Electronic States of SiO$_2$–M$_x$O$_y$ (M$_x$O$_y$=P$_2$O$_5$, TiO$_2$ and ZrO$_2$) Glasses

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SiO$_2$–M$_x$O$_y$ (M$_x$O$_y$=P$_2$O$_5$, TiO$_2$, ZrO$_2$) 系ガラスの電子状態

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The electronic states of the SiO$_2$–M$_x$O$_y$ (M$_x$O$_y$=P$_2$O$_5$, TiO$_2$ and ZrO$_2$) glasses, which have good passivation ability, were calculated by the DV-X$k$ cluster method. The energy level structure of glasses containing the transition metal oxides, TiO$_2$ and ZrO$_2$, is different from that of pure SiO$_2$ and SiO$_2$–P$_2$O$_5$ glasses. The bond order between oxygen and sodium ion diffusing to the glass matrix in the systems SiO$_2$–P$_2$O$_5$, SiO$_2$–TiO$_2$ and SiO$_2$–ZrO$_2$ is larger than that in SiO$_2$ glass. Such a result is probably the origin of the passivation ability of these glasses.

Key-words: Electronic states, Passivation ability, SiO$_2$–P$_2$O$_5$, SiO$_2$–TiO$_2$, SiO$_2$–ZrO$_2$, Molecular orbital calculation, DV-X$k$ cluster method, Glass

1. Introduction

In recent years, many studies of coating films prepared by the sol-gel method have been reported. Using the sol-gel method the surface of metal and glass substrates can be modified. For example, stainless steel sheets coated with the SiO$_2$–ZrO$_2$ glass films derived from the gel film containing fluoroalkylsilane have higher resistance to corrosion and oxidation than the sheets without coating.1) Especially the SiO$_2$–TiO$_2$ and SiO$_2$–ZrO$_2$ glass films are attractive since they have high chemical durability, hardness and refractive index. These glasses can also be applied to improve the weathering resistance of the metal substrates. Recently, the SiO$_2$–TiO$_2$ and SiO$_2$–ZrO$_2$ glass films which contain less than 20 mol% TiO$_2$ and ZrO$_2$ have been reported to have a high alkali passivation ability and have possibility of the alkali passivation for optical memory disk substrates.2) By the measurements of the secondary ion mass spectrometry (SIMS) it has been found that these coating films contain high concentrations of alkali ions diffusing from the glass substrates.3) These results suggest that the sodium ion is trapped strongly within coating films and is blocked to further diffuse to the surface. This behavior must be associated with the chemical bonding around the sodium ions in the SiO$_2$–TiO$_2$ and SiO$_2$–ZrO$_2$ coating films.

Thus the electronic state calculation for better understanding of the chemical bonding in the glasses seems to be very important. For such a purpose the discrete variational (DV)-X$k$ cluster method has been known to be very efficient.4) The method has successfully been applied to the calculation of electronic states in several inorganic compounds.5)–7) The DV-X$k$ method has many advantages over the ab initio Hartree-Fock molecular orbital method; for example, the computing time is much shorter not only for the simple molecules but also for the large clusters containing transition metal atoms. Therefore, the method is considered to be also appropriate for calculation of the electronic states and chemical bonding of the glasses. In the present work, we have applied this method to the calculation of several clusters which can be present in the glasses mentioned above and discussed the relationship between the electronic state of the Na$^+$ ion and the passivation ability of the SiO$_2$–M$_x$O$_y$ (M$_x$O$_y$=P$_2$O$_5$, TiO$_2$ and ZrO$_2$) glasses.

2. Calculation method

In the present work, we apply the DV-X$k$ cluster method to the calculation of the electronic states of model clusters for the SiO$_2$–M$_x$O$_y$ (M$_x$O$_y$=P$_2$O$_5$, TiO$_2$ and ZrO$_2$) glasses to investigate the valence level structure and covalent bonding in various types of the clusters. In this method, we use the Slater’s exchange correlation potential, $V_{xc}(i)$, written by Eq. (1).

$$V_{xc}(i) = -6\alpha \left\{ (3/8\pi) q(i) \right\}^{1/3}$$

where $q$ is the electron density and $\alpha$ is a parameter. We use $\alpha$ value of 0.7 for $\alpha$ which is known to be adequate for many molecular orbital calculations,9)–13) and thereby there are essentially no empirical parameters in Eq. (1). In the DV-X$k$ method, the $\ell$th molecular wave function is described by a linear combination of atomic orbitals (LCAO).

$$\phi_\ell = \sum_{\alpha} C_{\alpha\ell} \chi_\alpha$$

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where \( \chi_i \)'s are basis functions and \( c_{ij} \)'s are coefficients. As the basis functions, we use numerical atomic orbitals obtained by solving the Schrödinger equation for atoms in a cluster. The Mulliken population analysis is employed to obtain the orbital population and overlap population by analyzing the cluster charge. These data are useful to discuss ionicity and covalency.

Three cluster models calculated in this work are shown in Figs. 1 (a), (b) and (c). The cluster (a) is a model of the matrix of SiO\(_2\)-M\(_x\)O\(_y\) glasses. In this cluster, the SiO\(_4\) and the MO\(_4\) (M=Si\(^{4+}\), P\(^{5+}\), Ti\(^{4+}\) and Zr\(^{4+}\)) tetrahedral units are attached by sharing one oxygen. Three unshared oxygens in the SiO\(_4\), the TiO\(_4\) and the ZrO\(_4\) tetrahedra and two unshared oxygens in the PO\(_4\) tetrahedra are terminated with the Si(OH)\(_3\) units. These angles are taken from the experimental data for the SiO\(_2\) glasses.\(^{14}\) For simplicity, the bond angles of M-O-Si(OH)\(_3\), Si-O-Si(OH)\(_3\) and Si-O-H in the terminating units Si(OH)\(_3\) are fixed to be 180°.

As mentioned above, the SiO\(_2\)-TiO\(_2\) and the SiO\(_2\)-ZrO\(_2\) coating films are known to have a good passivation ability, nevertheless the concentration of sodium ion is relatively high in these films.\(^{3}\) This suggests that the sodium ion in the substrate easily diffuses to and is trapped in the SiO\(_2\)-TiO\(_2\) and the SiO\(_2\)-ZrO\(_2\) coating films. Such a phenomenon can be considered as a result of reaction of the sodium ion with the bridging oxygens in these films. After the reaction of the Na\(^+\) ion, we assume Si-O-M bond is broken and the Na\(^+\) ion penetrates to form Si-O-Na-O-M. In order to simulate this process we take a model cluster of the type (c). The stability of the sodium ion in the SiO\(_2\)-M\(_x\)O\(_y\) glasses is also discussed by using the cluster (c). In these glass films the Na\(^+\) ion seems to be surrounded by the non-bridging and the bridging oxygens (abbreviated as ONB and OB, respectively). The cluster has a sodium ion between the MO\(_4\) tetrahedral unit and the Si\(_2\)O\(_7\)\(^{6-}\) unit which is constructed by two SiO\(_4\) tetrahedral units sharing one OB. One of the ONB in the MO\(_4\) tetrahedra and an OB in the Si\(_2\)O\(_7\)\(^{6-}\) units are coordinated with the sodium ion. The bond angles and the distances in the cluster units are the same as in the cluster (b). In the cluster (c), each non-bridging oxygen is not terminated with any units, since in the clusters (a) and (b) the electronic states of the clusters terminated with Si(OH)\(_3\) units are qualitatively similar to those of the clusters without the Si(OH)\(_3\) terminating units. This cluster is one of the simplest clusters to study the electronic states around the Na\(^+\) ion in the SiO\(_2\)-M\(_x\)O\(_y\) glasses.

### 3. Results and discussion

The energy level diagram of the valence molecular orbitals for the cluster (a) is shown in Fig. 2. In the figure, the solid horizontal line denotes the occupied level and the dotted line the empty level. The energy levels mainly induced by the hydrogen atoms used as terminators, are eliminated from this figure.
In the cluster of \( M = \text{Si}^{4+} \) ion, the occupied levels are mainly composed of the O 2s and O 2p atomic orbitals and the unoccupied levels Si 3s, Si 3p and Si 3d orbitals. The highest occupied molecular orbital (HOMO) is of non-bonding and is composed of O 2p. The lowest unoccupied molecular orbital (LUMO) essentially consists of Si 3s. The energy gap between HOMO and LUMO is 7.65 eV. The optical band gap obtained by the experiment is about 7.7–8.2 eV in the SiO\(_2\) glass.\(^{10}\) The energy gap by the present calculation is slightly smaller than that by the experiment. Such a small difference is caused by the influence of the Si(OH)\(_3\) terminating units.

In the case of \( M = \text{P}^{5+} \) ion, the level structure is similar to the cluster with the Si\(^{4+}\) ion; the occupied levels are chiefly constructed by the O 2s and O 2p atomic orbitals and the unoccupied levels by the 3s, 3p and 3d atomic orbitals of the Si and the P ions. The main difference is that of energy gap between HOMO and LUMO of the two clusters. This is because that HOMO of the latter cluster is the non-bonding orbital composed of the O\(_{\text{NB}}\) 2p atomic orbital in the PO\(_4\) unit. In such a case, the energy gap is slightly smaller than that of the cluster with the \( M = \text{Si}^{4+} \) ion. The band gap is decreased by the addition of P\(_2\)O\(_5\) to the SiO\(_2\) glass. By the measurement of the absorption spectra, the band gap of the P\(_2\)O\(_5\) glass has been known to be 5.23 eV,\(^{17}\) being smaller than that of the SiO\(_2\) glass (7.7–8.2 eV). This is consistent with the present model cluster calculations. However, the main feature of the electronic state of the glass which contains only glass-forming oxides such as SiO\(_2\) and P\(_2\)O\(_5\) is similar to that of the pure SiO\(_2\) glass.

In contrast to the level structure of the cluster only composed of the typical elements like Si and P atoms, the level structure of the cluster which contains TiO\(_2\) and ZrO\(_2\) can be somewhat complicated since the 3d and 4d atomic orbitals of the Ti and Zr atoms participate in the formation of valence band. Thus it is guessed that the energy level structure in the SiO\(_2\)–TiO\(_2\) and the SiO\(_2\)–ZrO\(_2\) glasses is different from that in the SiO\(_2\) and the SiO\(_2\)–P\(_2\)O\(_5\) glasses. In the cluster containing the Ti\(^{4+}\) ion, the molecular orbitals composed of the Ti 3d atomic orbital exist in the HOMO–LUMO energy gap of the network of the SiO\(_4\) tetrahedral units. This level structure is also different from that in the cluster with the P\(^{5+}\) ion. As the result, LUMO of the cluster is constituted by the Ti 3d atomic orbital and the energy gap between HOMO and LUMO is reduced to 3.46 eV, being much smaller than that of the clusters with P\(^{5+}\) ion.

The energy level structure of the cluster containing the Zr\(^{4+}\) ion is similar to that with Ti\(^{4+}\), but is also different from that of the cluster of \( M = \text{P}^{5+} \) ion; LUMO of this cluster is constructed by the Zr 4d atomic orbital and the band gap between HOMO and LUMO is 4.13 eV. These results suggest that the electronic state of the glasses containing Ti\(^{4+}\) and Zr\(^{4+}\) ions, which are "intermediate" ions in the silicate glasses, is different from those which contain only "glass-forming" ions like Si\(^{4+}\) and P\(^{5+}\) ions.

The energy level diagram of the valence molecular orbitals of the cluster (b) is shown in Fig. 3. In the cluster of \( M = \text{Si}^{4+} \) ion, the molecular orbital level mainly constructed by the Na 3s atomic orbital is situated just below the LUMO of the network of the SiO\(_4\) tetrahedral units. Since this molecular orbital of the Na\(^{+}\) ion has lower energy than that of the Si\(^{4+}\) ion, the energy gap between HOMO and LUMO in this cluster becomes smaller than that in the cluster (a). The measurements of optical spectra have shown that the band gap of the sodium silicate glasses is decreased with increasing Na\(_2\)O content.\(^{16}\) This is well explained by the present cluster calculations.

For the cluster with the P\(^{5+}\) ion, a similar result is obtained. In this cluster, the molecular orbitals constructed by the Na 3s and the Na 3p atomic orbitals are also located near LUMO of the network of the SiO\(_4\) and PO\(_4\) tetrahedral units. Since the 3s orbital is

![Fig. 2. Valence energy level diagrams for the cluster (a). The energy scales of the cluster are shifted so that the top of O 2p levels are aligned to zero energy.](image)

![Fig. 3. Valence energy level diagrams for the cluster (b).](image)
located in the energy gap between HOMO and LUMO of the network which includes SiO₄ and PO₄ tetrahedral units, the energy gap between HOMO and LUMO becomes 6.27 eV, smaller than that in the cluster (a) with only P⁵⁺ ion. Thus it can be mentioned the energy gap of the glasses is decreased with the addition of the Na⁺ ion.

In the cluster (b), the energy level structure of the clusters with the Ti⁴⁺ and the Zr⁴⁺ ions is different from that of the cluster (a) where Na⁺ ion is not contained. In the cluster (b) with the Ti⁴⁺ ion, Na 3s and Na 3p atomic orbitals are located between the Si 3s and the Ti 3d orbitals. By an interaction of Ti 3d with Na 3s, the Ti 3d levels shift to lower energies. However, the reduction of the energy gap is only 0.75 eV.

For the cluster with the Zr⁴⁺ ion the level structure is similar to that of the cluster with the Ti⁴⁺ ion in analogy with the case of type (a); the molecular orbitals composed of the Na 3s and Na 3p are located between the Si 3s and the Zr 4d orbitals. The decrease of the energy gap due to the depress of the Zr 4d orbital is 1.04 eV.

The bonding states of Si-O and M-O and their changes by the addition of Na⁺ must particularly be important to discuss the reaction between the Na⁺ ion and the bridging oxygen in the SiO₂-MₓOᵧ glasses. We have employed the bond overlap population or the bond order of these bonds calculated by the Mulliken population analysis to discuss these bonding states. Figure 4 shows the bond order of Si-O in the Si-O-M bridge of the cluster (a). The bond orders in the clusters of M=Si⁴⁺, P⁵⁺, Ti⁴⁺ and Zr⁴⁺ ions are about 0.5-0.6 and not very different each other. However, in the case of cluster type (b), which contains the Na⁺ ion, the bond order of Si-O is somewhat smaller than that in the cluster (a), independent of the kind of the Mⁿ⁺ ions. This result indicates that the Si-O bond in the Si-O-M in the SiO₂-MₓOᵧ glasses is weakened by an addition of the Na⁺ ion as the result of interaction with the bridging oxyg- en.

In contrast to the small change in the bond order of Si-O with different Mⁿ⁺ ions, the bond order of M-O drastically changes. Figure 5 shows the bond order of M-O for cluster type (a). The bond order of M-O of the cluster of M=Si⁴⁺ ion is 0.55. The covalency of the P-O bond is stronger than that of the Si-O bond, showing a larger bond order of 0.75 for P-O bond. However, in the clusters with the Ti⁴⁺ and the Zr⁴⁺ ions, the value is only about 0.1. Thus the covalency of Ti-O and Zr-O bonds is substantially weaker than that of Si-O and P-O. In other words, the bonding nature of Ti-O and Zr-O is ionic in the glasses. When Na⁺ ion approaches to the bridging oxygen in M-O-Si, the bond order of M-O also becomes smaller, similar to that of Si-O (see Fig. 4).

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Especially in the clusters with Ti⁴⁺ and Zr⁴⁺, the bond orders of M-O diminish to essentially zero. Experimentally, the SiO₂-P₂O₅ glass shows a good passivation ability, similar to SiO₂-TiO₂ and SiO₂-ZrO₂ glasses. However, from the cluster model calculation, it is found the bonding nature in the SiO₂-P₂O₅ glass is considerably different from those in SiO₂-TiO₂ and SiO₂-ZrO₂ glasses. This suggests that the mechanism of the passivation of the SiO₂-TiO₂ and SiO₂-ZrO₂ glasses is different from that of the SiO₂-P₂O₅ glass.

Now we show the electronic states of the cluster (c) which is a model of the Na⁺ ion diffusing to the passivation films of the SiO₂-MₓOᵧ glasses. As described above, since the bridging oxygen in the Si-O-M bond tends to become the non-bridging oxygen more easily than that in the Si-O-Si bond, the non-bridging oxygen coordinated with the Na⁺ ion is one of the M-O bonds in the MOₓ unit. Furthermore since the bridging oxygen of the Si-O-Si bond is considered to coordinate to the Na⁺ ions which diffused to the SiO₂-MₓOᵧ glasses, we take a model cluster where the bridging oxygen of the Si₆O₁₈⁻ unit is coordinated with the Na⁺ ion.

The stability of the Na⁺ ion in the SiO₂-MₓOᵧ glass-
es seems to be associated with the bonding nature of Na-O, Si-O and M-O. Therefore the bond orders of Si-O in the Si-O-Si, of M-O in MO₄ units, of Na-O in Si-O-Si, and of Na-O in MO₄ units are very important to consider the stability of the Na⁺ ion. The bond orders of these bonds are shown in Fig. 6.

In the cluster (c) with M=Si⁴⁺, the bond orders of Si-Ob, Si-ONb, Na-Ob, and Na-ONb are 0.0, 0.48, −0.12 and 0.03, respectively. In addition to small covalent interaction between the Na⁺ ion and the oxygen ions, the bond strength of Si-Ob is very small. This means that the glass matrix becomes unstable in this cluster and that the Na⁺ ion is unstable and mobile in the SiO₂ glass. In contrast to this, in the cluster with the P⁵⁺ ion, the bond orders of Si-Ob, P-ONb, Na-Ob, and Na-ONb are 0.34, 0.91, 0.01 and 0.04, respectively, which are larger than the case of M=Si⁴⁺. In this cluster the cluster units surrounding the Na⁺ ion are stable, in addition to the fact that the interaction between the Na⁺ ion and the oxygen ions is larger than that in the cluster with the Si⁴⁺ ion. Thus the Na⁺ ion in the SiO₂-P₂O₅ glass is likely to be trapped strongly and is hard to move. The bond orders of Si-Ob, Na-Ob, and Na-ONb in the clusters with Ti⁴⁺ and Zr⁴⁺ take approximately the same values as in the clusters with P⁵⁺, although the change in M-ONb bond order with different M⁺ ions is very similar to that in the clusters (a) and (b). This implies that diffusibility of the Na⁺ ion is very small in the SiO₂-P₂O₅, the SiO₂-TiO₂ and the SiO₂-ZrO₂ glasses. This strong interaction between the Na⁺ ion and oxygens is probably the origin of the good passivation ability of the SiO₂-P₂O₅, the SiO₂-TiO₂ and the SiO₂-ZrO₂ glasses.

4. Conclusion

By the use of DV-Xα cluster method we have studied the electronic states of several model clusters for the SiO₂-MO₄ (MO₄=P₂O₅, TiO₂ and ZrO₂) glasses, which have good alkali passivation ability.

The bonding nature of Ti-O and Zr-O is more ionic than that of Si-O in these glasses, although that of P-O is more covalent. The Na⁺ ion diffusing to the SiO₂-MO₄ glasses must react with the bridging oxygen. The result shows that the bond which is broken by the Na⁺ ion in the SiO₂-TiO₂ and the SiO₂-ZrO₂ glasses seems to be different from that in the SiO₂-P₂O₅ glass, suggesting that the mechanism of the alkali passivation in the SiO₂-TiO₂ and the SiO₂-ZrO₂ glasses is different from that in the SiO₂-P₂O₅ glass.

In the clusters with the P⁵⁺, the Ti⁴⁺ and the Zr⁴⁺ ions, the bond order between the Na⁺ ion diffusing to the glass matrices and the oxygens is larger than that in the model clusters of the SiO₂ glass. Such a strong interaction between the Na⁺ ion and oxygens is probably the origin of the good passivation ability of the SiO₂-P₂O₅, the SiO₂-TiO₂ and the SiO₂-ZrO₂ glasses.

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