

Comparison with solubility of alkaline earth metal oxides by using DV-X α method

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Abstract : The molecular orbital calculation for alkaline earth metal oxides (MgO, CaO, SrO and BaO) was carried out using the discrete variational X α method. For the model cluster of bulk state, the order of magnitude for band gap obtained from calculation agreed with that of reference value, and distribution of these points was linear. Besides, the solubility of these compounds is discussed by using three model clusters. One is surface model, the others are hydration models. It is found that the difference of orbital energy between LUMO of compound and HOMO of water is related to the solubility of these compounds from calculation of surface model. Hydration is represented by coordinating OH ion or H₂O on their surface. And the five models with different height of water coordination are calculated. When OH ion approaches to surface, the bond O-H was strengthened. On the other hand, when H₂O approaches to their surface, the bond O-H in water was weakened. From these results, H₂O should bring about dissociative adsorption. The differential total overlap population between hydrated and unhydrated states (surface model) related to the solubility of compound.

Key words : DV-X α method, differential total overlap population, solubility, alkaline earth metal oxides, LUMO

1. INTRODUCTION

DV-X α method, which is one of calculation method of quantum chemistry, has applied to understanding property of inorganic materials due to development of computer. Feng et al.¹⁾ have applied DV-X α method to cement compounds. But calculation results as band gap are not valid. And we also have attempted to estimate for hydraulic activity of cement compounds²⁾. In the past paper, difference of total overlap population as indication of covalent bond between hydrated and unhydrated states should be available for estimation of hydraulic activity. But it is not clear that this evaluation procedure is enough. Then solubility for alkaline earth metal oxides with NaCl type structure is discussed as typical case. The order of solubility to water for alkaline earth metal oxides is MgO < CaO < SrO < BaO. In this paper, the purpose is the establishment of estimation procedure for hydraulic activity (solubility) by DV-X α method.

2. CALCULATION METHOD

Alkaline earth metal oxides with NaCl type structure, MgO, CaO, SrO and BaO are calculated using M₁₄O₁₃ (M=Mg, Ca, Sr and Ba) model cluster. The point charges are distributed at virtual atomic site around the cluster. The number of point charge is about 2000 points. Total charge of cluster and point charges is zero.

2-1 Bulk model

The validity of cluster was discussed by com-

parison with band gap between calculation results and reference value. The bonding state as covalent bond and ionicity are studied. The magnitude of covalent bond was evaluated from the overlap population, which is measure of overlap between orbitals.

2-2 Surface model

Displacing the end of point charges to end of cluster, the end of cluster is regarded as surface. In this paper, the calculation is performed about (001) plane (Fig.1).

Bonding state of the first layer (surface) was treated as covalent bond. Besides wave function of the lowest unoccupied molecular orbital, LUMO, is obtained owing to consider relationship between surface state and the solubility. The difference of orbital energy (ΔE) between the highest occupied molecular orbital, HOMO, of water and LUMO of compound was calculated.

2-3 Hydrated model

Water (OH ion or H₂O) was arranged above centered metal atom (Mc) with the surface (Fig.1). The distances between oxygen atom (Oh) in water and Mc were those of 0.95, 1.0, 1.1, 1.3 and 1.5 times of standard distance. The standard distance represents the sum of ionic radii of each metal atom with coordination number 6 and oxygen atom with coordination number 2.

At first, when water approaches to surface, bonding state (overlap population) of O-H in water

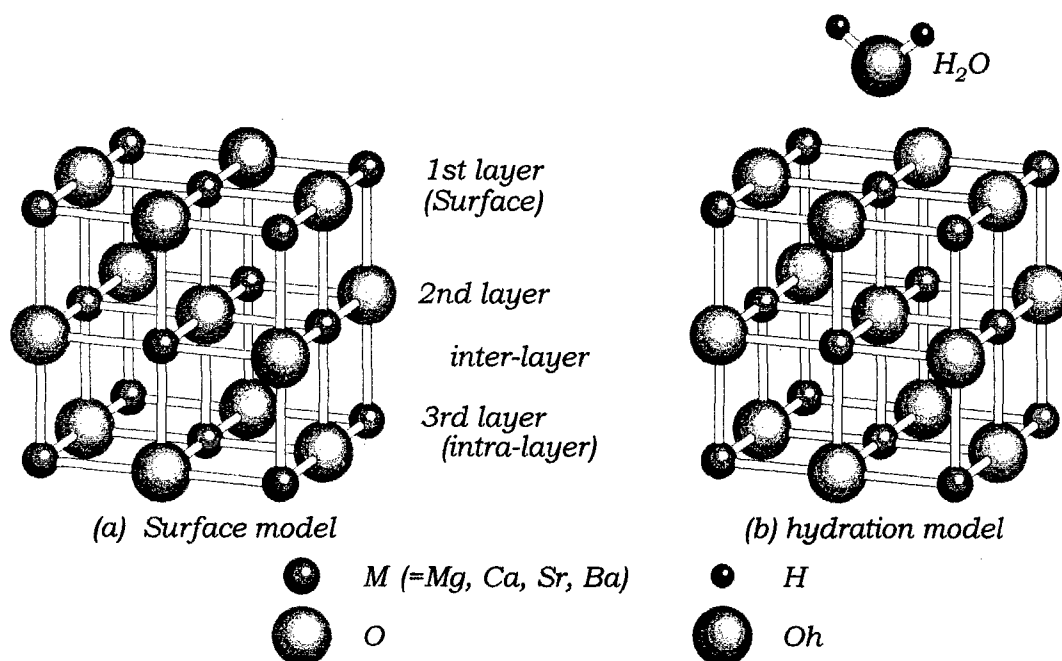


Fig.1 Model cluster $M_{14}O_{13}$ ($M=Mg, Ca, Sr$ and Ba) for calculation.

was discussed. Secondly, changes in overlap population of $Mc-O_h$ with distance of $Mc-O_h$ were obtained to consider the adsorption of water. Finally, bonding state of compound was discussed by means of differential total overlap population (ΔTOP), which is the difference of bond strength between hydrated and unhydrated states (surface model).

3.RESULTS AND DISCUSSION

3-1 Bulk state

The relationship between band gap obtained from the calculation and reference value³⁾ is shown in Fig.2. The results were calculated larger than reference for all compounds. But the order of magnitude for calculated band gap agreed with that of reference value, and the distribution of these points in Fig.2 was linear. Besides main component of molecular orbital for valence band was oxygen 2p orbital for all compounds, characteristic of oxide clearly appeared in band structure. From the results, it was found that this calculation method is applicable to these compounds, and model cluster $M_{14}O_{13}$ is available.

Overlap population (OP) of $M-O$ decreased with increasing the atomic number of metal (Table I). That is, MgO and BaO have high and low covalency, respectively. OP of SrO and BaO was negative value, ionicity of both compounds was expected high. From net charge, SrO and BaO were also found high ionicity. In this way, it was found that compound with high ionicity would have high solubility.

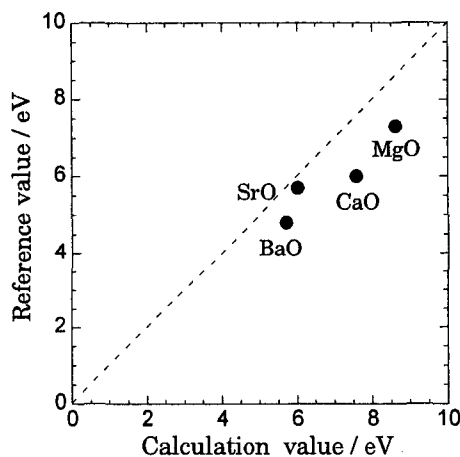


Fig.2 Relationship between calculation values and reference values for band gap.

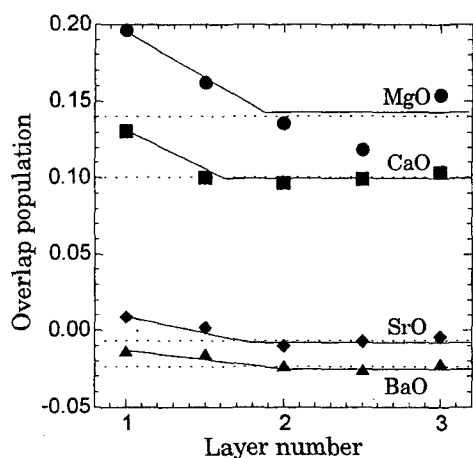
3-2 Surface state

The magnitude of overlap population for each layer is shown in Fig.3. Layer number 1, 2 and 3 represent intra-layer, and 1.5 and 2.5 represent inter-layer (Fig.1). OP of layer number 3 was same as that obtained from bulk model. From this result, the third layer can be regarded as bulk state. The OP of first layer (surface) was larger than that of below second layer for all compounds. MgO had the most increment of OP, and the bond $Mg-O$ was strengthened. To the contrary, BaO had the least increment of OP, the bond $Ba-O$ was not appreciably strengthened. The bond strengthening

Table I Overlap population and ionicity of bulk state

	MgO	CaO	SrO	BaO
OP of M-O	0.140	0.100	-0.006	-0.023
Ionicity of M and O	67.9	63.7	88.1	90.0

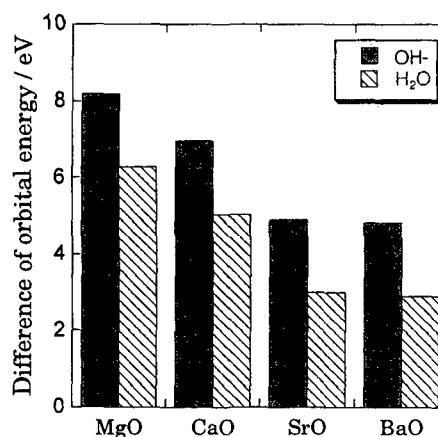
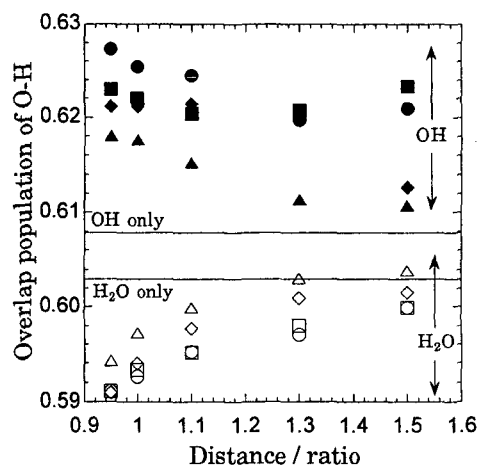
OP : overlap population

**Fig.3** Changes in overlap population M-O (M=Mg, Ca, Sr and Ba) with layer number. Layer number 1 represents surface. Broken lines show OP of bulk state for each compound.

at surface (first layer) should relate to solubility.

Net charge of the atom in first layer (coordination number 5) was almost the same as that of bulk (coordination number 6) for all compounds. This means that when surface is appeared, joint electron is separated in halves. Then the net charge of the surface atom should be kept that of the atom with 6-coordination number.

Lone pair electron of water would need to attack the lowest unoccupied molecular orbital (LUMO) of compound as the start of solution. Then spread of LUMO and difference of orbital energy between LUMO of compound and HOMO of water were discussed. The spread of LUMO had not enough relationship with solubility. The difference of orbital energy (ΔE) between LUMO of compound and the highest occupied molecular orbital (HOMO) of water is shown in Fig.4. Energy level was corrected on the basis of oxygen 1s orbital for all compounds. It was confirmed that oxygen 1s orbital does not form hybrid orbital with other orbital. LUMO of BaO was more close to HOMO of water than that of MgO. BaO was seemed to be easily accepted lone pair electron of water. The order of ΔE was corresponded with the order of solubility. This ΔE should be equivalent to activation energy for hydration. The ΔE of H_2O was smaller than that of OH ion for all compounds.

**Fig.4** Difference of orbital energy between HOMO of water and LUMO of compound.**Fig.5** Changes in overlap population of O-H in water with height of OH ion or H_2O from surface. Distance represents ratio based on sum of ionic radii for metal atom and oxygen. \circ , \bullet : MgO, \square , \blacksquare : CaO, \diamond , \blacklozenge : SrO, \triangle , \blacktriangle : BaO

3-3 Hydrated state

Changes in the overlap population of O-H in water with coordinated height are shown in Fig.5. The distance was represented as the ratio based on the sum of ionic radii for metal atom and oxygen. When water (H_2O or OH ion) approached to surface, the bond of O-H in H_2O and OH ion were weakened and strengthened, respectively. This result would

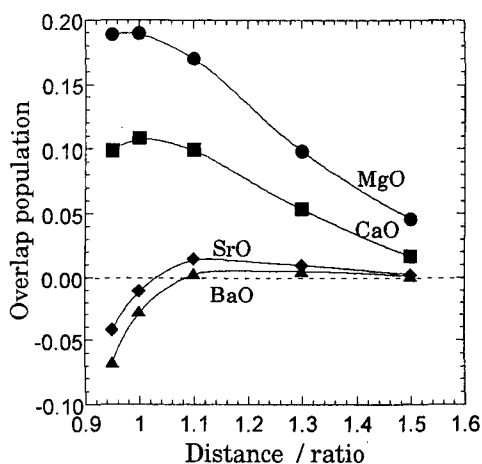


Fig. 6 Changes in overlap population of Mc-OH with height of OH ion from surface. Mc and Oh represent metal ion coordinated OH ion and oxygen in OH ion, respectively. Distance represents ration based on sum of ionic radii for metal atom and oxygen.

represent that H₂O dissociatively adsorbed and OH ion was stable on the surface. From this result, OH-model should be important in comparison with H₂O-model in estimation of hydration.

Changes in overlap population of Mc-OH with coordinated height are shown in Fig. 6. Mc and Oh represent metal atom at center of surface and oxygen of water, respectively. For SrO and BaO, overlap populations were very small, it was found that ionic bond is formed. On the other hand, for MgO and CaO overlap populations were relatively large, OH ion would chemically adsorb on the surface. The compound, whose bond of Mc-OH is ionic, would have high solubility.

The differential total overlap population (Δ TOP), which is the difference of bond strength between hydrated and unhydrated states, is shown in Fig. 7. Δ TOP was discussed at the distance where overlap population of Mc-OH is maximum. That is, the distance (ratio) of Mc-OH is 1.0 for MgO, 1.0 for CaO, 1.1 for SrO and 1.1 for BaO. Δ TOP of MgO and CaO was positive value, and the bond was strengthened. On the other hand, Δ TOP of SrO and BaO was negative value, and the bond was weakened. The order of Δ TOP was corresponded with the order of solubility. In this way, change in bond strength in hydration should relate to solubility. From above results, it was found that Δ TOP was available for the estimation of solubility.

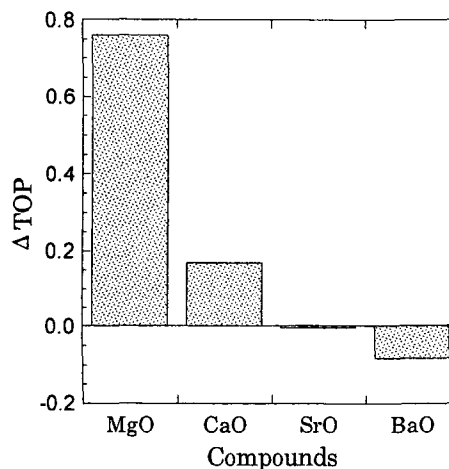


Fig. 7 Δ TOP of each compound for model coordinated OH ion at surface. Coordinated height is standard distance for MgO and CaO, is 1.1 times standard distance for SrO and BaO. Δ TOP represents value subtracted TOP of unhydrated state from that of hydrated state.

4. CONCLUSION

DV-X α method was applied to the property of solubility behavior of alkaline earth metal oxides. The results are summarized as follows;

- 1) The band gaps obtained from calculation agreed with reference values.
- 2) For surface model, overlap population of the first layer was larger than that of inner layer. The bond strengthening at surface (the first layer) should relate to solubility.
- 3) LUMO of BaO is more close to HOMO of water in comparison with that of MgO. Thus BaO should be easily accepted the lone pair electron of water.
- 4) Change in bond strength (Δ TOP) in hydration should relate to the solubility. Δ TOP is available for the estimation of solubility (hydration).

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