Effects of Reduced Coordination Number for Ca on the Electron Redistribution during Ca−O−Si Bridge Bonding from CaO or $Ca(OH)_2$ and SiO_2

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The discrete variational Xα method has been conducted to elucidate the formation of a heterobridging bond (HBB), Ca−O−Si, when a Si−O pendant bond of SiO_2 comes close to the Ca atom on the surface of calcium oxide or hydroxide. A decrease in the coordination number for Ca in CaO or $Ca(OH)_2$ increases the electron population density (PD) between Ca and O, and decreases the PD between Si and O. These simultaneous changes in PD favor the formation and stabilization of a Ca−O−Si HBB. The calculated results agree well with the experimental observation of precursor formation toward calcium silicate during milling of a mixture of $Ca(OH)_2$ and SiO_2.

1. Introduction

A mechanochemical process represented by milling a mixture has several unique features which are often superior over thermal processes.[1] First, local plastic deformation derived from shear stress at contact points of two particles results in structural disorder or partial amorphization,[2] and thus creates low coordinated (LC) atoms. These LC atoms have peculiar energy states which lead to reactivity higher than that of fully coordinated atoms in bulk.[3] Furthermore, atoms at the contact point of dissimilar particles under mechanical stress can approach so close to each other that chemical reaction can occur rapidly. The solid-state surface reaction mentioned above is accompanied by simultaneous dehydration when oxide with rich surface OH groups or hydroxides are involved.[4] This phenomenon is coined as mechanochemical dehydration, which is unique in the process of milling such a mixture. No dehydration is observed by milling $Ca(OH)_2$ or $Mg(OH)_2$ separately.[1]

During milling a mixture of metal oxides or hydroxides, e.g., a system comprising calcium hydroxide, $Ca(OH)_2$, and silica, SiO_2, we observe Ca−O−Si heterobridging bond (HBB) formation with simultaneous dehydration.[1] This leads to a highly reactive precursor toward a final product, i.e., calcium monosilicate on subsequent heating. Similar phenomena are observed between $Mg(OH)_2$ and TiO_2, or many other systems.[5−8]

Formation of a HBB requires a charge transfer between dissimilar metallic species across an oxygen atom between them.[9] We further proposed a principle of electronegativity equalization between two different metal atoms, M and M′, abridged by a central O atom,[10] when the coordination number (CN), n, of the construction unit of the oxide or hydroxide, MO_n or $M(OH)_n$, decreases from that of a perfect crystal, e.g., $n = 6$ in CaO or $Ca(OH)_2$ or $n = 4$ in SiO_2.

We examined binding energies of Si 2p electrons by X-ray photoelectron spectroscopy (XPS) for a milled mixture of $Ca(OH)_2$ and SiO_2, and found that only near surface Si atoms were reduced.[1] If the charge transfer from $Ca(OH)_2$ to SiO_2 occurs to form the Ca−O−Si HBB, some corresponding oxidation, i.e., the change of the valence number of Ca in $Ca(OH)_2$, must be postulated. However, we did not observe any valence change of Ca from XPS spectra of Ca 2p.[1] We therefore suggested that charge transfer from Ca to Si occurs due to electron redistribution, via a change of the CN for Ca, instead of the valence change of Ca. In this study, we try to examine whether and to what extent M−O−M′ bridging bonds are formed and stabilized with a decrease of CN by means of the electron population density (PD). The calculation is based on the discrete variational Xα (DV-Xα) method.[11,12]

The calculation in this study has two goals, i.e., (1) to calculate the overlap population or population density (PD) between Ca and O as well as Si and O when a Si−O pendant bond comes close to the Ca atom on the surface of CaO and the electron density redistribution in a Ca−O−Si unit as a criterion of the complex formation and (2) to elucidate the feasibility of mechanochemical dehydration by calculating the overlap population between O and H from the oxygen atom of $Ca(OH)_2$ and hydrogen atom from surface silanol groups. For both cases, we paid special attention to account for the effects of the decrease of CN for Ca on the formation of Ca−O−Si bonds.

2. Method of Calculation

2.1. Ca-O−Si Bridging Bond Formation at a CaO/SiO$_2$ Contact Point. A model of the CaO/SiO_2 interface between two model clusters, $CaO_x^{(2x-2)-}$ and SiO_4^{4-} (Figure 1), is adopted to calculate the electron density distribution of the cluster and the overlap population analysis. A self-consistent charge (SCC) method,[11] which creates a Coulomb potential around a molecule by combining spherical atomic potentials, was used to obtain the Coulomb potential of the whole cluster. For the purpose of better convergence of regression, the shape of the atomic orbital function was modified from infinite to finite. This was done by adding a finite well potential centered

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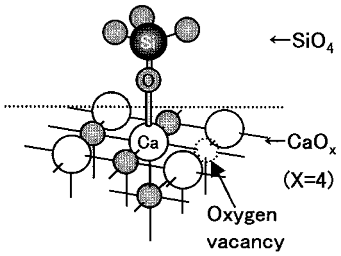

Figure 1. $CaO_x^{(2x-2)-}-SiO_4^{4-}$ cluster calculated for the $CaO-SiO_2$ interface.

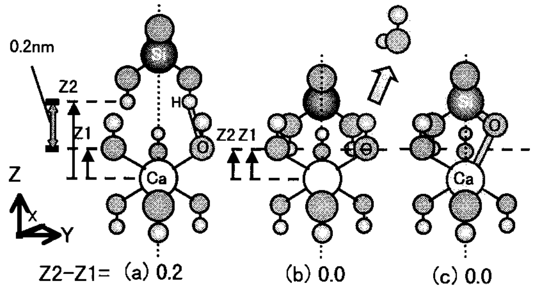

Figure 2. $Ca(OH)_6^{4-}-SiO_4H_2^{2-}$ cluster calculated for the $Ca(OH)_2-SiO_2$ interface: (a) the difference in the Z coordinates, $Z2-Z1$, is 0.2 nm, (b) $Z2-Z1 = 0.0$ nm. (c) $Ca(OH)_x^{(x-2)-}-SiO_4H_1^{3-}$ cluster after the dehydration at $Z2-Z1 = 0.0$. A Ca−O−Si bond is formed.

at each atom. To minimize the skew of the potential, and to reproduce the electronic structures for CaO and SiO_2, we chose the value of the well potential radius to be 2.0 ± 0.2 atomic units. We chose the depth as −2.0 hartrees as the smallest absolute value within the conversion limit. Since the orbital energy can be calculated within an error limit of 0.1 eV for the valence band area with 300 sample points,[12] we used 500 sample points per atom in a cluster. The molecular orbitals for these clusters were constructed by a linear combination of atomic orbitals (LCAO). The atomic orbitals used in these calculations were 1s−4p for Ca, 1s−3d for Si, 1s−2p for O, and 1s for H, which were numerically calculated for atomic Hartree−Fock equations. The electron density was evaluated from Mulliken population analysis.[13]

At the end of the atomic array in the cluster, 54 potential atoms and about 2000 point charges were laid around the CaO cluster. This was done for two reasons, i.e., (i) to suppress implausible spreads of molecular orbitals in a periodical atomic array in a CaO crystal and (ii) to take an electron cloud of the neighboring atoms into account. Around the SiO_2 cluster, only 150 potential atoms were laid, merely to terminate the pendant bonds. The number of potential atoms was determined to account for the Madelung potential within the radius of 1 nm. Reduction of the CN was manipulated by taking out one of the nearest neighbor O^{2-} ions with respect to the center atom to obtain the state of $x = 4$, as shown in Figure 1. Likewise, $x = 3-1$ clusters were constructed.

2.2. Mechanochemical Dehydration Reaction between Ca(OH)$_2$ and Surface Silanol. $Ca(OH)_6^{4-}$ and $SiO_4H_2^{2-}$ clusters, shown in Figure 2a,b, were brought into contact, and the overlap population between the oxygen atom from $Ca(OH)_2$ and the hydrogen atom from silanol was examined. To distinguish and clarify the role of each atom, a mirror plane common to the two clusters was provided to give C_s symmetry. For the purpose of rational conversion, a well potential depth for Ca was chosen to be −4.0 hartrees. All other conditions were the same as those adopted in section 2.1. Madelung potential atoms were again distributed within the spherical space of the radius not smaller than 1 nm, with their net charge being zero. To fulfill these conditions, 772 potential atoms were laid around the $Ca(OH)_2$ cluster, with the radius from the cluster center being 1.47 nm. For the silica cluster, a high-temperature crystobalite structure was adopted and 254 potential atoms were laid within the radius of 1.25 nm. The Z axis is defined in Figure 2. The distance between the oxygen atoms from the $Ca(OH)_6^{4-}$ cluster and hydrogen atoms from the $SiO_2(OH_2)^{2-}$ cluster, i.e., the difference between the Z coordinate of the two clusters, was varied between 0 and 0.4 nm.

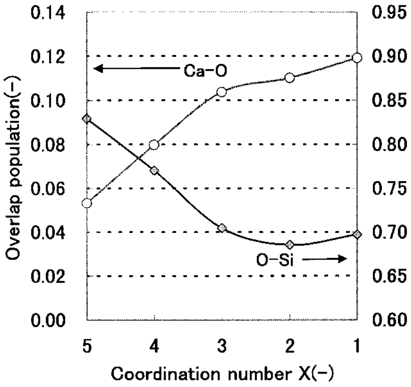

Figure 3. Bond overlap population between Ca and O, and O and Si in the $CaO_x^{(2x-2)-}-SiO_4^{4-}$ cluster.

We further calculated the overlap population between two clusters to examine the effect of the low coordination state for a Ca atom (Figure 2c). One cluster was $Ca(OH)_x^{4-}$ with some OH groups deleted, and the other $SiO_4H_y^{2-}$, with some hydrogen atoms deleted. All the remaining conditions were the same as those adopted in section 2.1. The difference in the Z coordinate between these defect-containing clusters was fixed at zero.

3. Results

3.1. Ca−O−Si Bond Formation in the System CaO−SiO$_2$. When an O atom from the SiO_4^{4-} cluster comes close to a Ca atom in the $CaO_x^{(2x-2)-}$ cluster, the PD between Ca and O increases with decreasing CN for Ca up to $x = 3$, with a simultaneous decrease in the PD between Si and O, as shown in Figure 3. The changes at x below 2 are small but in the opposite direction for Si−O. This is yet to be explained but seems not particularly significant, since the CNs of less than 2 are unrealistic for CaO in an actual solid state.

The contour maps of one of the molecular orbitals bonding Ca, O, and Si are shown in Figure 4. These maps exhibit the increase in the overlapping of the bonding orbital between Ca and O and corresponding increase in the electron density between Ca and O at $x = 4$, compared with those at $x = 5$. All the results shown in Figures 3 and 4 consistently demonstrate that, with decreasing CN for Ca, the electronic interaction between Ca and O increases and that between Si and O decreases. This makes the electron densities around Ca−O and Si−O come closer to each other, and, hence stabilizes the Ca−O−Si bridging bonds, in accordance with our experimental results reported previously.[1]

In the present calculation, oxygen vacancies were introduced by deleting O^{2-} ions. Therefore, there is no contribution of electrons trapped in the oxygen vacancy to the change of the PD between low coordinated Ca and O. Indeed, PD between low coordinated Ca and O had changed by use of the neutral oxygen vacancy in our preliminary calculation. We, therefore, disregarded the effect of electrons trapped at the oxygen vacancies.

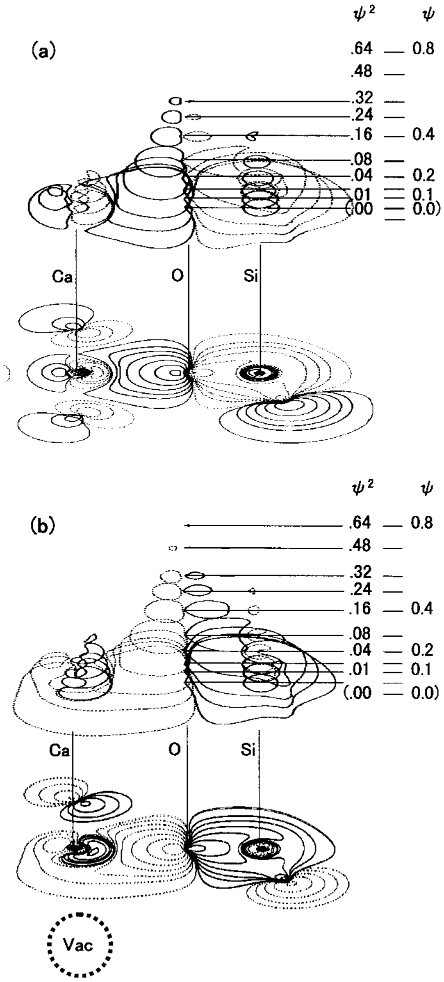

Figure 4. Contour maps of the bonding molecular orbitals for Ca, O, and Si in the $CaO_x^{(2x-2)-}-SiO_4^{4-}$ cluster and the amplitude of their wave function ψ. Different lines represent different phases; (a) $x = 5$ (surface). (b) $x = 4$ (surface with an oxygen vacancy).

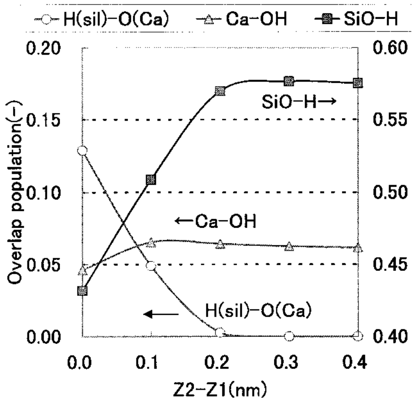

Figure 5. Bond overlap population between $H(X1,Y1,Z1)$ and $O(X2,Y2,Z2)$ in the $Ca(OH)_6^{-}-SiO_4H_2^{2-}$ cluster at $Z2-Z1 = 0$, H−O length 0.1 nm.

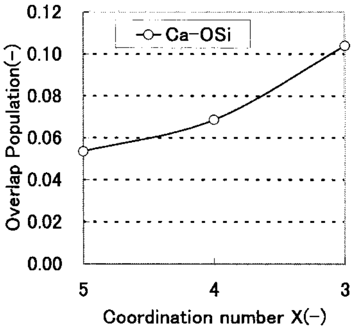

Figure 6. Bond overlap population between Ca and O in the $Ca(OH)_x^{(x-2)-}-SiO_4H_1^{3-}$ cluster.

3.2. Dehydration in the System $Ca(OH)_2-SiO_2$. As the distance between the $Ca(OH)_6^{4-}$ and $(SiO_4H_2)^{2-}$, $Z2-Z1$, defined in Figure 2, decreases, the PD between an O(Ca), i.e., the oxygen atom from $Ca(OH)_2$, and a H(sil), the hydrogen atom from the surface silanol, increases, as shown in Figure 5. At the same time, those between Ca and O within a formula unit $Ca(OH)_2$, and between O and H of the surface silanol unit, decrease. These synchronized changes clearly favor the formation of a new bond between the oxygen atom of $Ca(OH)_2$ and the hydrogen atom from silanol, with a simultaneous weakening of the two bonds in a reactant mixture, i.e., Ca−O and SiO−H. This favors our postulation that a water molecule is formed from $Ca(OH)_2$ and surface silanol, leading to a dehydration which was observed during mechanochemical processes.[1]

3.3. Bridging Bond Formation in the System $Ca(OH)_2-SiO_2$. According to the present calculation, the decrease of CN for Ca contributes to the Ca−O−Si HBB formation, but not to the dehydration itself. The increase in the PD between Ca and O in $Ca(OH)_2$ with decreasing CN for Ca might seem to hinder the OH desorption from Ca necessary for the dehydration. Nevertheless, we further calculated the PD between Ca from $Ca(OH)_2$ and O from silanol, in the cluster shown in Figure 2c, to represent one of the positions of atoms possibly found at the $Ca(OH)_2-SiO_2$ interface after dehydration. As shown in Figure 6, the PD between Ca from $Ca(OH)_2$ and O from silanol in Figure 3 still increases with decreasing CN for Ca in $Ca(OH)_2$. The tendency is the same as that in the system $CaO-SiO_2$.

4. Discussion

4.1. Electronegativity Equalization between Ca and Si. First, we will refer to electronegativity equalization between Ca and Si atoms in the present systems. Electronegativity is usually defined as the magnitude for a neutral atom to pull one electron. According to Pauling, the electronegativities of Ca and Si are 1.0 and 1.8, respectively.[14] When an atom forms a bond with another atom, however, charge transfer occurs to change the electronegativity from conventional ones.[15]

In our calculation, the PD between Ca and O, which is significantly lower than that between Si and O, increases with decreasing CN for Ca. Provided the increase in PD between Ca and O is attributed to the increase in the electronegativity of Ca and O atoms, the electronegativity of Ca must be higher by decreasing the coordination number. Formation of a Ca−O−Si HBB is, then, accompanied by the dissipation of the excess electronegativity. Thus, the electonegativity changes again toward equalization between those of Si and Ca. This speculation, however, should further be examined.

4.2. Origins of the Increase of the PD between Ca and O. The reason for the easier formation or stabilization of Ca−O−Si bridging bonds with decreasing CN for Ca is explained as follows. Ca−O bonds are fairly ionic. The degree of ionicity is reported to be 0.85 in a calcium oxide crystal,[16] although it is still a matter of controversy.[17] The high ionisity of a Ca−O bond is mainly attributed to the large energy difference between the valence electrons, i.e., those in Ca 4s orbitals and in O 2p orbitals. These electrons are known to be responsible for the bond formation between Ca and O, even in a hypothetical molecule such as CaOH.[18] Therefore, most of the electrons in Ca atoms are transferred to O 2p, forming Ca^{2+} and O^{2-} ions.

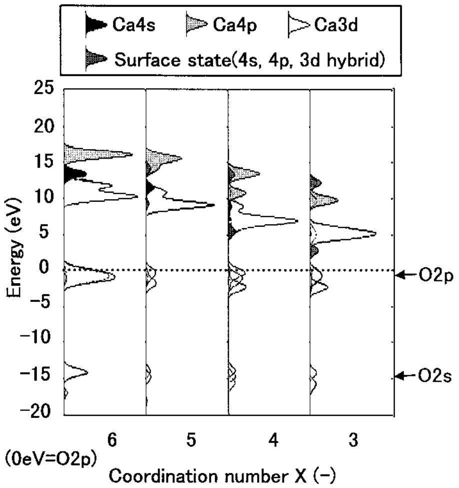

Figure 7. Density of states for the $CaO_x^{(2x-2)-}$ cluster.

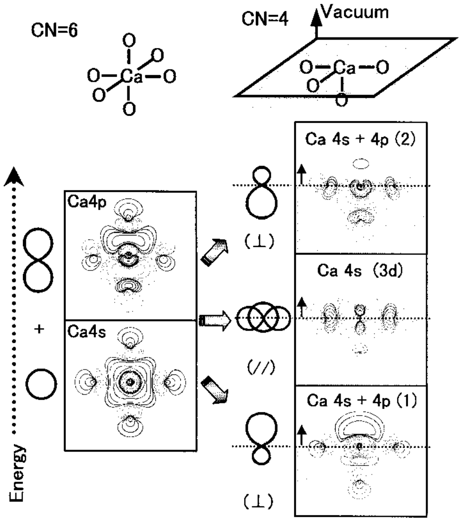

Figure 8. Contour maps of unoccupied molecular orbitals dominated by Ca 4s in the $CaO_x^{(2x-2)-}$ cluster.

In a calcium oxide crystal, the difference in the valence energy for the two ions forms the large band gap,[15] where the Madelung potential makes O^{2-} levels more stable and Ca^{2+} levels less stable. The value of the band gap is estimated in various studies, e.g., 5.5, 6.31, or 7.72 eV.[16,20,21]

However, when defects are incorporated, the CN of the atoms adjacent to the defects becomes smaller and the Madelung constant for the atoms decreases due to the partial disappearance of the surrounding atoms. Thus, the Madelung potential around the LC atoms becomes lower.[22] As a consequence, the electronic energy of 4s, 4p, and 3d orbitals for surface Ca atoms decreases with decreasing CN, as shown in Figure 7.

4.3. Surface Energy State. Furthermore, since atoms are subject to asymmetric Madelung potential at the surface, only Ca 4s and Ca 4p orbitals perpendicular to the surface make hybrid orbitals to stabilize those electrons, as shown in Figure 8. In a CaO crystal, those orbitals are generally orthogonal with each other when the calcium atoms are fully coordinated. With higher symmetry, hybridization becomes less likely and dissolution of degeneration tends to occur.[19] The lower energy states become lowest unoccupied molecular orbitals (LUMOs) for the clusters. These peculiar orbitals are specific to LC atoms and responsible for the surface state. The energy difference between a highest occupied molecular orbital (HOMO) and a LUMO corresponds to the band gap made from the oxygen 2p HOMO and the LUMO for the surface state. Thus, the effective valence levels of Ca^{2+} and O^{2-} come closer to each other, as shown in Figure 7. Consequently, hybridization of these Ca and O orbitals takes place in the surface state, where 4s orbitals predominantly contribute. When the surface Ca atom with lower CN combines with an O atom from the SiO_2 surface, the stabilized energy level of Ca with a smaller energy difference with respect to O 2p triggers a further hybridization between the orbitals of Ca and those of O, resulting in the formation of a chemical bond with higher covalency.

If surface relaxation and rumpling are taken into consideration, the electronic structure shown in Figure 7 may change considerably.[19,22] In this study, however, we do not take any surface relaxation into account since the degree of relaxation and related displacement of atoms during milling are not available.

4.4. Mechanism of Mechanochemical Reaction at the Contact Point. We have suggested hitherto that the increase of the PD between Ca and O in $Ca(OH)_2$ with decreasing CN may hinder the OH desorption from Ca necessary for the dehydration. According to our present calculation, however, the PD between Ca from $Ca(OH)_2$ and O from silanol in Figure 2c still increases with decreasing CN for Ca in $Ca(OH)_2$. Therefore, we suppose that the decrease of the CN in the $Ca(OH)_2-SiO_2$ system also causes an increase in the covalency of the Ca−O bond, stabilizing a Ca−O−Si bridging bond. This favors the formation of a Ca−O−Si HBB. This further explains why a $Ca(OH)_2-SiO_2$ mixture becomes more reactive in the mechanochemical process, which induces the energy state of LC atoms, e.g., the 4-fold coordinated Ca atoms against 6-fold coordinated ones in bulk.

The scheme discussed above is realized under two conditions. One is the decrease in the distance between Ca and O on the surfaces of $Ca(OH)_2$ and SiO_2, respectively, to the order of a few angstroms. The bond length between Ca and O in a calcium oxide or hydroxide lattice is 2.4×10^{-10} m.[23] The other is that the Ca atoms are low coordinated when a Ca atom comes close to an O atom. These conditions are met automatically when we mill a mixture of $Ca(OH)_2$ and SiO_2. During milling of a mixture, two dissimilar particles encounter repeatedly, whereby shear stress at the local contact point can easily reach the regime of gigapascals. This results in the creation of a nascent surface with simultaneous severe microplastic deformation.[3,24] As a result, an energy state of low CN is created everywhere around the dislocations or vacancies just created, and atomic transport called mechanical diffusion takes place, as is quite popular in the area of mechanical alloying.[25] Thus, those atoms at the contact point of dissimilar particles, i.e., Ca, Si, and O, have high enough probability to react with each other during milling of a mixture, without the aid of thermal excitation.

5. Conclusion

In the course of milling a mixture, bridging bonds, Ca−O−Si, are formed either from CaO and SiO_2 or from $Ca(OH)_2$ and SiO_2. The covalency increases between Ca and O, while it decreases between Si and O. These simultaneous changes favor the stabilization and further formation of Ca−O−Si bridging bonds with simultaneous dehydration, particularly when a mixture contains hydroxides.

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References and Notes

(1) Watanabe, T.; Isobe, T.; Senna, M. *J. Solid State Chem.* **1996**, *122*, 74.

(2) Smekal, A. In *Warmfeste und korrosionsbeständige Sinterstoffe*; Benesobsky, F., Ed.; Metallwerk Plansee: Reutte, 1956.

(3) Satoko, C.; Tsukada, M.; Adachi, H. *J. Phys. Soc. Jpn.* **1978**, *45* (4), 1333.

(4) Senna, M. *Solid State Ionics* **1993**, *63/65*, 3.

(5) Liao, J.-F.; Senna, M. *Solid State Ionics* **1993**, *66*, 313.

(6) Baek, J.-G.; Gomi, K.; Watanabe, T.; Isobe, T.; Senna, M. *Mater. Sci. Forum* **1997**, *235/238*, 115.

(7) Baek, J.-G.; Isobe, T.; Senna, M. *J. Am. Ceram. Soc.* **1997**, *80*, 973.

(8) Senna, M. *Trans. Inst. Chem. Eng.* **1998**, *76*, 767.

(9) Senna, M.; Isobe, T. *Solid State Ionics* **1997**, *101/103*, 71.

(10) Watanabe, T.; Isobe, T.; Senna, M. *Chem. Sustainable Dev.* **1998**, *6*, 165.

(11) Rosén, A.; Ellis, D. E.; Adachi, H.; Averill, F. W. *J. Chem. Phys.* **1976**, *65*, 3629.

(12) Adachi, H.; Tsukada, M.; Satoko, C. *J. Phys. Soc. Jpn.* **1978**, *45* (3), 875.

(13) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833, 1841.

(14) Pauling, L. *The Nature of Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(15) Sanderson, R. T. *Science* **1951**, *114*, 670.

(16) Barr, T. L. *J. Vac. Sci. Technol., A* **1991**, *9* (3), 1793.

(17) Pacchioni, G.; Illas, F. *Chem. Phys.* **1995**, *199*, 155.

(18) Kong, J.; Boyd, R. J. *J. Chem. Phys.* **1995**, *103* (23), 10070.

(19) Cox, P. A. *Electronic Structure and Chemistry of Solids*; Oxford University Press: Oxford, 1987; Chapters 3 and 7.

(20) Ching, W. Y.; Gan, F.; Huang, M.-Z. *Phys. Rev. B* **1995**, *52* (3), 1596.

(21) Kotani, T. *Phys. Rev. B* **1994**, *50* (20), 14816.

(22) Goniakowski, J.; Noguera, C. *Surf. Sci.* **1994**, *319*, 68; **1995**, *323*, 129.

(23) See, for example, Chaix-Pluchery, O.; Pannetier, J.; Bouillot, J. *J. Solid State Chem.* **1987**, *67*, 225.

(24) Senna, M.; Schönert, K. *Powder Technol.* **1982**, *32*, 217.

(25) Heinicke, G. *Tribochemistry*; Akademie-Verlag: Berlin, 1984; p 354.