Short-Range Structure of Vitreous P_2O_5 by MD Simulation

Yoshihiro Suzuki^{1,*}, Keiichi Takase², Isao Akiyama^{1,*}, Kentaro Suzuya³,
Norimasa Umesaki⁴ and Norikazu Ohtori¹

¹Graduate School of Science and Technology, Niigata University, Niigata 950-2181, Japan

²Department of Chemical Engineering and Materials Science, Doshisha University, Kyo-tanabe 610-0321, Japan

³Japan Atomic Energy Research Institute, Naka 319-1195, Japan

⁴Japan Synchrotron Radiation Research Institute, Sayo 679-5198, Japan

We have performed molecular dynamics (MD) simulations for vitreous P_2O_5 using isotropic pair potentials composed only of coulombic and repulsive interactions. The P–O pair distribution function obtained had the two distinguishable peaks expected from the results of neutron diffraction experiments, in the nearest-neighbor P–O correlation. The neutron-weighted real-space correlation function was also in semi-quantitative agreement with that obtained from the experimental results. The distribution of the coordination number for O around P and P around O showed that most P atoms form tetrahedral PO_4 units in the glass, and that three-fifths of O atoms are bridging oxygen atoms, O_B , and the remaining are terminal oxygen atoms, O_T . The pair distribution functions for P– O_B and P– O_T show that the PO_4 units have three long P– O_B bonds and one short P– O_T bond. We have concluded that the short-range structure obtained for vitreous P_2O_5 agrees well with the picture derived from many experiments. This fact indicates that the short-range structure of vitreous P_2O_5 can be described mainly by both charge ordering and packing based on the differences in ionic charge and size between cation and anion.

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1. Introduction

The structure and properties of phosphate glasses have not been investigated as systematically nor extensively in comparison with those of borate or silicate glasses.¹⁾ This may be partly because many phosphates are difficult to perform experiments due to their hygroscopicity and volatility. However, in recent years, because of technical improvements, phosphate glasses have been used as laser glasses,²⁾ biomedical uses,³⁾ and other practical uses.^{4,5)} Since phosphates have a relatively low melting point for glass-forming materials and are good solvents for many additives, they are promising materials for new functional glasses in the future. Accordingly, studies of the structure and properties of phosphate glasses have also become more important. Especially, knowledge of the pure glass is always important as a reference system for glasses including additives. However, since vitreous P_2O_5 is extremely hygroscopic, it has not been easy to prepare a sample and keep it stable during measurements. This property prevented the experimental study of the glass structure for a long time, but in recent years, technical improvements have enabled neutron and x-ray diffraction measurements^{6–12)} to be successfully performed. As a result, it has been found that the structural unit in vitreous P_2O_5 is tetrahedron consisting of a central P atom and four O atoms, of which three are bridging oxygen atoms, O_B , that form the network structure and one is a non-bridging atom, *i.e.*, the terminal oxygen atom, O_T . Hoppe *et al.*^{8–12)} obtained the neutron interference function, $Q \cdot i(Q)$, up to a high momentum transfer, Q , of $50 \times 10^{-2} \text{ pm}^{-1}$ and derived the real-space correlation function, $T(r)$, with high resolution. The first and second peaks were clearly distinguishable at 143 pm and 158 pm and assigned to the most probable nearest-neighbor distances, P– O_T

and P– O_B distance, respectively, in $T(r)$.

Molecular dynamics (MD) simulation has been useful for analyzing the short-range structure of many glasses such as silicates and borates, complementing the experimental methods. Although several MD calculations were performed for phosphate glasses,^{13–19)} apart from a recent one,¹⁹⁾ there is no report on vitreous P_2O_5 . In the report,¹⁹⁾ the peak separation was successfully reproduced using the three-body potentials incorporating an anisotropic interaction. However, the authors pointed out that it was hard to reproduce the two distinguishable peaks using the isotropic pair potential.¹⁹⁾ So far, we have studied the short-range structure of alkaline-earth borate glasses using the simple ionic pair potentials.^{20,21)} The purpose of the series of our researches is to elucidate the possibility of describing variation in the short-range structure depending on additives such as alkali and alkaline-earth oxides using such simple pair potentials. In other words, our main interest is to clarify the structural properties predominated by charge ordering and packing, *i.e.*, the charge and size of both cation and anion. In fact, the MD simulations using purely ionic pair potentials have been useful for the description of the short-range structure for the alkali borate glasses²²⁾ and the alkaline-earth borate glasses.^{20,21)}

Since it was found that the phosphate glasses have a clear anisotropic structure of O atoms around a P atom, they are not only interesting but also useful for examining the applicability of the isotropic pair potentials. In this paper, we describe the results of the MD calculation of vitreous P_2O_5 using the isotropic pair potentials and discuss the simulated short-range structure based on the following: the P–O pair distribution function; the distribution of coordination number of P around O and of O around P; the P– O_B and P– O_T pair distribution functions; the distance distribution functions between P and its first- to fourth-nearest O; and the P–O–P and O–P–O angular distribution functions, by reference to those from neutron

*Graduate Student, Niigata University.

diffraction experiments.

2. Calculation Method

The MD simulation for P₂O₅ glass was performed with constant N , V and total energy, E . The total number of atoms, N , was 1050 and the cell volume, V , in a glassy state was determined from the density⁷⁾ which was $2.385 \times 10^3 \text{ kgm}^{-3}$ at 300 K. The function used for the pair potential energy, U_{ij} , between the atoms i and j , was proposed by Speghini *et al.*¹⁷⁾ and composed only of the coulombic and the short-range repulsive interaction:

$$U_{ij}(r_{ij}) = \frac{e^2}{4\pi\epsilon_0} \frac{Z_i Z_j}{r_{ij}} + \frac{C_{ij}}{r_{ij}^6},$$

where Z is the effective ionic charge, e the unit charge, r the interatomic distance, and C the repulsive interaction parameter given by Speghini *et al.*¹⁷⁾ The effective ionic charge of the O atom was obtained by Uchino and Ogata²³⁾ who performed *ab initio* molecular orbital calculations of the electronic structure of H₄P₂O₇, which is a cluster, as a model for P₂O₅ glass. The charge of the P atom was adjusted to meet the charge neutrality of the entire system. The values of C and Z are collected in Table 1. The coulombic interactions were treated using the Ewald method²⁴⁾ under periodic boundary conditions.

The initial atomic configuration was generated randomly and the initial atomic velocities were also created randomly but in accordance with the Maxwell distribution of velocities corresponding to 3000 K. The equations of motion were integrated using the velocity version of the Verlet algorithm.²⁴⁾ In the beginning, the system was kept at 3000 K for 200 ps with a time step of 1 fs in order to obtain a fully disordered configuration in the equilibrium state. The molten state was confirmed by checking the mean square displacement of atoms. Subsequently, it was gradually cooled to 300 K for vitrification by scaling the velocities and the cell volume at a rate of 50 K/ps with a time step of 2 fs. In the course of cooling, the system was kept at 2000, 1000, and 300 K for 40, 40, and 240 ps, respectively, for the sake of structural relaxation. The positions and velocities for the subsequent 100 ps were analyzed to obtain structural information. The pair distribution functions, $g_{ij}(r)$, for P–O, O–O, and P–P pairs were calculated first from the obtained trajectory of the atoms. On the basis of these functions, the partial static structure factor, $S_{ij}(Q)$, in the Faber-Ziman form²⁵⁾ was evaluated for each

pair as follows:

$$S_{ij}(Q) = 1 + 4\pi\rho_0 \int_0^{r_{\max}} r^2 [g_{ij}(r) - 1] \frac{\sin(rQ)}{rQ} dr,$$

where ρ_0 is the average number density of atoms, and $r_{\max}$ is the cut-off value of r , *i.e.* 1300 pm, for the Fourier transformation. The neutron-weighted static structure factor, $S(Q)$, was calculated as follows:

$$S(Q) = \frac{\sum_i \sum_j x_i x_j b_i b_j S_{ij}(Q)}{\left(\sum_k x_k b_k \right)^2},$$

where b_i is the coherent scattering length of the i th nuclear species and x_i is the atomic fraction. The real-space correlation function, $T(r)$, was evaluated as follows:

$$T(r) = 4\pi\rho_0 r \times \sum_i \sum_j x_i x_j b_i b_j g_{ij}(r) / \left(\sum_k x_k b_k \right)^2.$$

The distribution of coordination number for P around O and O around P, and the O–P–O and P–O–P angular distributions were evaluated using the definition that the first minimum of $g_{PO}(r)$ is the outer sphere of the coordination shell. The P–O pair distribution function can be expressed as the sum of the P–O_B and P–O_T pair distribution functions.

3. Results and Discussion

Figure 1 shows a snapshot of the atoms in the equilibrium state at 300 K obtained from the MD calculation. As can be seen from this figure, the obtained atomic configuration was vitreous and no crystallization occurred.

Figure 2 shows the pair distribution functions for P–O, O–O and P–P correlations, obtained from the MD calculation of vitreous P₂O₅. Two clearly distinguishable peaks can be observed at 147 pm and 159 pm in $g_{PO}(r)$. The peaks for O–O

Fig. 1 Snapshot of the configuration of P(●) and O(○) atoms at 300 K obtained from the MD calculation.

Table 1 Potential parameters for P₂O₅ glass.

Ionic charge	Value
Z_P	1.9675
Z_O	−0.787
Short-range interaction parameter	Value/ $10^{-77} \cdot \text{Jm}^6$
C_{P-P}	1.216
C_{O-O}	1.197
C_{P-O}	0.2381

Fig. 2 Pair distribution functions obtained from the MD calculation.

Fig. 3 Neutron-weighted structure factor, $S(Q)$, obtained from the MD simulation. The dashed line denotes that from the neutron diffraction experiment.⁷⁾

and P–P pairs are observed at 253 pm and 320 pm. To our knowledge, this is the first report in which the peak split is clearly observed in $g_{PO}(r)$ obtained for P_2O_5 glasses using the isotropic pair potentials. It was found that the difference in the most probable distance between the two peaks depends on the effective ionic charge. Boiko *et al.*¹⁶⁾ performed MD calculation for $2ZnO \cdot P_2O_5 - 2Na_2O \cdot P_2O_5$ glass system using the isotropic pair potential, and reported that the $g_{ij}(r)$'s obtained for P– O_T and P– O_B had a peak at 150 pm and 154 pm, respectively, in the case of $2ZnO \cdot P_2O_5$ as a representative. However, the peak split was not observed in their total P–O pair distribution function. This is due to the small difference in the most probable distance between the two peaks, *viz.* 4 pm, which is far smaller than our result of 12 pm.

The neutron-weighted structure factor, $S(Q)$, is depicted in Fig. 3, and compared with the experimental results.⁷⁾ The $S(Q)$ from the present MD simulation is in good agreement with the neutron diffraction results in the middle and high Q range corresponding to the short-range structure, which shows that the isotropic pair potentials used are effective for simulation of the short-range structure of phosphate glasses and that this structure is appropriate for further discussion. On the other hand, $S(Q)$ from MD simulation in the low Q region agrees poorly with the experimental results. This fact

Fig. 4 Real-space correlation function, $T(r)$, obtained from the MD simulation. The dashed line denotes that from neutron diffraction experiment.¹¹⁾

indicates that there is still great room for improvement in order to discuss the long-range or middle-range structure. The $T(r)$ obtained from the MD calculation is illustrated in Fig. 4, and compared with experimental results.¹¹⁾ The peaks are observed at 147 pm, 159 pm, 254 pm and 320 pm which are reasonably assignable to the P–O, O–O and P–P correlations, respectively, on the basis of the pair distribution functions. Figure 4 shows that the positions of the first two distinguishable peaks are in very good agreement with those from experiment, while a poor agreement is found between their peak heights. In the experimental results, the higher intensity at the second peak is due to greater oscillatory behavior in $S(Q)$ up to a higher Q range.

The distribution of coordination number for O around P and P around O is shown in Fig. 5. Most P atoms are coordinated by four O atoms, whereas O atoms consist of one-coordinated O_T and two-coordinated O_B atoms; the ratio between O_B and O_T is 3 to 2. The former represents O atoms around a P atom forming a tetrahedral structure in the glass. The latter is a manifestation of the 3 to 1 ratio between P– O_B and P– O_T bonds, since one O_B atom participates in two P– O_B bonds and one O_T atom participates in only one P– O_T bond. On the basis of the results of spectroscopic studies, the structural unit in vitreous P_2O_5 has been thought as a tetrahedron consisting of four O atoms coordinated by a central P atom: three P– O_B bonds and one P– O_T bond.^{26–28)} This model is consistent with the experimental results by Hoppe *et al.*,⁸⁾ since their $T(r)$ shows that the peak intensity corresponding to the P– O_B correlation is three times higher than that corresponding to the P– O_T correlation. Apart from the ratio of the intensities between the first two peaks in $T(r)$ obtained from the MD calculation, our result for the ratio of P– O_B to P– O_T is in good agreement with the experimental results. Figure 6 shows the P– O_B and P– O_T components in the P–O pair distribution function. This is a clear representation of the fact that the bond length of P– O_T is smaller than that of P– O_B . Therefore, we conclude that the simulated structure accurately reproduces the real short-range structure of vitreous P_2O_5 .

Figure 7 depicts the distance distribution functions between P and its 1st- to 4th-nearest O. The distance distribution be-

Fig. 5 Distribution of coordination number for (a) O around P and (b) P around O.

Fig. 6 Pair distribution functions of P-O_B and P-O_T.

tween P and its 1st-nearest O agrees reasonably with the P-O_T pair distribution function. On the other hand, the distance distribution for the 2nd- to 4th-nearest O is far from that for the 1st-nearest O, which leads to the two distinguishable peaks in $g_{PO}(r)$. However, the three distance distributions for the 2nd- to 4th-nearest O are not also equivalent to each other. This is the reason why the second peak intensity in $T(r)$ from the MD calculation is smaller than that in the experimental intensity. In other words, in real vitreous P_2O_5 , there is little difference among the three P-O_B bond lengths. This disagreement

Fig. 7 Distance distribution functions between P and its 1st-6th nearest O.

Fig. 8 Angular distribution functions for (a) O-P-O and (b) P-O-P.

suggests the limit of the applicability of the isotropic pair potentials.

The angular distributions of O-P-O and P-O-P are displayed in Fig. 8. Peaks are observed at 107 and 169 degrees, and the full widths at half maximum are 20 and 19 degrees, respectively. The angle at the peak in the angular distribution of O-P-O supports the PO_4 tetrahedral model. Assuming O-P-O angle to be 107 degree and O-P distance to be 158 pm, we get 256 pm as O-O distance, in good agreement with the most probable distance, 258 pm, observed in the O-O pair distribution function as above described. Although the P-O-

P angle is larger than the experimental value given by Hoppe *et al.*,^{9,10)} the calculated result supports, not the edge-sharing tetrahedral, but the corner-sharing PO₄ tetrahedra, which is also in qualitative agreement with the experimental results. The larger P–O–P angle can be one of the reasons for disagreement of the $S(Q)$ from MD calculation with that from experiment in the low Q region. The larger P–O–P angle is traceable to our use of the two-body potentials, since it was found that a larger B–O–B or Si–O–Si angle than the experimental value was also obtained from the MD calculation for pure B₂O₃ or SiO₂ glass using the two-body potentials. In order to solve this problem, we must incorporate the many-body effect into MD simulation.

We performed several separate MD calculations with different initial atomic configurations. As a result, we confirmed that all kinds of the pair distribution functions and the angular distribution functions are independent of various vitreous configurations obtained from the separate MD calculations; hence, the results above stated are fully reproducible.

4. Conclusion

MD calculation has been performed for pure P₂O₅ glass using simple isotropic pair potentials. The P–O pair distribution function showed the two distinguishable peaks in the nearest-neighbor P–O correlation. The distribution of coordination number for O around P and P around O showed that most P atoms form tetrahedral PO₄ units in the glass, and that the three-fifths of O atoms are bridging oxygen atoms, O_B, and the remaining are terminal oxygen atoms, O_T. Hence, it turns out that the ratio of P–O_B to P–O_T bonds is 3 to 1. The pair distribution functions for P–O_B and P–O_T make it clear that the PO₄ units have three long P–O_B bonds and one short P–O_T bond. The neutron-weighted real-space correlation function was also in semi-quantitative agreement with that from the experimental results. We conclude that the short-range structure obtained for vitreous P₂O₅ agrees well with the picture derived from many experiments. It is worth noting that the anisotropic structure was reproduced using the isotropic pair potentials: the short-range structure of vitreous P₂O₅ can be described mainly by both charge ordering and packing, *i.e.*, the charge and size of both cation and anion.

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