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Electronic structure of the alkaline-earth silicon nitrides $M_2Si_5N_8$ (M = Ca and Sr) obtained from first-principles calculations and optical reflectance spectra

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Abstract
Results of first-principles band-structure calculations for the ternary alkaline-earth silicon nitrides $M_2Si_5N_8$ (M = Ca and Sr) are presented. In the structures of $M_2Si_5N_8$ (M = Ca, Sr and Ba), the N atoms show connections to two ($N^{[2]}$) and three ($N^{[3]}$) neighbouring silicon tetrahedral centres. Calculations show that the local electronic structure is strongly dependent on the local chemical bonding. The valence band is dominated by N 2p hybridized with the s, p states of the alkaline-earth-metal and silicon atoms. The upper part of the valence band is dominated by the 2p states of $N^{[2]}$ atoms, while the $N^{[3]}$ 2p states lie about 2 eV below the Fermi level. The bottom of the conduction band consists of the N 3s characters hybridized with s orbitals of the alkaline-earth metals, while the s character of Si atoms is higher in energy. $Sr_2Si_5N_8$ is a semiconductor with a direct energy gap at Γ, while $Ca_2Si_5N_8$ is an indirect semiconductor. Optical diffuse reflectance spectra show an energy gap of 4.9 eV for $Ca_2Si_5N_8$, 4.5 eV for $Sr_2Si_5N_8$, as well as 4.1 eV for $Ba_2Si_5N_8$, in fair agreement with the calculated values.

1. Introduction

More and more attention has been paid to nitrides in recent years [1–4]. Some binary nitrides, such as Si_3N_4, AlN and GaN, have been intensively investigated both experimentally and theoretically and are applied in industry [5–7]. Ternary nitrides have, however, not been considered in much detail, especially theoretically. The study for ternary nitrides has concentrated on preparation and characterization [1, 2]. Some of the ternary nitrides show peculiar structures and interesting physical properties, as well as outstanding thermal, mechanical and chemical stability.

Alkaline-earth silicon nitrides with a high metal–silicon ratio have been known for a long time [8]. However, during recent years the preparation and structure determination of novel

alkaline-earth silicon nitrides with low metal–silicon ratios (i.e. higher degree of cross-linking between the SiN_4 tetrahedra) have been reported [1–4, 9, 10]. The alkaline-earth-metal silicon nitrides, $M_2Si_5N_8$ (M = Ca, Sr and Ba), show two different structures (Ca [9] versus Sr and Ba [10]). The common feature is that half of the N atoms have two Si nearest neighbours (NSi_2, or $N^{[2]}$ for short) and the other half of the N atoms have three Si nearest neighbours (NSi_3, or $N^{[3]}$ for short) [9, 10]. It was found recently that $M_2Si_5N_8$ compounds doped with Eu have intense orange-red colours, and show peculiar red-band emission, which may provide the possibility for these ternary nitrides to be applied as environmental-friendly pigment materials as well as luminescent materials [11, 12]. For understanding the optical properties, as well as the chemical bonding of these compounds and related nitrides [1, 13, 14], knowledge of the electronic structure is important.

In this paper the results of first-principles band-structure calculations and optical diffuse reflectance spectra measurements for the ternary nitrides $M_2Si_5N_8$ (M = Ca, Sr and Ba) are presented. The bond valences in these ternary nitrides are discussed. The electronic structure of these alkaline-earth-metal silicon nitrides is also compared to those of the binary nitride Si_3N_4 with $N^{[3]}$ coordination and the ternary nitride $MgSiN_2$ with $N^{[2]}$ coordination.

2. Crystal structure of the ternary alkaline-earth silicon nitrides

The ternary alkaline-earth silicon nitrides $M_2Si_5N_8$ (M = Ca, Sr and Ba) were first synthesized by Schlieper *et al* [9, 10]. They also determined the crystal structures of the compounds by means of x-ray diffraction (table 1).

Table 1. Space groups and lattice parameters of the alkaline-earth silicon nitrides $M_2Si_5N_8$ (M = Ca, Sr and Ba) [9, 10].

		Lattice parameters (Å)					
Crystal	Space group	a	b	c	β (deg)	Z	Reference
$Ca_2Si_5N_8$	Cc	14.352	5.610	9.689	112.06	4	[9]
$Sr_2Si_5N_8$	$Pmn2_1$	5.710	6.822	9.341	—	2	[10]
$Ba_2Si_5N_8$	$Pmn2_1$	5.783	6.959	9.391	—	2	[10]

$Ca_2Si_5N_8$ has a monoclinic lattice, while the other two nitrides, $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$, which are isostructural with each other, have orthorhombic lattices. Although $Ca_2Si_5N_8$ has a symmetry different to the other two nitrides, the local coordinations in the structures are quite similar, as shown in table 2. Half of the nitrogen atoms (N1, N2, N5 and N7 for $Ca_2Si_5N_8$; N1, N2 and N5 for $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$) have two Si neighbours ($N^{[2]}$), while the other half of the nitrogen atoms have three Si neighbours ($N^{[3]}$). The average Si–$N^{[2]}$ distances are slightly shorter than that in $MgSiN_2$ (table 2). Meanwhile, the average $N^{[3]}$–Si distances in the $M_2Si_5N_8$ compounds are slightly larger than those in β-Si_3N_4 (table 2). It is noted that the N3 atom in $Ca_2Si_5N_8$ has no bonding with Ca and only three silicon atoms as nearest neighbours with an averaged N–Si distance of 1.735 Å, close to that in Si_3N_4 (about 1.732 Å [16]). In these ternary nitrides every Si atom is coordinated by four N atoms forming a tetrahedron (SiN_4). One type of silicon atom in the nitrides (Si1 in $Ca_2Si_5N_8$ [9] and Si2 in $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$ [10]) is only coordinated with $N^{[2]}$ atoms. The Si–N network is built from corner-sharing SiN_4 tetrahedra. Each Ca atom in $Ca_2Si_5N_8$ has seven nitrogen neighbours [9], while the alkaline-earth atoms in $Sr_2Si_5N_8$ and $Ba_2Si_5N_8$ occupy positions that are eight or nine coordinated by nitrogen atoms [10]. Predominantly, the N atoms which are coordinated to only two Si atoms are bonded to the alkaline-earth ions.

Table 2. Coordinations of N atoms in the ternary nitrides $M_2Si_5N_8$ (M = Ca, Sr and Ba) [9, 10].

d (Å)	$Ca_2Si_5N_8$ [9]	$Sr_2Si_5N_8$ [10]	$Ba_2Si_5N_8$ [10]	$MgSiN_2$ [15]	Si_3N_4 [16]
N1–Si	1.696	1.653	1.665		
N1–Si	1.740	1.730	1.726		
N1–M	2.343	2.542	2.677		
N1–M	2.645	2.891	2.925		
N2–Si	1.677	1.676	1.692		
N2–Si	1.717	1.718	1.718		
N2–M	2.315	2.627	2.753		
N2–M	2.471	2.720	2.823		
N2–M	3.128	3.181	3.160		
N3–Si	1.728	1.767	1.788		
N3–Si	1.732	1.769	1.794		
N3–Si	1.744	1.786	1.797		
N3–M		2.959	3.004		
N3–M		(3.231)	(3.171)		
N4–Si	1.754	1.748	1.741		
N4–Si	1.758	1.751	1.768		
N4–Si	1.759	1.751	1.768		
N4–M	2.848	2.861	2.931		
N5–Si	1.671	1.68	1.674		
N5–Si	1.751	1.69	1.709		
N5–M	2.398	2.57	2.706		
N5–M	2.596	2.894	2.930		
N5–M	2.956				
N6–Si	1.763	1.762	1.780		
N6–Si	1.777	1.762	1.780		
N6–Si	1.796	1.773	1.791		
N6–M	2.627				
N7–Si	1.705				
N7–Si	1.736				
N7–M	2.397				
N7–M	2.676				
N8–Si	1.741				
N8–Si	1.751				
N8–Si	1.780				
N8–M	3.059				
N8–M	3.070				
$\bar{d}_{(N^{[2]}-Si)}$	1.712	1.719	1.699	1.751	
$\bar{d}_{(N^{[3]}-Si)}$	1.757	1.766	1.782		1.732

3. Calculations and results

First-principles band-structure calculations were performed for $Ca_2Si_5N_8$ and $Sr_2Si_5N_8$ with the localized spherical wave (LSW) method [17] using a scalar-relativistic Hamiltonian. We used local density exchange–correlation potentials (LDA) [18] inside space-filling, and therefore overlapping, spheres around the atomic constituents. The self-consistent calculations were carried out including all core electrons. We performed iterations with 616 $\boldsymbol{k}$-points for

$Ca_2Si_5N_8$ and 384 $\boldsymbol{k}$-points for $Sr_2Si_5N_8$ distributed uniformly in an irreducible part of the Brillouin zone (BZ), corresponding to a volume of the BZ per $\boldsymbol{k}$-point of less than 1×10^{-6} Å^{-3}. Self-consistency was assumed when the changes in the local partial charges in each atomic sphere decreased to the order of 1×10^{-5}.

It was recently found that in ionic oxides (as such alkali and alkaline-earth oxides [19–21]) and nitrides (such as the binary nitride Mg_3N_2 and the ternary nitride $MgSiN_2$ [22]), the anion 3s states have a strong influence on the values of calculated energy gaps and the characters of the conduction bands. Therefore, in the construction of the LSW basis [17–23], the spherical waves were augmented by solutions of the scalar-relativistic radial equations indicated by the atomic symbols 4s, 4p and 3d for Ca; 5s, 5p and 4d for Sr; 3s, 3p for Si; and 3s and 2p for N. The internal l-summation used to augment a Hankel function at surrounding atoms was extended to $l = 2$, resulting in the use of 3d orbitals for N and Si, and to $l = 3$, resulting in the use of 4f orbitals for Ca and Sr. We also performed calculations with a basis set including N 2s orbitals. The Wigner–Seitz radius employed in the calculations is about 1.3 Å for N, 0.7 Å for Si, 1.4 Å for Ca and 1.7 Å for Sr. These radii of the spheres are close to the ionic radii [24]. Because the crystals of both nitrides are not very densely packed, it is necessary to include empty spheres in the calculations. The functions 1s and 2p, and 3d as an extension, were used for the empty spheres. The lattice parameters and coordinates of atoms used in these calculations are obtained from the experiments [9, 10].

For a better understanding of the electronic structure of $M_2Si_5N_8$ (M = Ca, Sr) it is useful to compare it with the electronic structure of the related binary nitride Si_3N_4, as well as a ternary nitride with a higher alkaline-earth-metal:silicon ratio ($MgSiN_2$). Si_3N_4 has two modifications (α and β), with the β-form more stable at high temperature [16, 25]. Xu and Ching performed band-structure calculations for α-Si_3N_4 and β-Si_3N_4 using the self-consistent orthogonalized linear combination of atomic orbitals (OLCAO) method [26]. They found that the electronic structures of α-Si_3N_4 and β-Si_3N_4 are similar, and their results for β-Si_3N_4 are also in agreement to the calculations made by Liu and Cohen using the first-principles pseudopotential total-energy approach within a localized orbital formalism [27]. The electronic structure of $MgSiN_2$ was calculated using the same method as is used here [22].

Figure 1 shows the Brillouin zone (BZ) of orthorhombic $Sr_2Si_5N_8$. Figure 2 shows the partial and total densities of states, and figure 3 the dispersion curve of the energy bands along the high-symmetry lines for $Sr_2Si_5N_8$ with N 3s orbitals included in the basis set. Figure 4 shows the partial and total densities of N 2s states for $Sr_2Si_5N_8$, obtained with N 2s orbitals in the basis set. The calculated partial and total densities of states for monoclinic $Ca_2Si_5N_8$ are shown in figure 5 (with N 3s in the basis set) and figure 6 (with N 2s in the basis set).

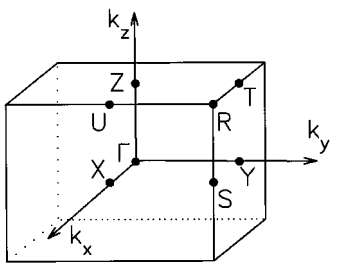

Figure 1. The BZ and high-symmetry points of $Sr_2Si_5N_8$.

Table 3 lists the major features of the electronic structures of the ternary nitrides $Sr_2Si_5N_8$ and $Ca_2Si_5N_8$, as well as those of $MgSiN_2$ [22] and Si_3N_4 [26, 27] for comparison. In the structure of $M_2Si_5N_8$, there are two different types of N atom ($N^{[2]}$ and $N^{[3]}$). The bandwidth of the 2p states of $N^{[3]}$ (N3, N4 and N6 for $Sr_2Si_5N_8$ and N3, N4, N6 and N8 atoms for $Ca_2Si_5N_8$)

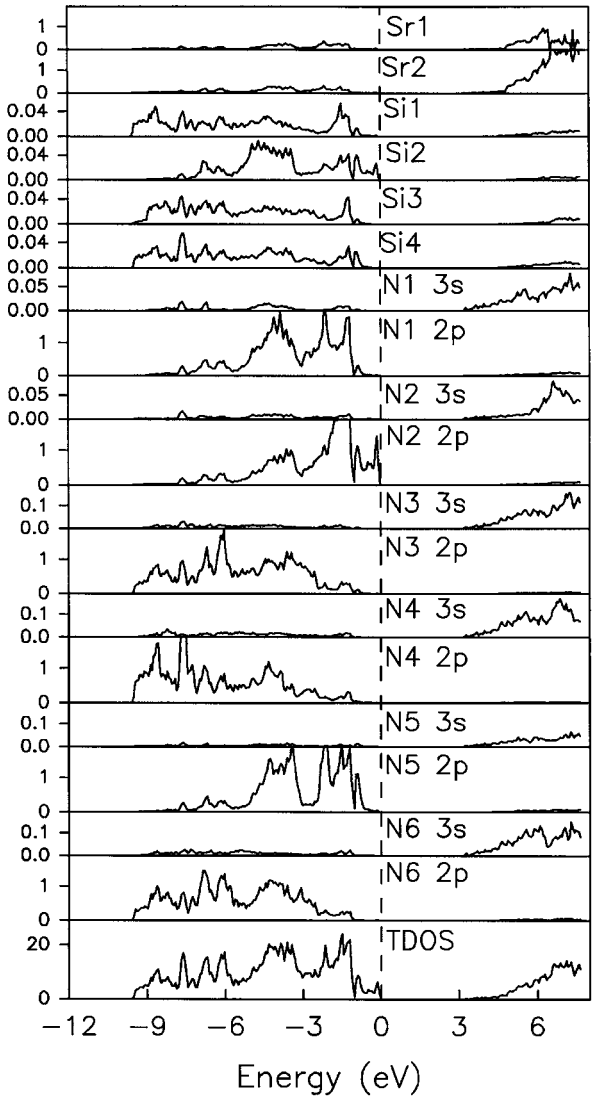

Figure 2. Partial and total densities of states for $Sr_2Si_5N_8$ with N 3s in the basis set. The Fermi level is at zero eV and the *y*-axis represents the partial and total densities of states (DOS). This is also the case for figures 4, 5 and 6.

is about 8 to 9 eV, close to that in Si_3N_4 (about 10 eV [26]). The 2p states of the $N^{[2]}$ atoms (N1, N2 and N5 for $Sr_2Si_5N_8$ and N1, N2, N5 and N7 for $Ca_2Si_5N_8$), which are dominant in the upper part of the valence band, have a smaller bandwidth of just about 6 eV, which is close to the value of about 6.5 eV for $MgSiN_2$ (table 3). The calculated partial density of states also shows the sensitivity of the local electronic structure to the Si–N distances: in $Ca_2Si_5N_8$ the two types of $N^{[2]}$ atom (N1 and N7) have their 2p states more predominant in a narrow energy range from about −2.0 to the Fermi level, while the other two $N^{[2]}$ atoms (N2 and N5) have their 2p states in the energy range from about −6.0 to 0.0 eV (figure 5). These differences are due to the fact that both N2 and N5 atoms have one very short N–Si bond (about 1.67 Å), while

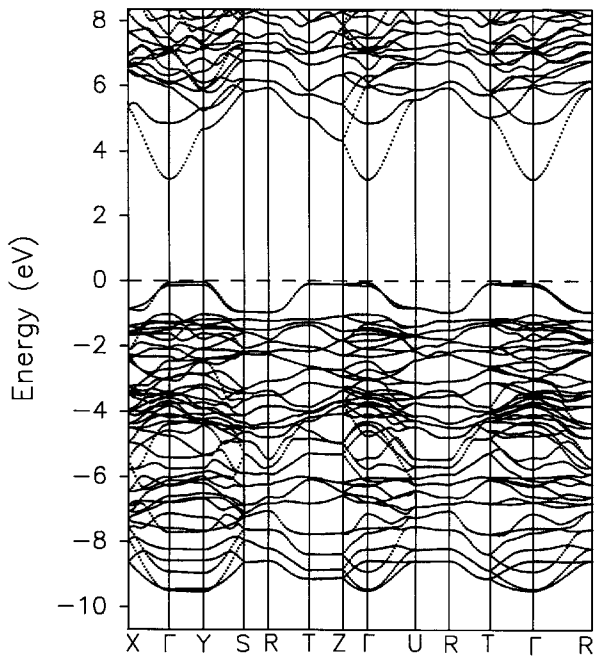

Figure 3. Dispersion of the energy bands for $Sr_2Si_5N_8$.

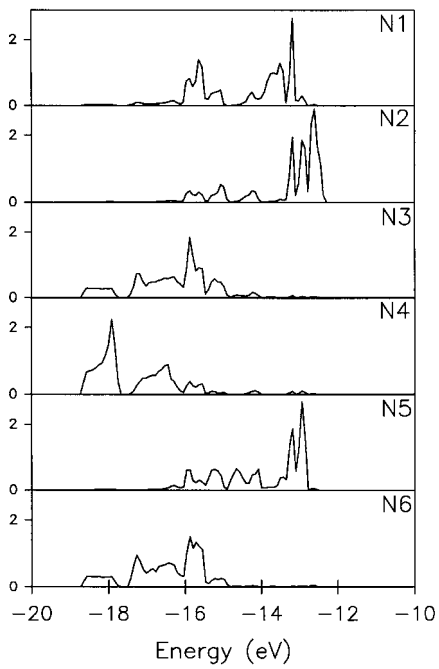

Figure 4. The partial density of N 2s states for $Sr_2Si_5N_8$ without N 3s in the basis set.

the shortest Si–N distances are about 1.71 Å for N1 and N7 (table 2). The top of the valence band is at Γ and Y for $Sr_2Si_5N_8$ in the BZ (figure 3), and on the line along Γ–Y for $Ca_2Si_5N_8$ (not shown). For $Sr_2Si_5N_8$ there are two energy bands, separated from the rest, at the top of the

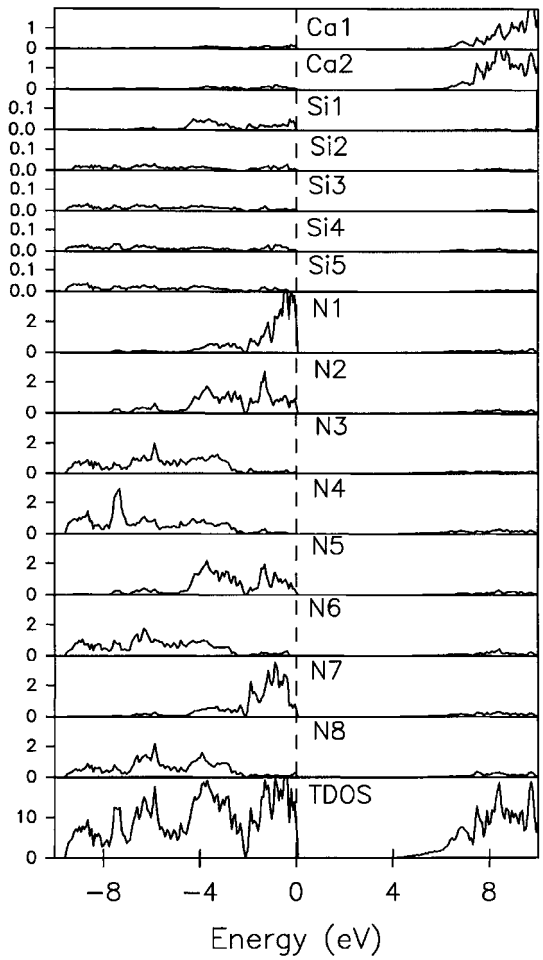

Figure 5. Partial and total densities of states for $Ca_2Si_5N_8$ with N 3s in the basis set.

valence band (figure 3), for which the density of states is mainly composed of $N^{[2]}$ 2p and Si 3s, 3p states, mainly of the N2 and Si2 atoms. It is noted that for $Sr_2Si_5N_8$ the Si2 atom has the partial density of states in a higher position (from −8.0 eV to the Fermi energy) as compared with those of other silicon atoms (from −9.7 to about −1.0 eV). This is because the Si2 atom is connected with only $N^{[2]}$ atoms (N1, N2 and N5 [10]). The shape of the partial DOS for the Sr atoms is similar to that for the 2p states of the $N^{[2]}$ atoms, which corresponds to the fact that the alkaline-metal atoms are connected dominantly to the $N^{[2]}$ atoms. Similar behaviour is observed for Si1 in $Ca_2Si_5N_8$. The bottom of the conduction band for both nitrides, mainly composed of N 3s and Ca 3s/Sr 4s states, is at Γ. The Si 3s states are positioned higher in energy. Therefore $Sr_2Si_5N_8$ is a semiconductor with a direct energy gap of 3.32 eV at Γ, while $Ca_2Si_5N_8$ is an indirect semiconductor with an energy gap of about 4.10 eV. The direct gap at Γ for $Ca_2Si_5N_8$ is about 4.35 eV, as shown in table 3.

Table 3 also shows the calculated results without N 3s orbitals included in the basis set for $Sr_2Si_5N_8$. There are hardly any differences between the two valence bands calculated with/without N 3s in the basis set. However, the conduction band is positioned higher in

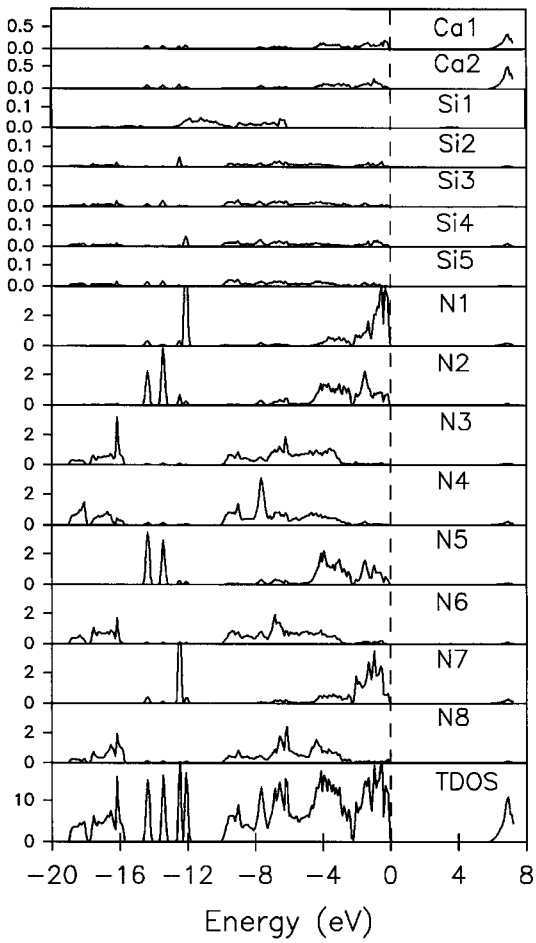

Figure 6. Partial and total densities of states for $Ca_2Si_5N_8$ without N 3s in the basis set.

energy, as found for other nitrides [22]. The energy gap for $Sr_2Si_5N_8$ is still direct at Γ, but with a larger value (about 5.8 eV). Figure 4 shows the partial density of the N 2s states calculated with 2s included in the basis set. Apparently, two different types of N atom can be classified: the $N^{[3]}$ atoms (N3, N4 and N6) have the 2s states in the energy range between −18.8 eV and −15.5 eV, similar for Si_3N_4 containing only $N^{[3]}$ [26, 27]; while $N^{[2]}$ atoms (N1, N2 and N5) have the 2s states in the energy range from −16.1 to −12.3 eV, similar to $MgSiN_2$ containing only $N^{[2]}$ [22]. The N2 atom has the 2s states mainly at the top of the 2s band with a rather narrow bandwidth (about 1.0 eV). Those differences are also in accordance with the N 2p states in the compound (figure 2).

Calculations for $Ca_2Si_5N_8$ without N 3s orbitals in the basis set also show hardly any differences from the valence bands with N 3s in the basis set, as listed in table 3. However, there are some differences in the conduction band. The bottom of the conduction band is composed of mainly Ca 4s states. The bottom of the conduction band is also higher in energy as compared to that calculated with N 3s in the basis set (figures 5 and 6). The $N^{[3]}$ atoms (N3, N4, N6 and N8) in $Ca_2Si_5N_8$ have partial DOS of the 2s states similar to those of Si_3N_4, as shown in table 3 and figure 6. The position of the 2s states of $N^{[2]}$ (N1, N2, N5 and N7)

Table 3. Comparison of calculated electronic structures of $M_2Si_5N_8$ (M = Ca and Sr), $MgSiN_2$ [22] and β-Si_3N_4 [26]. Data in parentheses represent the calculated energy gaps without nitrogen 3s orbitals in the basis set. The Fermi level is set at the top of the valence band.

	β-Si_3N_4 [26]	$Ca_2Si_5N_8$	$Sr_2Si_5N_8$	$MgSiN_2$ [22]
Top of VB	Γ–A	Γ–Y	Γ, Y	Γ, H
Bottom of CB	Γ	Γ	Γ	Γ
Position: $N^{[2]}$ 2p		−5.7 to 0.0	−6.0 to 0.0	−6.5 to 0.0
Width: $N^{[2]}$ 2p		5.7	6.0	6.5
Position: $N^{[3]}$ 2p	−9.8 to 0.0	−10.0 to −2.1	−9.7 to −1.0	
Width: $N^{[3]}$ 2p	9.8	7.9	8.7	
Position: $N^{[2]}$ 2s		−14.5 to −11.8	−16.1 to −12.3	−15.5 to −12.3
Width: $N^{[2]}$ 2s		2.7	3.8	3.2
Position: $N^{[3]}$ 2s	−18.2 to −14.0	−19.2 to −15.7	−19.5 to −15.9	
Width: $N^{[3]}$ 2s	4.2	3.5	4.0	
$E_{g,\mathrm{at}\,\Gamma}$ (eV)	5.25	4.35(5.35)	3.32(5.80)	4.35(6.45)
$E_{g,\mathrm{min}}$ (eV)	4.96	4.10(5.10)	3.32(5.80)	4.35(6.45)
Optical gap (eV)	4.6–5.5	4.9	4.5	4.8

is close to that of $MgSiN_2$. Moreover, the 2s states of $N^{[2]}$ show a more localized character, e.g. the 2s states for N1 and N7 have a single peak positioned at the top of the 2s band with a bandwidth of just about 0.3 eV. The 2s states for the N2 and N5 atoms have two narrow peaks positioned at −13.5 and −14.5 eV.

The top of the valence band, for both $Sr_2Si_5N_8$ and $Ca_2Si_5N_8$, is determined by $N^{[2]}$ 2p and Si 3s, 3p orbitals. The bottom of the conduction bands is mainly composed of N 3s states and s, p orbitals of the alkaline-earth metals.

For the alkaline-earth silicon nitrides $M_2Si_5N_8$ (M = Ca, Sr and Ba), until now no experimental data concerning the electronic properties have been reported. Optical diffuse reflectance spectra were measured for the ternary nitrides by a Perkin-Elmer LS-50B spectrophotometer in the range of 250–630 nm (2.0–5.0 eV). The direct energy gap is estimated from the spectra to be about 4.9 eV for $Ca_2Si_5N_8$, 4.5 eV for $Sr_2Si_5N_8$ and 4.2 eV for $Ba_2Si_5N_8$. The measurements show that with increasing main quantum number of the alkaline-earth metals, the energy gap decreases, in the same order as found in the calculations (table 3). The calculated direct band gaps at Γ (4.4 eV for $Ca_2Si_5N_8$ and 3.3 eV for $Sr_2Si_5N_8$) are in fair agreement with the experimental values, considering the fact that the local density approximation employed in our calculations generally underestimates the energy gaps for semiconductors [28].

4. Conclusions

First-principles band-structure calculations were performed for the ternary alkaline-earth silicon nitrides $Ca_2Si_5N_8$ and $Sr_2Si_5N_8$. The coordination number of nitrogen with silicon shows a strong influence on the partial electronic structure of these atoms. The calculations also show that the conduction bands are determined by N 3s states hybridized with Ca/Sr 4s/5s states. The inclusion of N 3s states is important in the calculations, especially for the character of the bottom of the conduction bands and the energy gaps of these nitrides. The calculations show that both compounds are semiconductors, with a direct energy gap (at Γ) of 3.3 eV for $Sr_2Si_5N_8$ and an indirect gap of 4.1 eV for $Ca_2Si_5N_8$. The energy gap, deduced from the optical diffuse reflectance spectra, is about 4.9 eV for $Ca_2Si_5N_8$, 4.5 eV for $Sr_2Si_5N_8$ and 4.2 eV for $Ba_2Si_5N_8$. The calculated results are in fair agreement with the experimental data.

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