CHEMICAL BINDING AND ELECTRONIC STRUCTURE OF ORTHORHOMBIC O'-SIALON AND SILICON DIOXYNITRIDE WITH SUBSTITUTION IMPURITIES (C, Al, Ga, Be, Mg)

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The self-consistent X₉ discrete variation ab initio method is used to study the electronic structure and chemical binding in model clusters of orthorhombic O'-sialon and silicon oxynitride containing substitution impurities in cation sublattices. Changes in the local interatomic interactions and effective atomic charges induced by iso- and heterovalent substitutions of Si in Si₂N₂O (Si → C, Al, Ga, Be, Mg) are discussed.

INTRODUCTION

Silicon oxynitride (Si₂N₂O) belongs to the class of high-melting nonmetal compounds possessing a number of interesting properties [1], including chemical inertness and high resistance to oxidation [2-6]. The latter is particularly important for its application as protecting films applied on silicon nitride ceramics and composites to enhance their performance in corrosive media [7, 8]. Efforts were made to design oxidation-resistant Si₂N₂O-containing materials (e.g., Si₂N₂O/ZrO₂ [8]).

Silicon oxynitride can be used as a starting phase to produce Si–Al–O–N (so-called sialon) four-component solid solutions possessing high hardness and thermal stability along with low density and low friction coefficient (9, 10). The sialons synthesized from Si₂N₂O (O'-phase [11]) are four-component monophase solid solutions Si₂₋ₓAlₓN₂₋ₓO₁₊ₓ (0.04 < x < 0.40) [12], which are also chemically inert. Recently, the O'-phases were used to synthesize complex composites (e.g., O'-sialon/ZrO₂) [13].

O'-sialons are formed by simultaneous substitutions Si⁴⁺→Al³⁺ and N³⁻→O²⁻ in Si₃N₄ tetrahedra, which are basic structural units of the initial orthorhombic phase Si₂N₂O. The composition and properties of the Si₂N₂O and O'-phases can also be modified using other p and d and rare earth metal atoms as substituents [9-15]).

First efforts were recently made to simulate the electronic structures of some multiple phases in Si–Al–O–N systems using computational quantum chemistry methods. The X₉ discrete variation cluster method was used [16] to study the effect of lanthanide impurity atoms on the system of interatomic interactions in ß-sialon (Si₆₋ₓAlₓOₓN₄₋ₓ). The semiempirical band structure method was employed [17] to describe the conditions of formation of concentrational polytypes — wurtzite-like alumosilicate oxynitrides Alₓ₋₉Si₆₋ₓOₓN₄₋ₓ (x = 4, y = 2n, where n is an integer). The effect of the Si→C substitution in Si₂N₂O as well as the band structure and chemical binding in hypothetical "carbon oxynitride" were studied by the linear muffin-tin orbital (full-potential) method [18]. The nature of chemical binding in O'-sialon was first considered in [19].

In this work, we performed ab initio calculations of the electronic structure and interatomic interactions of orthorhombic O'-sialon and considered the effect of partial substitution of silicon atoms (Si⁴⁺) by tetravalent (C⁴⁺), trivalent (Al³⁺, Ga³⁺), and bivalent (Be²⁺, Mg²⁺) ions on the electronic characteristics of the initial phase (Si₂N₂O).

MODELS AND CALCULATION TECHNIQUE

The initial silicon oxynitride (Si₂N₂O) phase was represented by the [Si₂ON₆]¹²⁻ cluster; the presence of substitution...
impurities (M = C, Al, Ga, Be, Mg) was simulated by \([\text{SiMON}_6]^{4+m-20}\) fragments, where \(m\) is the impurity ion charge (4+ for C, 3+ for Al and Ga, and 2+ for Be and Mg). The impurities were assumed to occur in \(\text{Si}_2\text{N}_2\text{O}\) in low concentrations.

\(\text{O}^-\)-sialon is an extended solid solution with variable Si/Al and O/N contents [9-15] where the charge balance condition for the \(\text{Si}^{4+} \rightarrow \text{Al}^{3+}\) substitution is provided by the variation of the composition of the anion sublattice as a result of simultaneous inclusion of \(\text{O}^{2-}\) atoms at \(\text{N}^{3-}\) sites. Hence electron concentration calculation for the cluster will depend on the composition of the model solid solution.

In the first step, the effects of Al or O impurities on the electronic structure of the substance were studied using the \([\text{SiAION}_6]^{13-}\), \([\text{SiAION}_6]^{12-}\), and \([\text{SiO}_2\text{N}_2]^{12-}\) clusters. \(\text{O}^-\)-sialon was represented by the \([\text{SiAlO}_2\text{N}_5]^{12-}\) fragment, which was also employed to simulate possible types of short-range atomic ordering in the solid solution.

The calculations were fulfilled by the spin-limited \(X_\alpha\) discrete variation \textit{ab initio} method [20]. Numerical integration was performed using 6000 points per cluster. The Gunnarsson–Lundqvist exchange correlation potential [21] was employed. Orbital population and overlap population analyses were carried out by the Mulliken method [22]. The interatomic distances in the clusters corresponded to those in silicon oxynitride (space group \(\text{Cmc21}\); unit cell parameters: \(a = 8.843\), \(b = 5.473\), \(c = 4.835\) Å [23]).

The calculations were accomplished in the unsymmetrized molecular orbital approximation using the basis set optimization procedure. The numerical AO basis set incorporated the orbitals with the principal quantum numbers \(n = 4\) (Ga), \(n = 3\) (Si, Mg, Al), and \(n = 2\) (C, N, O, Be); the core states of atoms were calculated in the “frozen” core approximation. We calculated the atomic charges \(Q_i\), the total and partial overlap populations of valence orbitals \((N_i)\), the partial densities of states \(n_i(e_i)\), and the total energies \(E_i\) of the clusters defined as [24]

\[
E_i = E_{\text{sum}} + E_{\text{exc}} + E_{\text{coul}} + E_{\text{NN}},
\]

where \(E_{\text{sum}}\) is the sum of the one-electron energies, \(E_{\text{exc}}\) is the electron exchange energy, \(E_{\text{coul}}\) is the Coulomb energy of electron interactions in the cluster, and \(E_{\text{NN}}\) is the energy of Coulomb nuclear repulsion.

### RESULTS AND DISCUSSION

**Silicon oxynitride.** The electronic energy structure of \(\text{Si}_2\text{N}_2\text{O}\) was previously studied by the band OLCAO [25, 26], FP-LMTO [18], and LMTO tight binding [27] band structure methods. The electronic energy structure parameters of silicon oxynitride calculated in this work and published elsewhere [18, 26], are listed in Table 1. According to our calculations, the valence band of \(\text{Si}_2\text{N}_2\text{O}\) contains three subbands (Fig. 1). The lowest-energy subband has a predominant contribution from the O2s states. The higher energy subband has a peak of one-electron states with a prevailing contribution from the N2s AO, which is 3.33 eV higher in energy and \(\sim 2.73\) eV wide; this is consistent with the results of [26]. The width of the third subband (9.50 eV) involving the (O, N)2p-Si3p states also shows reasonable agreement with the estimate 10.41 eV [26]. The discrepancies between the cluster and band structure representations of a number of energy intervals in the

<table>
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<th>Parameters</th>
<th>Our calculations</th>
<th>[18]</th>
<th>[26]</th>
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