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Prediction of spinel structure and properties of single and double nitrides

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Lattice constants, bulk moduli, band gaps, electronic bonding, and the stability of 20 new nitrides with spinel structure are studied by first-principles calculations. Double nitrides AB_2N_4 are found to be stable when the counterparts BA_2N_4 are metastable except for $TiZr_2N_4$. The four single nitrides C_3N_4, Si_3N_4, Ge_3N_4, and Sn_3N_4 have direct band gaps at the Γ point ranging from 1.14 to 3.45 eV while Zr_3N_4 and Ti_3N_4 have small indirect gaps. For double nitrides, both metallic and insulating band structures are possible. The total bond orders of the stable double nitrides are larger than those of constituent single nitrides. Among them, CSi_2N_4 shows exceptionally strong covalent bonding and a large bulk modulus. A simple scaling law based on bond lengths can describe the bulk moduli of these spinel nitrides quite well.

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Double oxides having spinel or perovskite structures are extensively used in modern technology since their properties can be ''tuned'' in a wide range by appropriate combination of cations.[1] Normal spinel oxides are denoted by AB_2O_4, where A and B are, respectively, the tetrahedrally and octahedrally coordinated cations at the $8a$ and $16d$ sites. The formal charges of the two cations are generally different. For example, $ZnAl_2O_4$ is composed of Zn^{2+} and Al^{3+}, and is called a 2-3 spinel. $GeMg_2O_4$ and $MoNa_2O_4$ are examples of 4-2 and 6-1 spinels. Although magnetite Fe_3O_4 appears to be an exception, it is actually a double spinel with $A=Fe^{2+}$ and $B=Fe^{3+}$. Spinel belongs to the space group of $Fd3m$ (No. 227) with one internal parameter u for the anion. It is well known that significant cation disorder can occur in the spinel structure by interchanging of A and B cations. In the extreme case of the so-called inverse spinel, all the $8a$ sites and half of the $16d$ sites are occupied by cation B and the other half of the $16d$ sites by cation A. The distribution of cations is often somewhere between the normal and the inverse spinels. The oxygen sublattice in the spinel structure is a nearly cubic close-packing (ccp or fcc) structure. Assuming a hard-sphere model of the ccp sublattice of anions, the spherical radius that can fit into the tetrahedral interstitial site is smaller than that for the octahedral site. As a result, cations with smaller ionic radii tend to occupy the tetrahedral site. On the basis of these premises, the property of spinel compounds can be ''tuned-up'' by optimizing cations with different ionic radii and formal charges.[1]

Other than oxides, only a few chalcogenides, such as Co_3S_4 and Co_3Se_4, are known to have the spinel structure. The discovery of cubic silicon nitride (c-Si_3N_4) in 1999 (Ref. 2) was a major breakthrough in the synthesis of new materials. c-Si_3N_4 was first synthesized under an extreme pressure of 15 GPa and a high temperature of 2000 K. Immediately after the discovery, we have predicted some very interesting physical properties of c-Si_3N_4 by first-principles calculations.[3] It exhibits a direct band gap of 3.45 eV, much smaller than those of hexagonal α- and β-Si_3N_4, which have larger and indirect band gaps. The c-Si_3N_4 has a higher covalency and larger static dielectric constants compared with the α- and β-Si_3N_4.[3] In c-Si_3N_4, Si atoms are located at both the octahedral and the tetrahedral sites of the N sublattice. Sixfold coordinated Si has been found only in stishovite, a high-pressure phase of SiO_2, and the perovskite-analogous $(Mg,Fe)SiO_3$. Very recently, an oxonitridosilicate with sixfold coordinated Si has been synthesized.[4] The interesting properties of c-Si_3N_4 should be related to the presence of the sixfold-coordinated Si. However, the nature of the role played by the sixfold-coordinated cations in determining the properties of these compounds has not yet been fully clarified.

The formation of double spinel nitride was proposed by the present authors.[5] Contrary to oxides or chalcogenides, nitrides may exhibit 4-4, 2-5, or 6-3 spinels. c-Si_3N_4 is a typical 4-4 spinel. Since the ionic radius to fit the octahedral site is greater than that for the tetrahedral site, the substitution by larger ions to Si^{4+} at the octahedral site or smaller ones to Si^{4+} at the tetrahedral site may stabilize the compound. Spinel $SiTi_2N_4$ was then proposed as a stable new phase.[5] The c-$SiTi_2N_4$ phase is found to defy the simple rule of mixing. It is metallic, although c-Si_3N_4 has a wide band gap and c-Ti_3N_4 has a narrow gap.[5]

Less than a year after the discovery of c-Si_3N_4, much progress has been made in the synthesis and characterization of the new spinel nitrides. c-Ge_3N_4 has been synthesized by at least two different groups.[6,7] Synthesis and characterization of spinel Si_3N_4 have been reported by two more groups.[8,9] We are now at an early stage of research in that an entirely new class of nitride compounds is open for investigation. In the present paper, we report a systematic investigation for the new single and double nitrides. Our study will provide a guiding principle in the synthesis of additional new compounds.

Six single nitrides c-C_3N_4, c-Si_3N_4, c-Ge_3N_4, c-Sn_3N_4, c-Ti_3N_4, and c-Zr_3N_4, and most of their double compounds were examined in the present study. All the calculations were done by the first-principles orthogonalized linear combinations of atomic orbitals (OLCAO) method within the

TABLE I. Calculated properties of the 20 spinel nitrides.

		Lattice parameters			Band gap		Bulk modulus		Mulliken charge			Bond orders/length				
Crystal		a (Å)	u	ΔE (eV/A_3N_4)	E_g direct (eV)	E_g indirect (eV)	B (GPa)	B'	Q^*_{tet}	Q^*_{oct}	Q^*_{N}	Total bond order	Bond order A-N	Bond length A-N (Å)	Bond order B-N	Bond length B-N (Å)
c-C_3N_4		6.8952	0.3833		1.14		377.6	3.36	3.70	3.63	5.27	8.647	0.358	1.592	0.241	1.669
c-Si_3N_4		7.8372	0.3844		3.45		280.1	3.76	2.65	2.58	6.05	8.670	0.362	1.824	0.241	1.889
c-Ge_3N_4		8.2110	0.3841		2.22		268.6	3.14	2.81	2.80	5.90	7.900	0.327	1.907	0.220	1.981
c-Sn_3N_4		8.9658	0.3845		1.29		203.6	4.98	2.71	2.70	5.97	6.958	0.284	2.089	0.195	2.160
c-Ti_3N_4		8.4459	0.3833		0.25	0.07	265.6	3.56	3.09	3.20	5.62	8.474	0.353	1.950	0.236	2.044
c-Zr_3N_4		9.1217	0.3830		0.40	0.23	225.3	4.17	3.06	3.17	5.65	8.609	0.356	2.101	0.240	2.210
c-CSi_2N_4	LF	7.5209	0.3811	−0.64	1.34	1.26	309.5	2.72	4.14	4.44	4.75	11.231	0.299	1.708	0.368	1.835
c-SiC_2N_4	HE	7.2867	0.3885	3.09	Metal		327.7	4.69	2.45	3.71	5.53	8.260	0.359	1.748	0.225	1.729
c-CGe_2N_4	0	7.7407	0.3701	0.00	1.36		266.0	3.53	3.67	2.79	5.68	8.284	0.361	1.610	0.225	1.974
c-GeC_2N_4	HE	7.4284	0.3943	3.84	0.71		310.1	4.22	2.85	3.67	5.45	7.816	0.317	1.857	0.220	1.726
c-$SiGe_2N_4$	LE	8.0871	0.3773	−0.26	1.85		277.1	3.02	3.10	2.91	5.77	9.999	0.564	1.783	0.229	2.003
c-$GeSi_2N_4$	HE	8.0011	0.3899	0.44	2.64	2.55	258.3	2.04	3.02	2.53	5.98	8.260	0.320	1.939	0.238	1.889
c-CTi_2N_4	LE	7.8351	0.3637	−1.95	Metal		300.3	3.99	3.71	3.23	5.46	9.005	0.383	1.543	0.248	2.051
c-TiC_2N_4	HE	7.5400	0.3936	4.51	0.97	0.62	317.3	3.13	2.97	3.77	5.37	8.030	0.352	1.875	0.217	1.756
c-$SiTi_2N_4$	LE	8.2168	0.3749	−1.42	Metal		274.5	1.99	2.51	3.31	5.72	9.075	0.366	1.778	0.256	2.055
c-$TiSi_2N_4$								Unstable								
c-$GeTi_2N_4$	LE	8.4002	0.3829	−0.43	Metal		253.2	1.98	2.90	3.18	5.68	8.657	0.323	1.934	0.253	2.036
c-$TiGe_2N_4$	HE	8.3158	0.3837	0.90	2.27	1.87	266.6	2.82	3.08	2.91	5.77	8.231	0.378	1.926	0.217	2.009
c-$TiZr_2N_4$	HE	8.9276	0.3800	0.95	0.32	0.15	227.5	2.46	3.14	3.14	5.64	8.482	0.339	2.010	0.240	2.188
c-$ZrTi_2N_4$								Unstable								

local approximation of the density-functional theory. The details have been described elsewhere.[3,5] A full basis set consisting of core- and valence-electron orbitals and additional excited-state orbitals is employed. For each phase, the total energy (E_t) is minimized by varying both the lattice constant and the internal parameter.[10,11] The number of k points in the irreducible part of the Brillouin zone ranges from 56 to 84, which gave a convergence in E_t to better than 0.001 eV per unit cell. The effective charges Q^*_α on atom α and the bond order $\rho_{\alpha\beta}$ for each atomic pairs α and β were calculated from the crystal wave functions and overlap integrals according to the Mulliken population analysis scheme.[12] A separate minimal-basis calculation was carried out for this purpose. The bulk modulus B and its pressure coefficient B' were obtained by fitting the total energy data at eight different volumes (with internal parameter relaxed) to the Murnagham equation of states.[13]

Table I summarizes the calculated results for 20 single and double spinel nitrides. To investigate the stability of double nitrides, we calculate the total energy difference ΔE_t between AB_2N_4 and a simple mixture of the two constituent nitrides according to

$$\Delta E_t = E_t(AB_2N_4) - [\tfrac{1}{3}E_t(A_3N_4) + \tfrac{2}{3}E_t(B_3N_4)]. \qquad (1)$$

In Eq. (1), E_t is the total local-density approximation (LDA) energy at the optimized geometry. Since E_t at the equilibrium geometry corresponds to the free energy of the compound at zero temperature and zero pressure. And spinel nitrides are most likely to be formed at high temperature and high pressure. ΔE_t as defined by Eq. (1) represents the stability of the double nitride in the zeroth-order approximation. Other thermodynamic variables such as temperature and pressure will also play a role. Nevertheless, we can still consider E_t to be a reasonable indicator as to whether AB_2N_4 will be stable or not. Accordingly, we label AB_2N_4 as LE (low energy) in Table I if ΔE_t from Eq. (1) is negative, and as HE (high energy) if ΔE_t is positive. Thus a double spinel with a LE is likely to be stable and that of a HE could be metastable. Of the 12 double spinels whose geometry were optimized, five are HE, six LE, and one showed $\Delta E_t = 0$. The E_t of two more compounds, c-$TiSi_2N_4$ and c-$ZrTi_2N_4$, failed to converge, reflecting the unstable nature of these two compounds. It is instructive to note that when AB_2N_4 is a LE compound, the counterpart, BA_2N_4 is a HE compound.

The bond lengths (BL's) of the spinel nitrides from the optimized geometry are summarized in Fig. 1. In the rigid-sphere model, the BL is determined by the sum of two ionic radii. Shannon made an extensive list of effective ionic radii as a function of coordination number and formal charge on the basis of a large database of experimental BL's.[14] Figure 1 shows the BL obtained from the sum of the ionic radii of N and cations at both the tetrahedral and octahedral sites and compared with our theoretical values. The theoretical BL's are found to be scattered within ±10% of the values predicted by the rigid-sphere model. This implies that the rigid-sphere model is still useful as a rough estimate of the BL of

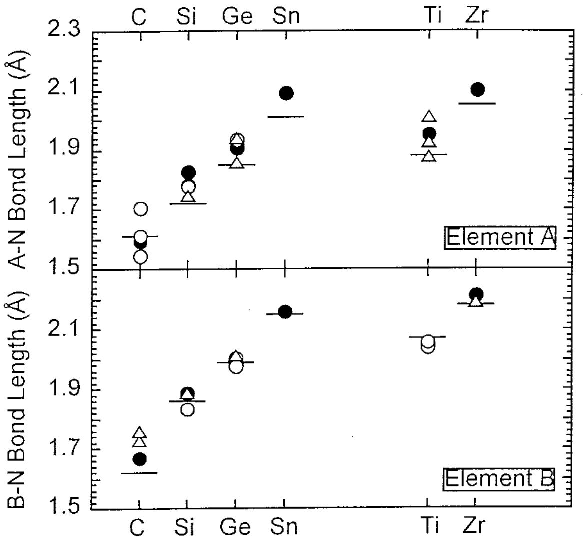

FIG. 1. Calculated bond lengths B-N and A-N in single and double spinel nitrides. Open circles for the LE phases, open triangle for the HE phases and solid circles for the single spinels. The bars represent the bond lengths estimated from the Shannon's radii.

these spinel nitrides, but for more accurate analysis, a rigorous *ab initio* quantum-mechanical treatment is desirable. To relate the stability of the double nitrides, we plot in Fig. 2 the A-N BL with the B-N BL for all the stable and metastable spinel nitrides. The data for the six single nitrides fall closely on a straight line. It is interesting to note that the stable phases are distributed on the upper left of this line, and most of the metastable HE phases are on the lower right of the line. The only exception is c-$TiZr_2N_4$, while c-$TiGe_2N_4$ falls almost on the line. Figure 2 demonstrates more vividly that in double spinel nitrides, the tetrahedral site is favored by a smaller cation, and the octahedral site by a larger cation. However, the existence of the metastable phases where the preference of the site occupation is reversed cannot be totally ruled out.

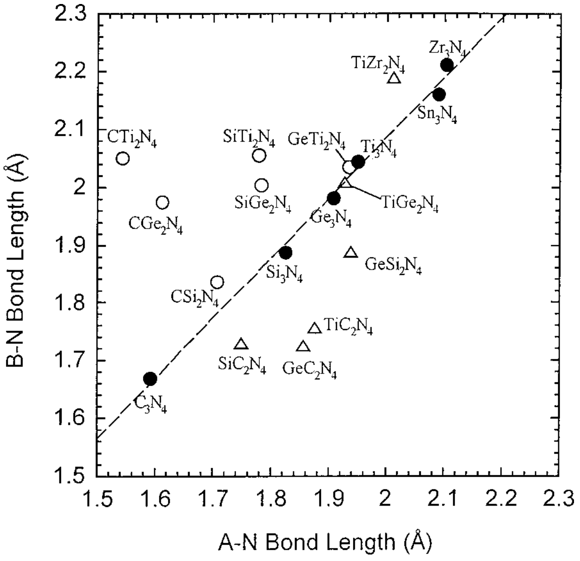

FIG. 2. Plot of bond lengths A-N vs bond lengths B-N for double and single spinel nitrides. Symbols are the same as Fig. 1.

The band structures for the single and double spinel nitrides have all been calculated. Those of C_3N_4, Si_3N_4, Ti_3N_4, and $SiTi_2N_4$ can be found in the previous reports.[3,5] Others will be presented elsewhere. The gap values are listed in Table I. The four single nitrides, C_3N_4, Si_3N_4, Ge_3N_4, and Sn_3N_4 with cations from column IV B of the periodic table, have direct band gaps at Γ ranging from 1.14 to 3.45 eV. c-Zr_3N_4 and c-Ti_3N_4 have small indirect band gaps of 0.23 and 0.07 eV and direct gaps of 0.40 and 0.25 eV at Γ, respectively. The fact that c-Zr_3N_4 and c-Ti_3N_4 have smaller, indirect band gaps is related to the electron states near the gap being dominated by the Ti $3d$ or Zr $4d$ orbitals. It should be pointed out that the LDA calculation generally underestimates the gap value of an insulator. This underestimation apparently depends on the crystal structure and also on the orbital compositions of the wave functions near the gap. Since no gap measurement for any of the cubic spinel nitrides has been reported, we may use β-Si_3N_4 as an illustrative example. In β-Si_3N_4, the reported experimental gap ranges from 4.6 to 5.5 eV while the calculated indirect band gap using the same OLCAO method is 4.96 eV.[15] However, in the silicon nitride case, the measured gap value is complicated by the presence of defects and the way the gap value was extracted by extrapolation from the optical absorption spectrum.[15]

One would expect the double nitrides formed from the insulating single nitrides to have gap values that fall somewhere in between. This was the case for most double nitrides whose cations do not contain d electrons in the valence shell except for the metastable c-SiC_2N_4. However, of the four double nitrides with Ti, three have metallic bands. Only the metastable c-$TiZr_2N_4$ has a small indirect gap. Obviously, a rather complex interplay of the Ti $3d$ orbitals with the N $2p$ and the s and p orbitals of the other cation is at work. As has been shown in Ref. 5 for c-$SiTi_2N_4$, Si orbitals are significantly admixed with those of Ti near the Fermi level, excluding the formation of a band gap.

The effective charges on each atom and the bond order for each pair of atoms are calculated using crystal wave functions and overlap integrals according to the Mulliken scheme.[12] The total overlap population or crystal bond order was obtained by summing up all bond orders in the unit cell. It serves as a single parameter in assessing the overall bond strength in a crystal. Results for the spinel nitrides are summarized in Table I. It is interesting to note that the effective charge of 4.75 for N in c-CSi_2N_4 is 0.25 electron less than the neutral N. It means N can be thought as an ''cation'' rather than ''anion.'' On the other hand, both Si and C in c-CSi_2N_4 can be recognized as ''anions.'' This rather unconventional scenario can be ascribed to the extraordinarily strong covalent bonding between Si/C and N in c-CSi_2N_4. As a matter of fact, the total bond order of 11.23 in c-CSi_2N_4 is remarkably higher than all other crystals listed in Table I. It should be noted that the total bond orders of the double nitrides with negative ΔE such as c-CSi_2N_4 is always larger than that of their constituent single nitrides. Obviously, double nitrides, by virtue of different sizes of the *A* and *B* cations, can pack themselves in a much more effective manner so as to produce very strong covalent bonding in these crystals.

The bulk moduli *B* of all the single and double nitrides are calculated in the manner described before.[10] c-C_3N_4 shows the highest *B* of 377.8 GPa. Substitution of octahedral C by Si, Ge, or Ti results in significant decrease in the bulk modulus by approximately 20%. On the other hand, the substitution of the octahedral Si by Ge or Ti in c-Si_3N_4 does not change the bulk modulus significantly. *B* increases monotonically with the decrease of *a* or *d*, the weighted average of BL's of *A*-N and *B*-N. A simple rule for classical ionic crystals states that *B* should be proportional to $V^{-4/3}$ where *V* is the unit-cell volume. However, experimental data from a number of oxides and alkali halides show a V^{-1} dependence for *B*.[16] For covalent materials, Cohen[17] proposed an empirical formula to estimate *B* (GPa) of zinc-blende solids based on the BL *d* (Å):

$$B=(1971-220\lambda)d^{-3.5}, \tag{2}$$

where $\lambda=0,1,2$ for homopolar, III-V, and II-VI compounds, respectively. Liu and Cohen[18] used $\lambda=\frac{1}{2}$ in the discussion of *B* for β-C_3N_4. For the spinel nitrides, the above equation cannot reproduce the *B* values from Table I independent of the choice of the λ value as shown in Fig. 3(a). Instead, a simple empirical formula of $B=Cd^{-n}$ appears to hold pretty well. A log-log plot shown in Fig. 3(b) gives $n=2.0$. This is certainly very different from a number of oxides. Alternatively, it may be more fruitful to consider the bulk modulus in spinel nitrides in terms of polyhedral bulk moduli for the octahedral and tetrahedral sites.[19]

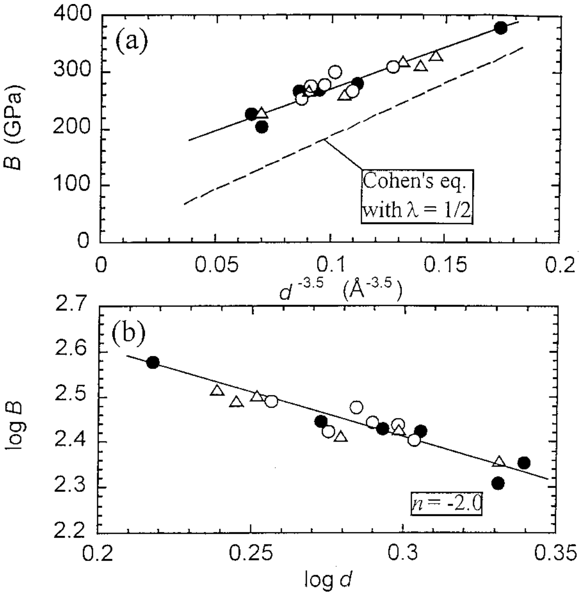

FIG. 3. (a) Calculated bulk moduli of the spinel nitrides as a power laws of the average bond lengths; (b) a log-log plot of the same data. Symbols are the same as Fig. 1.

In conclusion, we have made an extensive study of the structure and properties of the new class of materials, nitrides with a spinel structure. Double nitrides AB_2N_4 are most likely stable when the counterparts BA_2N_4 are metastable. All of the stable double nitrides show higher covalency than their constituent single nitrides. Some of the compounds show a bulk modulus exceeding 300 GPa. Most of them are semiconductors with varying band gaps. Some are expected to be metallic. These results offer a real hope for synthesizing these compounds in laboratory, which will potentially find a variety of applications in ceramic and semiconductor industries.

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