

Electronic state calculation of ceramics
by DV-X α cluster method

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The electronic state calculations for various types of ceramic materials have been performed by the use of DV-X α cluster method. The molecular orbital levels and wave functions for model clusters have been computed to study the electronic properties and chemical bonding of the ceramics.

For β -sialon($\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$) which is a high temperature structural material based on β - Si_3N_4 , we have made model cluster calculations to estimate the strength of chemical bonding between atoms by the Mulliken population analysis. It is found that the covalent bonding between Si and N atoms is very strong in pure β - Si_3N_4 , but the covalency around solute atom is considerably weakened when Si atom is substituted by Al. This tendency is enhanced by an additional substitution of oxygen atom for N. The result calculated can well explain the experimental data of changes in mechanical properties such as the reductions of Young's modulus and Vickers hardness with increment of z-value in β -sialon.

Various model clusters for transition metal oxides which show many interesting physical and chemical properties have also been calculated. High-valent perovskite-type iron oxides MFeO_3 (M=Ca and Sr) possess very interesting magnetic and chemical properties. In these oxides, iron exists as Fe^{4+} state, but the experimental measurement of Mossbauer effect suggests that disproportionation $2\text{Fe}^{4+}=\text{Fe}^{3+}+\text{Fe}^{5+}$ takes place for CaFeO_3 at low temperatures. The model cluster calculations for these compounds indicated the existence of considerably strong covalent bonding of Fe-O. The calculations of hyperfine interaction at iron nucleus show very good agreement with the experimental Mossbauer measurements. The result calculated also implies that the disproportionation reaction is strongly possible by assuming the quenching of breathing phonon mode at low temperatures.