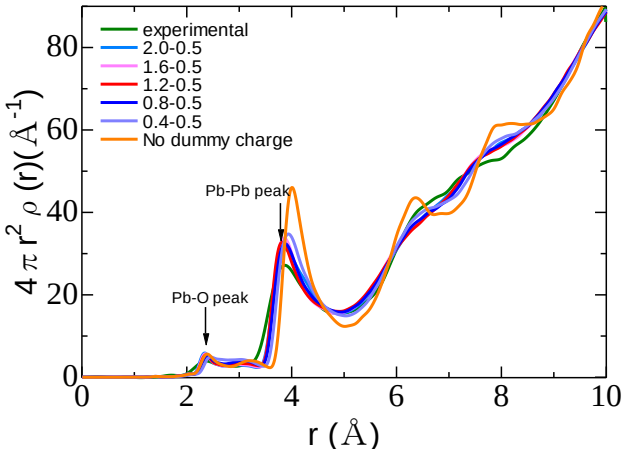

Fig. 1. X-ray weighted RDF for 66.7PbO-33.3B_2O_3 glass

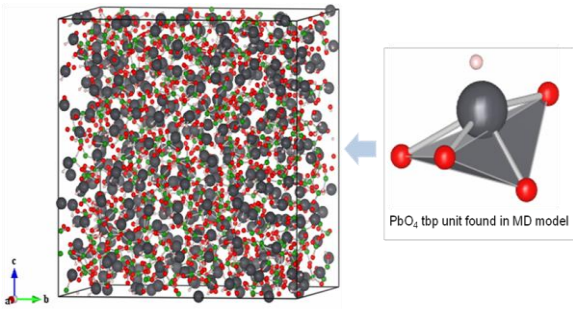

Fig. 2. MD model for 66.7PbO-33.3B_2O_3 glass obtained from the best parameter set

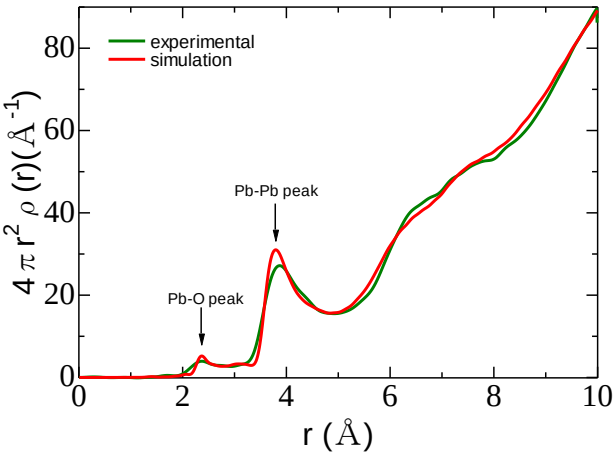

Fig. 3. X-ray weighted RDF for 66.7PbO-33.3B_2O_3 glass calculated from the MD model shown in Fig. 2

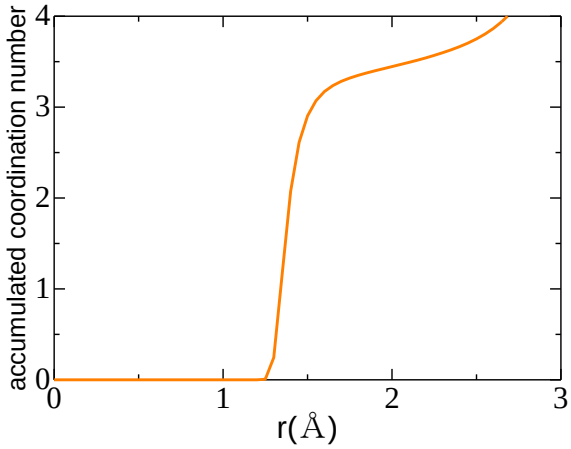

Fig. 4. The accumulated coordination number of boron atoms in the MD model shown in Fig. 2

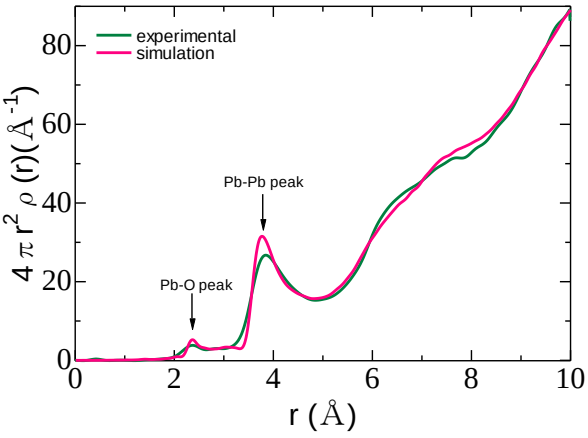

Fig. 5. X-ray weighted RDF for ternary 65PbO-5ZnO-30B_2O_3 glass