Chemical bonding state of sodium silicates

Tokuro Nanba*, Tatsuya Hagiwara, Yoshinari Miura

Department of Environmental Chemistry and Materials, Okayama University 3-1-1 Tsushima-Naka, Okayama 700-8530, Japan

Abstract

The chemical bonding state of sodium silicates was estimated by a DV-X α cluster MO method and a population analysis. Cluster models were constructed from the silicate crystals, pure silica, sodium disilicate and sodium metasilicate. The MO calculations successfully reproduced the experimental observations in XPS valence band spectra and core-orbital energies. According to the overlap population, covalent character increased with increasing Na₂O content, and it was also the case for Na ions. The exceptional change was found in bridging oxygen (BO), where anti-bonding overlap between Si and BO was clearly seen around the top of the occupied levels and its contribution increased with increasing Na₂O content. Correlations between the experimental core-orbital energies and the theoretical electronic populations were also examined, where the best correlation was found in the case of using a total atomic population given by the sum of the net atomic population and the overlap population.

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1. Introduction

It is well known that core-orbital signals in X-ray photoelectron spectra (XPS) shift chemically according to the electronic state of a material. The reason for the chemical shift is commonly understood as a change in the chemical bonding character, that is, ionicity or covalency of a chemical bond. Charge potential model (1) is the most famous theoretical model, from which we can obtain a simplified equation (2), indicating that the chemical shift is proportional to the charge on an atom. According to the theories, O1s shift in oxide materials is interpreted as follows. When ionicity in the bonding character increases, it leads to an increase in the electronic density of oxide ions, resulting in lower binding energy shift of the O1s signal. In the case of alkali silicate glasses (3), O1s signals move to lower binding energy side with increasing the amount of alkali oxides, which is interpreted as an increase in the negative charge on oxide ions due to the increase of ionicity in the chemical bonding character.

Point charge model (4) is often used in the estimation of atomic charges, where it is assumed that charge is localized on atoms and electrons are transferred in a chemical bond according to the difference in electronegativity. When an oxygen gets electrons from a neighboring silicon, the neighboring silicon is sure to lose electrons due to charge neutrality. In this case, electronic density of the oxygen increases and that of the silicon decreases. It is consequently expected in XPS measurement that O1s and Si2p signals shift to the opposite direction. Contrary to the expectation, all the XPS signals in alkali silicate glasses move to the lower binding energy side with increasing the alkali oxide content, not excepting the alkali ions (3). The experiments suggest that electronic density of all the glass constituents increases along with the addition of alkali oxides. It is not explainable from the standpoint of ionicity such as the point charge model.

Charge sharing model on the basis of covalency seems to be required to explain the concurrent increase or decrease in electronic density of all the glass constituents. According to the concept, the chemical shift of the XPS signals is associated with the change in the amount of electrons shared between cation and anion in a chemical bond, that is, a chemical shift to the lower binding energy side is interpreted as an increase in the shared electrons due to an increase in covalent character of the chemical bond. According to the interpretation, however, the experimental chemical shift indicates that the covalency of R–O bonds also increases with increasing an alkali oxide (R_2O) content, which seems to be in conflict with the general understanding that R_2O is more ionic than SiO₂.

Neither ionicity nor covalency explains the experimental chemical shifts. Then, what is the appropriate model to explain the chemical shifts, and how does the chemical bonding character in alkali silicate system change along with the composition? In the present paper, chemical bonding state in the sodium silicate system is investigated on the basis of theoretical MO calculations to interpret the experimental observations.

2. Investigation Procedures

Three compositions were chosen to the investigation, that is, SiO_2 , $Na_2O\cdot 2SiO_2$ and $Na_2O\cdot SiO_2$. The binary glasses were prepared by a conventional melt-quenching method, and the binary crystals were also obtained by heat-treatment of the glasses. As for SiO₂, commercial products both in vitreous and crystalline states were used as specimens.

XPS measurements were carried out using a monochromatic Al-K α radiation (hv = 1486.6 eV). Fresh surfaces of the rod-shaped specimens were analyzed just after being fractured in a high vacuum ($\approx 7 \times 10^{-8}$ Pa). Neutralization of the surface charge was performed by both an electrically grounded Ni-mesh screen and a low energy flood gun (5). Binding energy was corrected by referencing the C1s signal for an adventitious hydrocarbon accumulated in the vacuum as 284.6 eV (5).

The discrete variational X α (DV-X α) method (6) was used to examine the chemical bonding states of the sodium silicates, where Mulliken population analysis (7) was adopted for the evaluation of net charge and bond overlap population. Cluster models shown in Fig. 1 were constructed from the respective crystal structures (8–10). The basis atomic orbitals used in the MO calculations are O = 1s-2p, Si = 1s-3d and Na = 1s-3d. The population analyses were done only for the atoms around the center of the clusters in order to reduce the effects of bond termination. The cluster size, that is, the number of atoms in a cluster was chosen as an objective atom was surrounded by at least two layers of SiO₄ tetrahedra. The cluster was also embedded in the Madelung potential to reduce the termination effects.

According to the Mulliken population analysis (7), ionicity and covalency of a chemical bond A–B are evaluated by net charge ΔQ_A and bond overlap population Q_{AB} , respectively given in Eqs. 1 and 2, where both quantities are commonly obtained from the sums of overlap population Q_{ij}^l given in Eq. 3.

$$\Delta Q_{\rm A} = Z_{\rm A} - Q_{\rm A}, \ Q_{\rm A} = \sum_{i \in {\rm A}} Q_i, \ Q_i = \sum_l Q_i^l, \ Q_i^l = \sum_j Q_{ij}^l$$
(1)

$$Q_{AB} = 2 \sum_{i \in A, j \in B} Q_{ij}, \ Q_{ij} = \sum_{l} Q_{ij}^{l}$$
 (2)

$$Q_{ij}^{l} = n_{l}c_{il}c_{jl}S_{ij}$$
⁽³⁾

 Q_{ij}^{l} is the partial overlap population, that is, electronic population of the overlapped region between the atomic orbitals χ_i and χ_j in the molecular orbital ϕ_l ,

which is the product of n_i : the number of electrons in MO ϕ_l (usually $n_l = 2$), c_{il} and c_{jl} : the contribution of AOs χ_i and χ_j in MO ϕ_l , and S_{ij} : the overlap integral between AOs χ_i and χ_j . In Eq. 1, Q_A is the gross atomic population or gross atomic charge on atom A, which is given by the sum of atomic orbital population Q_i . Subtracting Q_A from atomic number Z_A , that is, the number of electrons in the neutral state, the net charge ΔQ_A is obtained. It is also noted in the Mulliken population analysis (7) that the gross atomic population Q_A is given by the sum of









Fig. 1. Cluster models used in the MO calculations prepared from (a) α -cristobalite SiO₂ (7).(b) α -Na₂Si₂O₅ (8) and (c) Na₂SiO₃ (9) crystals, respectively. The numbered spheres represent oxygen atoms, 1: bridging oxygen surrounded by no Na (BO1), 2: bridging oxygen also coordinated by Na (BO2) and 3: non-bridging oxygen (NBO). The numbers of sample points are 34500, 93600 and 88800 for the respective clusters (a), (b) and (c).

net atomic population (Q_{AA}) and half of total overlap population ($\frac{1}{2}\Sigma Q_{AB}$), that is, $Q_A = Q_{AA} + \frac{1}{2}\Sigma Q_{AB}$, where Q_{AA} is given by the summation for $j \in A$ in Eq. 1,

$$Q_{AA} = \sum_{i \in A} \sum_{l} \sum_{j \in A} n_l c_{il} c_{jl} S_{ij}$$
(4)

and $\frac{1}{2}\Sigma Q_{AB}$ is equivalent to the summation for $j \notin A$ in Eq. 1.

Theoretical intensity of the X-ray photoelectron peak for an MO ϕ_l is estimated from Eq. 5 (11).

$$I_l \propto \sum_i Q_i^l \sigma_i \tag{5}$$

where Q_i^l is the partial AO population given in Eq. 1 and σ_i is the photoionization cross-section of AO χ_i (12). X-ray photoelectron spectra were simulated by assuming a Gaussian lineshape, in which σ_i s for the AOs, Si3d, Na3p and Na3d were assumed as zero because σ_i s for the AOs vacant in the ground state were expected to be negligibly small compared with those of the occupied AOs. Density of states (DOS) and overlap population diagrams were also obtained from the AO and overlap populations, respectively.

3. Results and Discussion

3.1. Validity of MO calculation

The experimental valence band (VB) spectra of the sodium silicates are shown in Fig. 2. It is seen from Fig. 2 that the crystalline silicates show almost the same spectra with the vitreous ones, and it is also the case for core-orbital spectra, indicating the similarity in electronic states between the crystalline and vitreous silicates. It is probably due to the analogy in local structure, and it is hence deduced that the evaluation with the cluster models based on the structure of silicate crystals is valid also for the silicate glasses.

The simulated VB spectra are also shown in Fig. 2, where energy was corrected to agree with the experimental ones on the peak positions. As shown in Fig. 2, the relative intensity of the peaks is also in good agreement, indicating that the simulation satisfactorily reproduces the electronic states of the silicates. Two main peaks are seen at 5-10 and 10-15 eV, and the low binding energy (BE) peak increases in both relative intensity and width with increasing Na₂O content. Contribution of AOs to the XPS spectra is estimated by comparing the XPS spectra with DOS shown in Fig. 3. The low BE peak consists mostly of O2p, in which the higher BE component is assigned to BO2p and the lower BE component is associated with NBO2p. Relative amount of the NBO2p component increases with increasing Na₂O content, resulting in the increase of relative



Fig. 2. Experimental valence band XPS spectra for the vitreous and crystalline silicates, and the theoretical spectra simulated from the cluster models.



Fig. 3. Density of states (DOS) calculated from the cluster models. Continuous and broken vertical lines indicate occupied and unoccupied levels, respectively.

intensity and width for the low BE peak.

As shown in Fig. 2, the MO calculations successfully reproduce the electronic states of valence shell region. Then, how is the core-orbital region? Fig. 4 shows the correlation in core-orbital energy between the experiments and simulations, where the theoretical energies are corrected for the same quantity as in the case of the valence shell region. The experimental binding energies for the crystalline silicates are shown in Fig. 4, and it is also the case in the subsequent figures. It is seen a good correlation between the experiments and the simulations. In particular, the plot for O1s binding energy shows an almost straight line. It should be noted, however, that the theoretical energy is corrected according to the experiments and the uncorrected energy is not valid for the comparison. In other words, MO calculation does not predict the chemical shift of XPS signals without experiments. As predicted in the theories (1,2), if the chemical shift is proportional to the atomic charge, MO calculation will be useful also in the prediction of the chemical shift.



Fig. 4. Correlation in binding energy of core-orbitals between experiments and simulations for the silicates, (a) SiO_2 , (b) $Na_2O \cdot 2SiO_2$ and (c) $Na_2O \cdot SiO_2$. Experimental data for the crystalline silicates are shown here.

3.2. Chemical bonding character

Chemical bonding character was evaluated with net charge ΔQ_A and bond overlap population Q_{AB} . Fig. 5 shows the correlation between theoretical ΔQ_A and experimental binding energy E_b of core-orbital levels. It is seen a common trend in BO, Si and Na that E_b decreases and ΔQ_A also decreases with increasing Na₂O content. However, NBO shows the opposite change. It has been generally convinced in R_2O -SiO₂ system that ionicity of the system increases with increasing R_2O content. In such case, both the negative charge on oxygen and positive charge on Si and Na should increase with increasing R_2O content. Only BO follows the expectation.

On the other hand, all the constituents, O, Si and Na commonly show the lower binding energy shift with increasing Na₂O content in both the experiment and simulation (Fig. 4). If chemical shift is ruled by atomic charge as expected from the theories (1,2), NBO is exception. In Fig. 5, if $\Delta Q_{\text{NBO}}(c)$ were smaller than $\Delta Q_{\text{NBO}}(b)$ and the plots for BO and NBO lay on a straight line, the experimental XPS chemical shift would be explained by atomic population.



Fig. 5. Correlation between net charge and binding energy of core-level XPS signals for the silicates, (a) SiO_2 , (b) $Na_2O \cdot 2SiO_2$ and (c) $Na_2O \cdot SiO_2$.

When it is assumed as another case that the XPS chemical shift is ruled by overlap population, bond overlap population Q_{AB} should increases with increasing Na₂O content. In Fig. 6, E_b is plotted against the sum of Q_{AB} , that is, total overlap population which is obtained by summing Q_{AB} over the neighbors of an atom A. In obtaining ΣQ_{AB} , the interacting atoms B were chosen assuming two cases. In the case given by the open markers in Fig. 6, all the atoms in a cluster excepting atom A were chosen for B, and in another case given by the filled markers, only the neighboring bonding atoms were chosen for B. For example in the latter case, bridging oxygen BO2 in sodium disilicate (b) is surrounded by two Si and one Na, and hence the total overlap population ΣQ_{AB} for BO2 is obtained by $2 \times Q_{Si BO2} + 1 \times Q_{Na BO2}$. As expected, ΣQ_{AB} for A = NBO, Si and Na increases with increasing Na₂O content in the both cases, indicating the increase in the valence shell population. BO is however exceptional. As shown in Fig. 5, negative charge on



Fig. 6. Correlation between sum of bond overlap population (BOP) and binding energy of core-level XPS signals for the silicates, (a) SiO_2 , (b) $Na_2O \cdot 2SiO_2$ and (c) $Na_2O \cdot SiO_2$. Open and filled markers represent sum of BOP for all the atoms in the cluster and for the neighboring bonding atoms, respectively.

BO increases with increasing Na₂O content, suggesting the increase in ionic character, that is, the decrease in overlap population of BO. Hence, the change in $\Sigma Q_{AB}(BO)$ shown in Fig. 6 seems consistent with the change in atomic charge on BO seen in Fig. 5. It is also seen a large difference in $\Sigma Q_{AB}(BO)$ between the two cases, which is due to a large anti-bonding interaction between the neighboring O–O pairs. The change in $\Sigma Q_{AB}(BO)$ against the composition is also interpreted by the chemical bonding state of BO.

Overlap population diagrams are shown in Fig. 7, in which bond overlap populations Q_{AB} are also indicated. All the bonds, except Si–BO1 and Si–BO2, increase in Q_{AB} with increasing Na₂O content. Comparing Q_{AB} for the Si–O bonds, Si–BO2, Si–BO1 and Si–NBO, Q_{AB} increases in this order. Anti-bonding overlap is clearly seen in Si–BO bonds around the top of the occupied levels even in the pure silica (a). In particular, the decrease in $Q_{Si BO2}$ is remarkable, which leads to the decrease in ΣQ_{AB} (BO) shown in Fig. 6. The structural change in the silicates is also interpreted on the basis of bond overlap population. When Na₂O is added to a silicate, electrons are introduced into the MO levels around the top of the occupied levels. Then, Si–BO bonds decrease in overlap population due to the increase in anti-bonding overlap, resulting in the elongation and dissociation in Si–BO bonds. Covalency in Si–NBO bonds seems much higher than Si–BO bonds (13). As shown in DOS (Fig. 3), Si3d and NBO2p orbital populations overlap each other, resulting in the formation of π -bonding.



Fig. 7. Overlap population diagrams calculated from the cluster models. The continuous and broken lines indicate bonding and anti-binding overlap, respectively. The numerical values shown indicate bond overlap population, Q_{AB} .

3.3. Chemical shift of core-level XPS signals

In the Mulliken population analysis (7), gross atomic population Q_A is given by $Q_{AA} + \frac{1}{2}\Sigma Q_{AB}$, where Q_{AA} is the net atomic population and ΣQ_{AB} is the total overlap population. Large negative charge on oxygen means high gross atomic population. The negative charge on NBO in metasilicate (c) is much smaller than disilicate (b) (Fig. 5), while the total overlap population of NBO is slightly larger (Fig. 6). The small negative charge on NBO(c) is, therefore, due to low net atomic population, that is, small amount of electrons localized on NBO. It is said in general that NBO carries much lone pair electrons than BO, suggesting the higher net atomic population of NBO. As opposed to the expectation, NBO in metasilicate has lower net atomic population than BO. Overlap population also contributes to gross atomic population, where total overlap population is divided into halves to conserve the total amount of electrons. Evaluating the contribution of overlap population to the XPS chemical shift not in half but in full, the total atomic population of NBO in metasilicate becomes higher than that of BO. The total atomic population (AP) of an atom A is given by $Q_{AA} + \Sigma Q_{AB}$. Fig. 8 shows the correlation between the total AP so determined and the experimental XPS chemical shift. Except for oxygen in metasilicate (c), a linear correlation (dotted line in Fig. 8) is seen for oxygen in pure silica (a) and disilicate (b). Si2p also



Fig. 8. Correlation between total atomic population (AP) $Q_{AA} + \Sigma Q_{AB}$ and binding energy of core-level XPS signals for the silicates, (a) SiO₂, (b) Na₂O·2SiO₂ and (c) Na₂O·SiO₂.

shifts linearly against the total AP.

As mentioned, the results shown in the figures are only for the atoms around the center of the clusters because it was expected that the outer atoms received much bond termination effect than the inner atoms. Actually, oxygen atoms have larger negative charge as they separate from the center, indicating that the results are strongly dependent on the size and shape of the clusters. If different atomistic configuration were used for the cluster model for sodium metasilicate (c), the better correlation might be achieved. Even in the case, it should be kept in mind that the present model for the sodium metasilicate (Fig. 1) gave good agreements both in the valence and core-orbital regions (Figs. 2 and 3). In the original theoretical model (1), the XPS chemical shift is given by a change in electrostatic potential q/r, where q is charge and r is radius. In the approximation (2), however, r is treated as constant. In the present study, only the q dependence has been investigated. The results obtained may suggest that the r dependence is not negligible.

4. Conclusion

The chemical bonding states of sodium silicates, pure silica, disilicate and metasilicate were investigated on the basis of theoretical MO calculations. The theoretical expectations were compared with the experimental observations in XPS. The simulations were in good agreement with the experiments both in the valence band spectra and the atomic core-orbital energies of all the constituents.

Except for NBO, the net charge of BO, Si and Na decreased and the gross atomic population increased with increasing Na₂O content, which was opposed to the general empirical knowledge that ionic character would increase along with the addition of alkali oxides. In the case of covalency, however, an exceptional change in the overlap population was found not in NBO but in BO, that is, the overlap population of BO decreased with increasing Na₂O content, which was due to the increase in anti-bonding contribution in Si-BO bonds. The structural change in silicate was, however, consistent with the theoretical estimation in the chemical bonding character, that is, Si-BO bonds have longer bond distance than Si–NBO bonds and they grow in bond distance with increasing Na₂O content. The chemical shift of core-orbital binding energies was also discussed on the basis of atomic and overlap populations. In the Mulliken population analysis of gross atomic population, half of the overlap population is added to the net atomic population. Assuming full contribution of the overlap population, the best correlation was obtained between the experimental chemical shift and the theoretical total atomic population.

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