Electronic structure and hybridization effects in hypothetical orthorhombic carbon oxynitride

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The quantum-chemical examination of the electronic structure and hybridization of the valence states in the orthorhombic Si_2N_2O and hypothetical C_2N_2O compounds suggests that the cohesive properties can be improved by the substitution of carbon for silicon in a silicon oxynitride crystal.

Sialons (SiAlONs) are solid solutions with the general formula $Si_{6-x}Al_xO_xN_{8-x}$.[1,2] A large class of sialon ceramic materials, which are of crucial technological and commercial importance, is presently known.[3–5] Intensive studies are carried out in the field of modification of unique properties of sialon materials combining hardness, high abrasive ability, wear resistance, thermal stability, chemical inertness, *etc.*[1–5]

A serious effort was made to search for optimum composition and microstructure of ceramics whose functional properties depend on the grain characteristics (SiAlONs) and are controlled by the morphology, structure and chemical composition of the grain-boundary phase.[3–5] As a preliminary, it is reasonable to consider the microscopic properties of simple compounds of this system such as AlN, β-Si_3N_4, Si_2N_2O.

One of the possible ways to optimise the cohesive properties of the Si_2N_2O phase can be isovalent substitution of carbon atoms for silicon in its lattice. Recent theoretical results predicting extreme thermomechanical properties of the crystalline carbon nitride C_3N_4 with the basic structure β-Si_3N_4 allow this supposition (see ref. 6 for a review).

In this work, we report on a quantum-chemical study of the electronic structure, chemical bonding and cohesive energy of the orthorhombic Si_2N_2O and the hypothetical isostructural phase C_2N_2O.

The calculations were carried out by the self-consistent *ab initio* full-potential linear muffin-tin orbital method (FLMTO).[7] The lattice parameters of Si_2N_2O corresponded to those given in ref. 8. The unit cell included four formula units. The FLMTO calculations were performed in a scalar relativistic version; Si 3*s*, 3*p*, 3*d* and (C,N,O) 2*s*, 2*p* orbitals were inserted into the basis as valent states.

To take into account the lattice relaxation effect in C_2N_2O, which is associated with differences in the atomic radii of Si and C, the total energy (E_{tot}) of the crystal was calculated as a function of the unit cell volume (V). The miminum E_{tot} was obtained at $V/V_0 = 0.80$ (V_0 is the volume of a Si_2N_2O cell), which corresponds to the mean decrease in interatomic distances in the hypothetical compound C_2N_2O by ~7%.

Table 1 Charges in the muffin-tin spheres (q, e), cohesion energies E_{coh} (eV atom^{-1}) and forbidden band gaps (eV) for Si_2N_2O and C_2N_2O.

		Si_2N_2O	C_2N_2O	C_2N_2O
V/V_0[a]		1.00	1.00	0.80
Si, C	q_s	0.62	1.19	1.02
	q_p	0.87	1.87	1.92
	q_d	0.34	—	—
N	q_s	0.85	0.88	0.68
	q_p	1.89	1.59	1.49
O	q_d	0.99	1.05	0.85
	q_p	2.39	2.18	1.98
$-E_{coh}$		7.08	5.99	6.89
ΔE_v		0.95	—	—
$\Delta E'_v$		2.83	0.64	—
ΔE_g		3.24	1.14	2.04

[a] V is the cell volume of the calculated oxynitrides; V_0 is the cell volume of the real Si_2N_2O phase.[8]

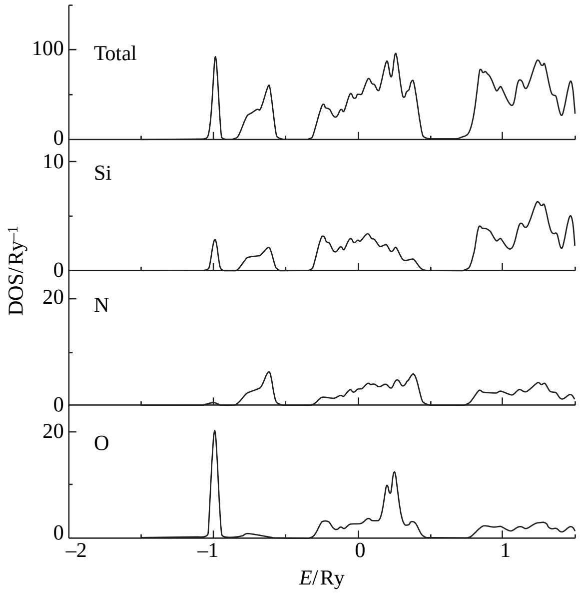

Figure 1 Total and local densities of states of the orthorhombic Si_2N_2O.

Total and local densities of states for Si_2N_2O and C_2N_2O are given in Figures 1 and 2. The energy spectrum of Si_2N_2O (Figure 1) contains three valence bands. The lower energy band is composed predominantly of O 2*s* states with an admixture of Si 3*s* states, and the next band includes the contributions of N 2*s* and Si 3*s*,3*p* states. The upper valence band exhibits a mixed character and contains hybridized *p* states of Si, N and O. The conduction band is made up of antibonding N 2*p*, O 2*p* and Si 3*p*,3*d* states. The three valence bands are separated by the forbidden gaps ΔE_v, $\Delta E'_v$ and ΔE_g (between the valence band and the conduction band) (Table 1). The results of our FLMTO computations are in good agreement with the recent calculations of Si_2N_2O performed by the OLCAO method.[9]

The main differences in the electronic spectrum of C_2N_2O are attributed to a noticeable widening of the basic valence bands of this hypothetical compound, which reflects an increase in the degree of hybridization of *p* states of the constituting atoms (Figure 2). For the equilibrium volume $V/V_0 = 0.80$, the forbidden gaps ΔE_v and $\Delta E'_v$ disappear; the ΔE_g value decreases by ~37% (Table 1).

Table 1 presents the cohesive energies (E_{coh}) of silicon and carbon oxynitrides. The cohesive energy is calculated as $E_{coh} = E_{tot} - \sum E_{at}$, where E_{tot} is the total energy of the crystal and E_{at} is the energy of free atoms constituting its sublattices.[7] The maximum E_{coh} value corresponds to Si_2N_2O. When lattice ‘compression’ occurs, E_{coh} of C_2N_2O dramatically increases approaching the cohesive energy of silicon oxynitride at $V/V_0 = 0.80$ (Table 1). The E_{coh} value is an integrated characteristic of the chemical bonding energy and describes the total effect of interatomic interactions.

According to our computations, the chemical bonding in silicon and carbon oxynitrides is of a combined covalent-ionic

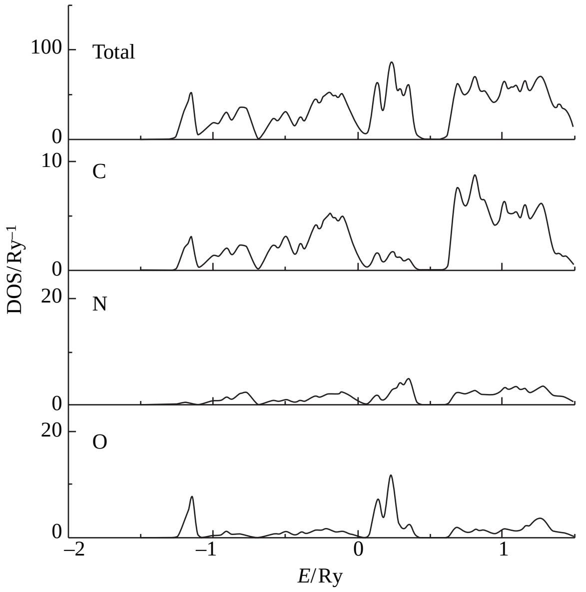

Figure 2 Total and local densities of states of the hypothetical orthorhombic carbon oxynitride C_2N_2O (for the 'equilibrium' cell volume $V/V_0 = 0.80$, see the text).

type. When substituting C for Si, the charges in the muffin-tin spheres of N and O decreased and those in the muffin-tin spheres of carbon increased as compared to silicon.

The above effect of *p*–*p* hybridization strengthening (covalent bonding) for C_2N_2O is readily illustrated by the maps of valence charge densities (Figure 3). It can be seen that the degree of hybridization of C–N bond states increases in comparison with Si–N. It also follows from Figure 3 that the charge density distribution (CDD) is essentially non-spherical with different degrees of CDD delocalization along the directions of particular interatomic bonds (Si–N, Si–O, C–N, *etc*.). The channels (along the *c* axis) with low CDD are responsible for anisotropic properties of oxynitrides.

In our calculations, the lattice relaxation for C_2N_2O was simulated by uniform compression of a cell of the initial Si_2N_2O crystal, *i.e.*, all interatomic distances decreased simultaneously. However, in real situations, we usually have low concentrations of an impurity, which results in local distortions around the dopant atoms preserving the crystal structure as a whole. Such local displacements (relaxation) of the nearest atoms around the impurity will lower the total energy and, therefore, increase the absolute value of the cohesive energy. Based on the performed analysis of hybridization effects, we can anticipate that the cohesive energy of Si_2N_2O with a C dopant will increase owing to stronger hybridization of covalent C–N and C–O bond states.

These tentative results of the quantum-chemical simulation of the hypothetical carbon oxynitride allow us to suppose that the doping of the orthorhombic Si_2N_2O structure will improve the cohesive properties of $Si_{2-x}C_xN_2O$ as compared with the isoelectronic Si_2N_2O. We also suggest that partial or complete isovalent substitution of C for Si in the lattice of sialons can be an efficient way of modifying the functional properties of SiAlON-based ceramic materials, and theoretical and experimental studies in this field can be of great practical importance for the development of a new class of non-metallic ceramic materials based on the C–Al–O–N system.

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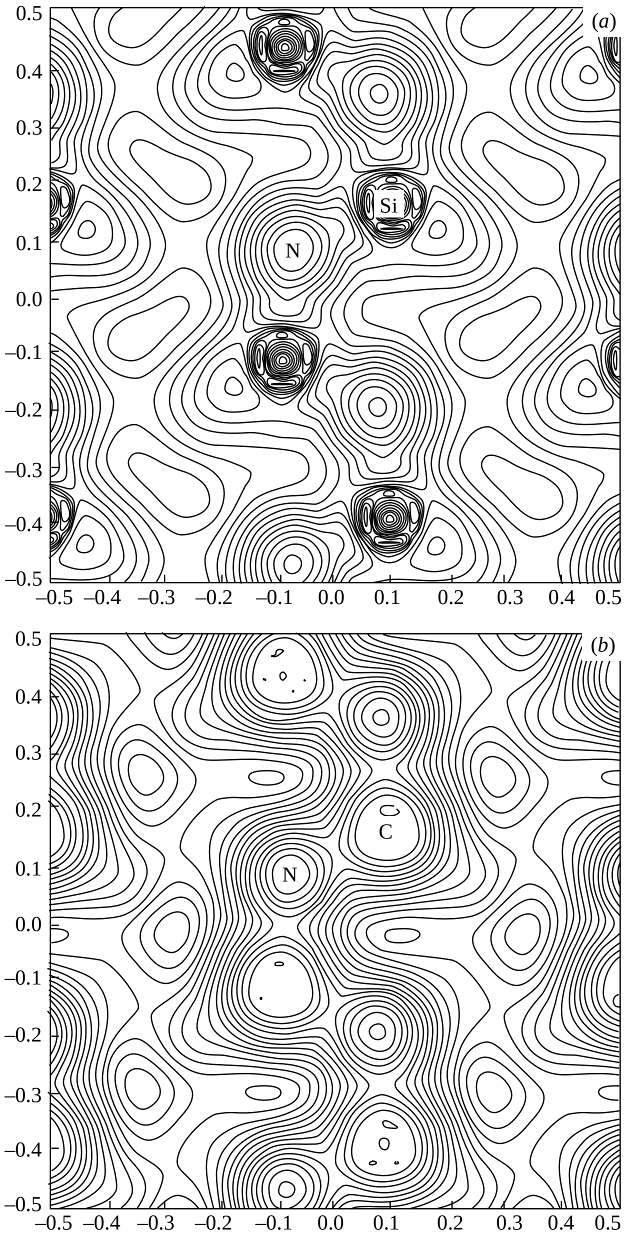

Figure 3 Maps of the valence charge density distribution in the plane (*yz*) of (*a*) Si_2N_2O and (*b*) C_2N_2O cells. FLMTO calculations.

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