O/N Ordering in $Y_2Si_3O_3N_4$ with the Melilite-type Structure from First-Principles Calculations

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Received November 3, 1999. Revised Manuscript Received December 28, 1999

First-principles calculations based on density-functional theory in the pseudopotential approach have been performed for the energetics and crystal structure of $Y_2Si_3O_3N_4$ with the melilite-type structure. The calculations show the following ordering of the O/N atoms in the crystal: N atoms fully occupy the bridging site (2c) and O atoms fully occupy the terminal site (4e) with 2 O and 6 N atoms at the bridging 8f site. These conclusions are in good agreement with the experimental results obtained with neutron diffraction. In addition, the calculations show that there is a preferential distribution of the O and N atoms at the 8f site, resulting in two different local coordinations of Y, as compared to only a single averaged crystallographic Y site. All the nitrogen ions exhibit similar electronic structure, in contrast to the oxygen ions. However, there are slightly more electrons (about 0.1 electrons per ion) for nitrogen at the 2c site than those at the 8f site, while the silicon atoms have almost the same charge distribution.

I. Introduction

In recent years interest in (oxy)nitrides has been rapidly growing, as these materials show promising physical properties and potential applications in industry.[1−3] The Si_3N_4-based materials show high strength at elevated temperatures, making them suitable candidates for replacement of the super-alloys in e.g. motor engines and gas turbines. Many of the oxynitrides are refractory materials and resistant to aggressive chemical agents at high temperature.[3−5] However, as compared with oxides and sulfides, relatively little is known about oxynitrides. One general question existing for a long time for many oxynitrides is the O/N ordering,[6] for which most routinely used techniques, such as X-ray diffraction, neutron diffraction, etc., only give statistically averaged results for the anion occupations. Additional techniques, such as NMR, may provide information about the local structures. However, in many cases analyzing the information from different techniques is a complicated task, which may even cause confusion. One such example is the crystal structure of N-melilite (nitrogen-containing melilite) $Y_2Si_3O_3N_4$.

Yttrium silicon oxynitrides are formed when yttrium oxide is used to promote sintering in silicon nitride and sialons.[5,7,8] Moreover yttrium silicon oxynitrides appear to be efficient host lattices for luminescent materials.[9−12] For a detailed interpretation of the luminescence properties of the rare-earth doped Y−Si−O−N compounds, the local coordination of the Y-ions is required, e.g., O/N ordering around the Y sites. $Y_2Si_3O_3N_4$, one of the most commonly encountered compounds in sintering, is named N-melilite because of its similarities with the melilite-type minerals, of which the end members are akermanite ($Ca_2MgSi_2O_7$) and gehlenite ($Ca_2Al_2SiO_7$). The suggested structure of $Y_2Si_3O_3N_4$ was derived from akermanite by substitution of Ca by Y, of Mg by Si and of four of the seven oxygen atoms by nitrogen. The positions of Y and Si atoms are well-established. However, the O/N distribution has been a subject of discussion.[5,13−19] Three different models con-

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10.1021/cm991168q CCC: $19.00

Table 1. Specification of the Occupation of the Anions Sites by O/N Atoms for the Different Models of $Y_2Si_3O_3N_4$ with the Melilite-type Structure

site	model I	model II	model III
2c	O	O/N	N
4e	O	O/N	O
8f	N	O/N	O/N

Table 2. Calculated Coordinates of the Atoms in $Y_2Si_3O_3N_4$ with the Melilite-type Structure (Model I),[a] As Compared with the Literature[15]

atom	Wyckoff	calculated coordinates	experimental coordinates [15]
Y	4(e)	0.3298,0.1702,0.5034	0.3363,0.1637,0.5028
Si1	2(a)	0,0,0	0,0,0
Si2	4(e)	0.1450,0.3550,0.9459	0.1442,0.3558,0.9407
O1	2(c)	0.5,0.0, 0.1805	0.5, 0.0,0.1942
O2	4(e)	0.1315,0.3685,0.2780	0.1435,0.3565,0.2827
N	8(f)	0.0758,0.1682,0.7949	0.0926,0.1623,0.7948

[a] The space group and lattice parameters are in Table 3.

cerning the occupation of the anions have been suggested (Table 1). Roult et al.[14] were the first who studied the structure of N-melilite $Ln_2Si_3O_3N_4$ (Ln = Y, lanthanide) using multicomponent profile analysis of time-of-flight neutron diffraction data. They suggested that the favored structure is such that oxygen atoms are at the 2c and 4e sites while N atoms are at the 8f site, with two Si atoms (at 4e) in a SiO_2N_2 tetrahedral and the third Si (at 2a) forming a SiN_4 tetrahedon (we give it the name “the ideal structure”, or model I), as shown in Figure 1 (also Tables 1 and 2). This model was used satisfactorily for refinement of the structure of $Y_2Si_3O_3N_4$ by X-ray powder diffraction, on the basis of the Rietveld whole-pattern fitting technique.[15] Dupree et al.[16] performed high-resolution ^{29}Si NMR for the N-melilite $Y_2Si_3O_3N_4$. They found a single broad peak at about −56.7 ppm in the chemical shift, which was explained to be related to SiO_2N_2 clusters in the compound. Therefore, they suggested that in the favored structure N atoms would partially occupy the 4e site and of importance is partial occupation of the 8f site by oxygen to removing presence of SiN_4 tetrahedra. MacKenzie et al.[17] carried out crystal structure refinements for this compound. The X-ray diffraction data they obtained were insufficient to furnish unambiguous details of the O/N ordering. However, they reached a satisfactory refinement of the powder data by assuming that the anion sites are occupied randomly with O/N (model II). Later on, Koroglu et al.[18] performed ^{15}N NMR studies for N-melilite. In contrast to the work based on the ^{29}Si NMR results, they suggested that O and N are ordered in a way according to Pauling’s second rule: N atoms occupy the bridging site (2c) and O atoms occupy the terminal site (4e) (model III) in the two $Si_2(O,N)_7$ units with Si at 4e, while for the remaining two tetrahedra for Si at 2a in the unit cell, oxygen and nitrogen atoms (at 8f) are disordered but with an overall composition of three nitrogen and one oxygen in each tetrahedron ($SiON_3$).[18] Furthermore, they proposed an O/N ordering at the 8f site according to the intensity of the three peaks in the ^{15}N NMR spectra. Finally Wang et al.[19] investigated the O/N ordering by Rietveld refinement using neutron powder diffraction data. It was found that the 2c site was occupied by 1.7 N and 0.3 O, while the remaining 6.3 N atoms are disordered at the 8f site. They also performed refinements for the above-mentioned models (models I and III). The final *R* values among the different structures showed no significant differences, but model III is preferred. These conclusions are also true for a recent X-ray single-crystal structure determination for $Sm_2Si_3O_3N_4$ by Lauterbach and Schnick.[20]

In this work, results of ab initio calculations for site occupations of the O/N in $Y_2Si_3O_3N_4$ with the melilite-type structure are presented. The calculations are based on density functional theory (DFT) and the pseudopotential method. The bulk modulus of the compound has been calculated. Ordering of the O/N atoms is investigated. Furthermore, information on the electronic structure of the compound is presented, to understand the NMR spectra and optical properties for the related materials.

II. Details of the Calculations

For the calculations we used the ab initio total-energy and molecular-dynamics program VASP (Vienna Ab Initio Simulation Program), developed by the Institut für Theoretische Physik of the Technische Universität Wien (who also supplied the pseudopotentials).[21−23] Vanderbilt-type ultrasoft pseudopotentials[24,25] were used for Y, O, and N, while for Si a norm-conserving pseudopotential was employed. For Y the 4p semi-core states were included in the calculations (i.e., a frozen $[Ar]3d^{10}$ $4s^2$ core). Nonlinear core corrections[26] were applied for Y and Si. The Kohn−Sham orbitals were expanded in plane waves with a kinetic energy cutoff of 36 Ry. Exchange and correlation were treated in the generalized gradient approximation (GGA) using the functional of ref 27. The Brillouin Zone (BZ) was sampled with a $2 \times 2 \times 2$ Monkhorst-Pack grid,[28] resulting in 1−4 *k* points in the irreducible part, depending on the symmetry. Tests on denser *k* point meshes, from $1 \times 1 \times 1$ (1 *k* points), $2 \times 2 \times 2$ (1 or 4 *k* points), $4 \times 4 \times 4$ (12 *k* points), to $4 \times 4 \times 8$ (24 *k* points), showed that this sampling is adequate.

Calculations were first carried out at the optimized volume with only relaxation of the atomic positions. Then calculations were performed with relaxation of both atomic positions and cell parameters. Cell relaxation was always small and thus the quality of the *k* point sampling is not affected by the relaxation. This procedure was repeated several times to give a set of total energies as a function of cell volume. From this the equilibrium volume and bulk modulus were obtained by a fit to a Murnaghan equation of state.[29]

III. Results and Discussion

a. Structure Models of $Y_2Si_3O_3N_4$. As a starting point we begin with the structure of model I obtained by Wang et al.[15] We assumed the symmetry of the

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Table 3. Calculated Lattice Parameters and Bulk Modulus for $Y_2Si_3O_3N_4$ with the Melilite-type Structure (Model I) (Space Group: $P\bar{4}2_1m$)

	B (GPa)	lattice parameters (Å)		V (Å^3)
		a	c	
this work	158	7.652	4.960	290.4
experiments				
Wang et al.[15,19]		7.6137	4.9147	284.9
MacKenzie et al.[17]		7.6083	4.9113	284.3

Table 4. Calculated Results (Lattice parameters, Total Energies) for $Y_2Si_3O_3N_4$ with the Melilite-type Structure

	E_{rigid} (eV)	E_{relaxed1} (eV)	E_{relaxed2} (eV)	space group
a. O(2c, 4e), N(8f) (model I)		205.512	−205.615	$P\bar{4}2_1m$
b. 2O in 2c; 1N+3O in 4e; 7N+1O in 8f	−204.166	−205.151	−205.216	$P1$
c. 2N in 2c; 1N+3O in 4e; 5N+3O in 8f (c)	−202.255	−205.328		$P1$
d. 1N+1O in 2c; 4O in 4e; 7N+1O in 8f	−204.904	−205.739	−205.815	$P1$
model III: 2O/6N ordering at 8f[a]				
e. 4 and 2	−204.000	−205.830	−205.871	$P1$
f. 1 and 2	−203.996	−205.843	−205.866	$P1$
g. 4 and 7	−204.446	−205.883	−205.906	$P1$
h. 4 and 8	−204.382	−205.900	−205.915	$P2_1$
i. 4 and 1	−204.456	−206.026	−206.133	$P2_1$

[a] The numbers represent the occupation of O atoms at 8f, shown in Figure 1.

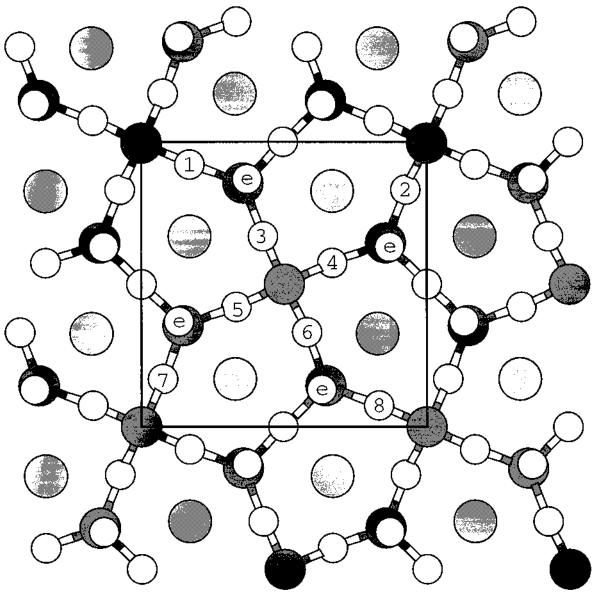

Figure 1. Schematic projection along [001] for $Y_2Si_3O_3N_4$ with melilite type structure (model I). The large lighter circles represent the Y atoms. The large darker circles represent the Si atoms. The medium open circles represent the anions: e for the 4e site, circles on lines for the 2c site, and the numbers for the 8f site.

crystal under pressure to remain the same as in the equilibrium case. The minimum in the total-energy curve gives an equilibrium volume of 290.4 Å^3, which is about 2% larger than the experimental data,[15,17,19] as shown in Table 2. Such results are typical for the GGA approximation.[27] By fitting the calculated data points to the equation of state,[29] we obtained a bulk modulus of 158 GPa. Calculations with broken symmetry confirm the symmetry and the space group ($P\bar{4}2_1m$). Tables 2 and 3 show the lattice parameters and coordinates of the atoms from the calculations and the experiments for model I.[15] The calculated coordinates are in good agreement with the experimental data (Table 1). There are only minor differences in the coordinates of the Y, O, and N atoms as compared with the experimental data, while the coordinates of the Si atoms are almost the same.

Calculations were also performed for different orderings of the O and N anions. Table 4 lists the calculated total energies for several different structural configurations. The total energy E_{rigid} represents only an interchange of O and N ions, while the total energies E_{relaxed1} and E_{relaxed2} were obtained after relaxation of the positional parameters and of both the positional parameters and lattice parameters, respectively.

First we discuss the plausibility of model II. Direct interchange of one N at 8f with one O at 4e causes a rise of about 0.45 eV per unit cell (case b vs case a in Table 4). This interchange is still unfavorable even after structural relaxation. The calculations also show that exchange of one O at 4e with one N atom at 8f is also not favorable even with two N ions at 2c (case c vs case a in Table 4).

Direct interchange of one N atom at the 8f site with one O at the 2c site causes a rise of the total energy of about 0.7 eV per unit cell (Table 4 case d vs case a). Relaxation of the coordinates of the atoms and lattice parameters reduces the total energy to about 0.2 eV per unit cell lower than that of model I. Further interchange of another O at 2c with one N at 8f results in the structure of model III. In this case with the relaxation of the positions of the atoms and the lattice parameters the total energies are reduced to about 0.3 to 0.5 eV per unit cell lower than for model I, as shown in Table 4 (cases e to i vs case a).

Next we discuss the possible ordering of O/N at the 8f sites (model III). There are five possible configurations for two oxygen atoms at the 8f site (Figure 1), for which the calculated total energies are listed in Table 4 (cases e−i). These configurations are stable as compared to model I with about 0.3−0.5 eV lower energy. The most stable configuration is case i, which has an energy about 0.52 eV lower than that of model I. It is also apparent that the total energy depends on the distance between the two oxygen ions at 8f: in cases e and f the two oxygen ions are connected at the same Si atom, while in case i the distance between the two oxygen ions is the largest. Relaxation of lattice parameters causes reduction of the lattice symmetry from a tetragonal cell to an orthorhombic cell (the deviations of the angles from 90° are less than 1°). There are small deviations of the *a* and *b* axis (about 1%) from the *a* axis of the tetragonal lattice, while the *c* axis is almost constant. However, the relaxation of lattice parameters does not change the order of the energies of the five configurations, except for the cases e and f.

As shown in Table 4, the calculations show that the occupation of the 4e site by N atoms causes a sizable rise of the total energy, which indicates that model II is unlikely. The favored O/N ordering is such that N occupy the bridging 2c and O the terminal 4e sites with 6 N and 2 O at the 8f site (model III), with the preferential configuration shown in Figure 2, case i in Table 4. These conclusions are in good agreement with the Pauling second rule[30] and with the experimental results from the neutron-diffraction refinements.[19]

Table 5. Interatomic Distances (Å) for the Favorable Structure as Compared with Experimental Results

			model III		
	model I		calcd		
	calcd	exp.[15]	Y(Si)1	Y(Si)2	exp[19,a]
Y−N1			2.34	2.42	2.346
Y−O1	2.44	2.325			
Y−O2	2.42, 2.57 (2×)	2.341, 2.57 (2×)	2.42	2.38	2.360
			2.46, 2.64	2.56, 2.62	2.551 (2×)
Y−N3	2.42 (2×),	2.346 (2×),	2.37, 2.38	2.44	2.397 (2×)
	2.70 (2×)	2.775 (2×)	2.80	2.61, 2.65	2.754 (2×)
Y−O3			3.15	2.47	
Si(a)−N3	−1.74 (4×)	1.744 (4×)	1.71 (3×)		1.701 (4×)
Si(a)−O3			1.74		
Si(e)−N1			1.69	1.67	1.702
Si(e)−O1	−1.69	1.688			
Si(e)−O2	−1.65	1.681	1.67	1.65	1.661
Si(e)−N3	1.70 (2×)	1.685 (2×)	1.72, 1.74	1.72	1.714 (2×)
Si(e)−O3				1.70	

[a] The space group used in the structure refinement is $P\bar{4}2_1m$, the same as in model I

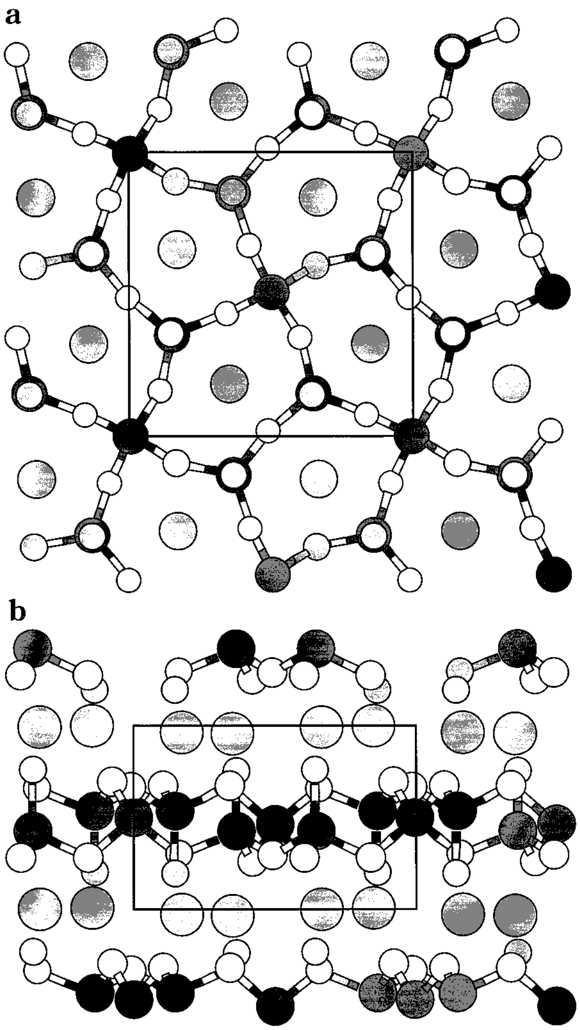

Figure 2. Favored structure of $Y_2Si_3O_3N_4$ along the [001] (a) and [010] (b) directions. The definition of the circles is the same as Figure 1. The medium filled circles represent O and the medium open circles represent N atoms.

b. Structure and Bonding in $Y_2Si_3O_3N_4$. Figure 2 shows the projections of the preferential structure (case i in Table 4) along the [001] and [010] directions. Table 5 lists interatomic distances for the favored configuration (case i in Table 4), as compared to the neutron diffraction data by Wang et al.[19] and to the calculated (case a in Table 4) and experimental data[15] for the structure with the highest symmetry (model I).

In model I, the discrepancies in interactomic distances between the experiment[15] and calculation are minor. The largest discrepancy occurs for some of the Y−O/N distances (~0.1 Å).

For the preferential structure, the calculations show that the Si−N network is distorted (Figure 2) as compared with model I (Figure 1). There are two crystallographically different Y atoms (Table 5), in contrast to only one for the experimentally determined (averaged) structure.[19] The Y atoms also show a shift along the [010] axis, as shown in Figure 2b. It is noted that although Y1 has the same number of coordinating anions (YO_4N_4) as Y2 (YO_4N_4), there is a long interatomic distance (3.1 Å) between Y1 and O as shown in Figure 2. Obviously, the calculations yield valuable information about differences in local coordination, as compared to the experimental results obtained with neutron diffraction, which only gives averaged site coordination.

The difference in the interatomic Si−O/N distances between the experimental and the calculated results is very small. The Si atoms at the 2a site have a tetrahedral coordination by three nitrogen ions and one oxygen ion ($SiON_3$), with a Si−N distance of 1.71 Å, and a Si−O distance of 1.74 Å (Table 5). The Si−N/O distances are very close to the corresponding experimental data for Si atoms at the 4e sites. Si(e)1 is coordinated by three N atoms and one O atom ($SiON_3$), Si(e)2 by two N and two O atoms (SiO_2N_2). The ratio between the numbers of ($SiON_3$) and (SiO_2N_2) is 2 to 1. In this structure there are three different kinds of O and four kinds of N atoms. The O atoms at the bridging 8f site have two Si and one Y coordinating atom (OSi_2Y), while the O atoms at the terminal 4e site have one Si and three Y coordinating atoms ($OSiY_3$). The N atoms at 2c and 8f have two Si and two Y coordinating atoms (NSi_2Y_2).

In model I, the Si1 atom at the origin has a tetrahedral coordination by 4 N atoms (SiN_4) at the 8f site. There is $\bar{4}$-point symmetry for Si1. This symmetry is destroyed when two N atoms at 8f are exchanged with the two O atoms at the 2c site. The space group for model I from the experiments, as well as from the calculations, is $P\bar{4}2_1m$ (D_{2d}^3), as shown in Tables 2 and 3. This symmetry has been used to refine the structure for this class of crystals,[15] even for model III.[19,20]

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Table 6. Calculated Electronic Configurations of the Ions in $Y_2Si_3O_3N_4$

	s	p	d	total
O1 (8f)	1.92	5.20	0.13	7.24
O2 (4e)	1.90	5.07	0.10	7.06
O3 (4e)	1.90	5.05	0.09	7.04
N1 (2c)	1.82	4.67	0.14	6.62
N2 (8f)	1.80	4.56	0.12	6.49
N3 (8f)	1.80	4.56	0.12	6.49
N4 (8f)	1.80	4.55	0.12	6.48
Si1 (4e)	0.22	0.28	0.10	0.60
Si2 (4e)	0.22	0.28	0.10	0.60
Si3 (2a)	0.22	0.27	0.09	0.58
Y1 (4e)	0.09	5.85	0.59	6.52
Y2 (4e)	0.08	5.84	0.56	6.48

Exchange of O atoms at the 2c site with N atoms at the 8f site would reduce the symmetry. For the preferential structure, there is only C_2 symmetry still available. Therefore, the real symmetry has been reduced to a monoclinic cell (or even triclinic), although approximately an orthorhombic, or even a tetragonal lattice was obtained.

c. Charge Distribution in $Y_2Si_3O_3N_4$. As mentioned before, to determine the crystal structure of the N-melilite $Y_2Si_3O_3N_4$, different techniques have been employed.[14−20] In the NMR spectroscopy experiments, the ^{29}Si spectra show a broad single peak, which was believed to be due to similar environments for all the Si atoms in the structure.[16] The ^{15}N spectra exhibit three peaks,[18] which was interpreted as three different possible environments for the N atoms. Our calculations show that for the most favored structure of the N-melilite $Y_2Si_3O_3N_4$, there are four different kinds of N atoms.

The calculations show that the density of oxygen 2s states has a very narrow band (with a width of about 0.2 eV). The density of the 2s states of the oxygen atoms at 8f is positioned at about −19.5 eV, while the oxygen atoms at 4e have their density of the 2s states positioned at about −18.0 eV. On the other hand, the calculations show the N 2s states of the nitrogen ions at almost the same position (about −15 eV) with a width of about 2.1 eV. The partial density of 2p states is also similar for the N atoms at the 2c and 8f sites. That is understandable since all the N atoms are in bridging sites.

NMR spectra have been used to probe the chemical environments of atoms in condensed matter. The absolute value of the magnetic field at a particular nucleus comprises not only contributions from the electrons of the atom containing the nucleus, but also from the nuclei and electrons of surrounding atoms, as it is sensitive to the local chemical environment. The combined effect leads to a chemical shift of the resonance. Although the electronic structure of the various nitrogen ions is similar, the charges on nitrogen ions show differences. Table 6 lists the calculated electronic configurations for the four different nitrogen atoms in the favored structure. There are about 1.82 electrons at the 2s orbital for the nitrogen at the 2c site, which is slightly more than those at the 8f sites (1.80 electrons). The occupation of electrons on the 2p orbital of the nitrogen atom at the 2c site is also about 0.11 electrons more than those of the nitrogen atoms at the 8f sites. These results are in agreement with the fact that nitrogen atoms at 2c have a slightly different chemical environment from those at 8f. Therefore, a different chemical shift is expected. The signal ratio in the NMR spectra between the two kinds of nitrogen ions is expected to be 1:3. The NMR results showed that there are three different peaks at −210, −217, and −228 with a ratio of the intensities of approximately 1:4:15 by dissolving a broad peak.[18] However, the small peak at −210, which occupies about 5% of the total intensity, may originate from the impurity of the sample (purity of the sample is about 95% from X-ray diffraction [18]).

Table 6 also lists the charge distribution for Y, O, and Si atoms in the structure. The difference of charge distributions between the two different Y atoms is rather small, although Y1 has a rather long Y−O distance. However, the difference for the charge distribution of the three different kinds of oxygen ions is apparent: the O ions at 8f have about 0.2 electrons more than those at the 4e site.

The calculations show that in the structure the silicon atoms have different coordination by oxygen and nitrogen ($SiON_3$ and SiO_2N_2) (Table 5). However, the charge distribution of the various Si atoms shows no significant differences (about 0.02 electrons Table 6). The NMR experiments also showed that there is just a broad peak in the ^{29}Si spectra, in good agreement with the calculations. This conclusion may also be important to explain the related experimental results obtained for the other yttrium silicon oxynitrides.[31,32]

IV. Conclusions

Self-consistent first-principles calculations have been performed for the energetics and structure of $Y_2Si_3O_3N_4$ with the melilite-type structure using density-functional theory and the pseudopotential approach. The calculations show ordering of the O/N in the crystal. N atoms fully occupy the bridging site (2c) and O atoms fully occupy the terminal site (4e) with 2 O and 6 N at the bridging 8f site. These conclusions are in good agreement with the experimental neutron diffraction results. Moreover, the structure optimizations also show that there is a preferential distribution of the O/N ions at the 8f site, resulting two different types of yttrium and three different types of silicon atoms. The averaged interatomic distance between Si and the anions is about 1.70 Å (1.67−1.74 Å). The calculations also show that the electronic structure and charge distribution for the oxygen ions at the bridging 8f site are different from those of the oxygen ions at the terminal 4e site. However, both nitrogen ions at the bridging 2c and 8f sites have only slightly different charge distribution from each other, while the silicon atoms with different (O, N) coordinations have almost the same charge distribution.

Acknowledgment. Dr. Joost van Krevel is acknowledged for beneficial discussions and critical reading of the manuscript. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) and was made possible by financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

CM991168Q

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