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Electronic structure calculation of cohesive properties of some $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ spinels

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Abstract

The structures of a spinel form of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ are investigated using techniques of ab initio density functional plane wave electronic structure theory with soft pseudopotentials. Four spinel configurations are considered corresponding to $z = 0, 1, 2,$ and 4 . In the case of $z = 2$ (Si_2AlON_3 spinels), that has now been synthesized, a normal or inversed configuration is considered. Very small energy differences are found suggesting that a mixed random atomic structure is very likely for the Si_2AlON_3 spinels. Results across the other range of spinels show that incompressible structures are associated with larger concentrations of N. These structures also have the larger cohesive energies. All spinels have direct energy band gaps varying between 3 and 4 eV in the spinel 56-atom unit cell depending upon oxygen concentration.

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1. Introduction

Elaborate crystal structures are rapidly emerging as having potential ultra-hard properties. In particular, oxides and nitrides are useful with electronic structure calculations offering much insight into the fundamental atomic bonding [1,2].

Calculational procedures have now advanced to a degree of reliability where predictions of a variety of properties can now be studied with great confidence. Whilst there are a variety of subtle calculational approaches, it is now proving that the most accurate and widely used is the approach based upon pseudopotentials and invoking a converged plane wave basis. It is the purpose of this paper to make application of this technique to study an exciting new class of ceramic silicon–aluminium–oxygen–nitrogen (SiAlON) system materials that has recently emerged with the spinel structure [3].

As a binary material both spinel Si_3N_4 [4] and Ge_3N_4 [5] have now been synthesized [6] and their structures extensively studied [7–9]. The theoretical predictions and appropriate synthesis have now demonstrated the potential of the spinel lattice as an ultra-hard structure. In either of these binary structures, cations occupy both tetrahedral and octahedral sites, but it has been suggested that incorporation of a third element can enhance the properties of the structure especially refractory and electronic properties [7]. Carbon appears to be the main element affecting the compressibility of the structures and when C occupies tetrahedral locations in the spinel structure ab initio calculations predict a significant increase in the bulk modulus. As yet, however, the synthesis of a ternary C containing nitride ceramic has not been realized—yet if so its properties would be far superior than its binary parent.

The explicit crystal structure of the spinels has been examined at length by several authors [10–12]. Essentially, it consists of a series of interpenetrating pseudo cubic sub-lattice structures that can be categorized into either four- or 12-fold symmetries. In ternary spinel

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AB_2O_4 structures, the relative ionicity of the metals dictates how the metals occupy the sites with octahedral or tetrahedral symmetry. Verway and Heilman [12] pointed out that for metals A and B being divalent and trivalent, respectively, the divalent metal entirely occupies the tetrahedral sites whereas with metals A and B being quadrivalent and divalent cations octahedral and tetrahedral sites are occupied in equal proportions. The former category of occupancy between the octahedral and tetrahedral sites has been termed “normal spinel” and the latter “inversed spinel” [11].

Quaternary spinels on the other hand have not received much attention despite the fact that the rather large cubic cell of the spinel structure—consisting of 56 atoms—offers quite a large variation in site occupancy. In the case of a quaternary structure in the configuration $Si_{6-z}Al_zO_zN_{8-z}$, the ionicity of the anions will also affect the overall effective ionic character of the cations Si or Al. As such the fundamental observation made by Verway and Heilman [12] of designating the structure of the spinels as being normal or inversed depending upon occupancy of the cation sites may still be applicable even though the relative distribution of cations among the octahedral and tetrahedral sites may possibly affect the overall material properties as is the case with ternary metal spinels [13].

The SiAlON system has been extensively studied with respect to composition at high temperatures [3,14–16]. Static pressures of 11 GPa are needed to clearly obtain the Si_2AlON_3 spinel phase starting from the β - Si_2AlON_3 phase. This is consistent with theoretical predictions of the β - to spinel-phase transformation of Ge_3N_4 [8] and possibly indicating similar compressibility of the two materials. Rietveld analysis of the high-pressure phase indicated a single phase of spinel symmetry from which a lattice parameter of $a_0 = 7.823 \text{ \AA}$ was determined [3]. We add that in the Rietveld refinement scattering curves for neutral atoms were used but the use of similar curves for charged atoms lead to nearly the same result. No significant differences between a similar analysis using solely N or N and O could be seen. This meant that it was not possible to obtain explicit Wyckoff coordinates through which the cation site occupancy could be determined and for this reason an ab initio calculation was undertaken.

Other spinel SiAlON configurations are also possible for the general popular formula $Si_{6-z}Al_zO_zN_{8-z}$ which follows from the assumption that such a structure is ionic which is tentative. In this work, we have modelled such structures using a 56-atom cubic cell with a lattice constant a . The purpose of the calculation to identify optimum properties of the structure as measured both by cohesive elastic properties as well as structural features namely the cell constant, a , and the cohesive energies.

2. Computational procedure

To elucidate the various structures we have applied ab initio techniques of density functional theory within the local density approximation employing soft Troullier Martins pseudopotentials [17] and a plane wave basis [18]. The cutoff radii describing each of the pseudopotentials is given in Table 1.

The plane wave approach is now quite widely respected giving a useful description of material properties at the fundamental atomic level even though the calculational constraint is near the zero temperature limit. A criterion of at least 10^{-4} eV/atom was placed on the self-consistent convergence of the total energy and the calculations reported here used a plane wave cutoff of 64 Ry. Here we have used throughout a 56-atom cubic cell to represent the various SiAlON spinel structures with a $[2 \times 2 \times 2]$ grid corresponding to four special k-points. The cell was subsequently compressed to obtain the bulk modulus through a least-squares fit to the Birch equation of state [19]. The cohesive energy, E_{coh} of a particular SiAlON is further obtained from the expression

$$E_{\text{coh}} = E_{\text{tot}}(Si_{6-z}Al_zO_zN_{8-z}) - (6-z)e(\text{Si}) - ze(\text{Al}) - ze(\text{O}) - (8-z)e(\text{N}),$$

where E_{tot} is the total energy of the appropriate unit cell and $e(\text{Si})$, etc. the total energy of the pseudoatom including spin correlation corrections. The value of E_{coh} in principle can be measured—yet the value also gives some insight into the relative stability of a particular structure and thus the potential of the structure to resist extreme mechanical conditions. We estimate that the calculational uncertainty in calculated total energies of the procedure is of the order 0.005 eV/atom . In some cases, we have quoted results well below this level of accuracy to highlight, as we shall see, situations where a very closeness of the finally deduced energy can impact on the overall physical significance of the results.

3. N- and O-rich SiAlONs

In the quaternary N-rich structure $z = 2$ SiAlONs (Si_2AlON_3) when the anions are restricted to various four-fold sub-lattices for O and N, respectively, then the

Table 1
Cutoff radii (a.u.) of pseudopotentials used in the present work

Element	r_s	r_p	r_d
O	1.45	1.45	—
N	1.12	1.20	—
Si	1.88	1.88	1.88
Al	2.48	2.89	1.88

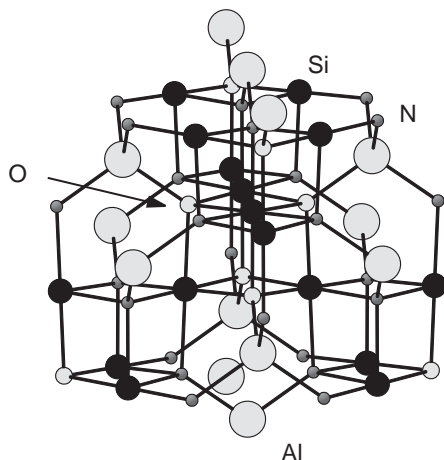


Fig. 1. A direct structure of Si_2AlON_3 ($z = 2$) spinel (Al only on tetrahedral sites, Si on octahedral sites). Some atoms lying outside the cubic unit cell are included to highlight the specific tetrahedral and octahedral sub-structures.

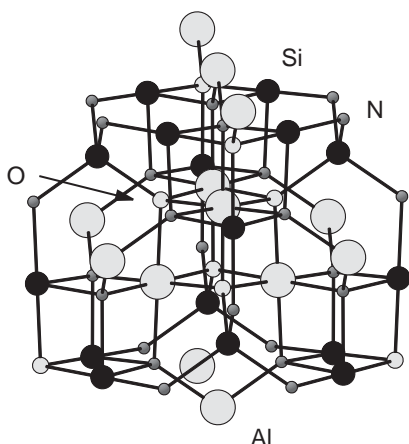


Fig. 2. An inversed structure of Si_2AlON_3 ($z = 2$) spinel (Al and Si on both octahedral and tetrahedral sites).

normal or inversed spinel cation structure can be examined. Figs. 1 and 2 schematically show the 56-atom unit cells in the two cases where the Al atom occupies either all the tetrahedral sites as for the normal spinel structure or part of the octahedral sites as for the inversed spinel structure.

To model other forms of the spinel SiAlONs we have considered some representative 56-atom unit cells shown in the figures. Such 56-atom cells are representative of the two conditions of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ for $z = 1$ and for $z = 4$, respectively, and are shown in Figs. 3 and 4, respectively. The range of structures can therefore be considered as reflecting N- and O-rich SiAlONs. We also make comparison with Si_3N_4 which is the $z = 0$ limit in the SiAlON family. In Table 2 we explicitly list all the fractional coordinates of the Si_3N_4 spinel

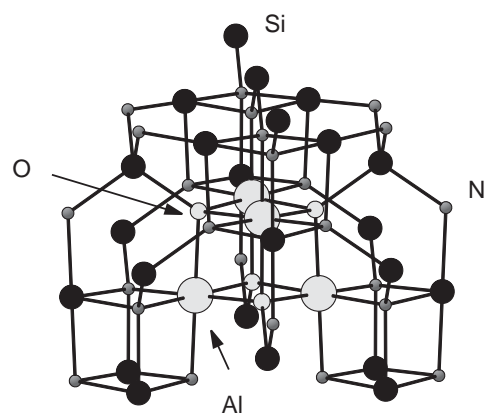


Fig. 3. Structure of Si_5AlON_7 ($z = 1$) spinel.

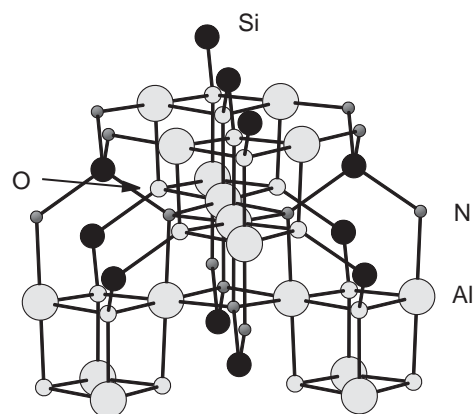


Fig. 4. Structure of $\text{SiAl}_2\text{O}_2\text{N}_2$ ($z = 4$) spinel.

structure and the atomic occupancies of these sites as used to specify either nominal stoichiometry of the $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ that have been considered here. The nominal symmetry of this cubic spinel system corresponds to the space group $Fd\bar{3}m$, as discussed at length by Serghiou et al. [5] for the case of the cubic spinel Ge_3N_4 system. Formally, the cubic A_3B_4 spinel system can be represented by Wyckoff coordinates $A(1) : 8a(1/8, 1/8, 1/8)$, $A(2) : 16d(1/2, 1/2, 1/2)$ and $B : 32e(x, x, x)$. The extensive listing of the coordinates for the cubic cell as shown in Table 2 embraces this space-group symmetry even though there are chemical variations reflecting the SiAlON stoichiometry.

3.1. Cohesive properties

The results obtained for the $z = 2$ SiAlONs are given in Table 3 with the bulk moduli being obtained from the Birch equation of state. Somewhat surprising is that a very small energy difference between the normal and inversed cation topology is found—but the inversed distribution is marginally lower in energy although this

Table 2
Fractional coordinates of the cubic spinel lattice considered here

Atom	Fractional coordinates for $z = 0$	$z = 0$	$z = 1$	$z = 2$ (direct)	$z = 2$ (inversed)	$z = 4$
1	0.0000, 0.0000, 0.0000	Si	Si	Al	Al	Si
2	0.0000, 0.5000, 0.5000	Si	Si	Al	Al	Si
3	0.5000, 0.0000, 0.5000	Si	Si	Al	Al	Si
4	0.5000, 0.5000, 0.0000	Si	Si	Al	Al	Si
5	0.7498, 0.7498, 0.2502	Si	Si	Al	Si	Si
6	0.7498, 0.2502, 0.7498	Si	Si	Al	Si	Si
7	0.2502, 0.7498, 0.7498	Si	Si	Al	Si	Si
8	0.2502, 0.2502, 0.2502	Si	Si	Al	Si	Si
9	0.6250, 0.6250, 0.6250	Si	Al	Si	Al	Al
10	0.6250, 0.3750, 0.3750	Si	Al	Si	Al	Al
11	0.3750, 0.6250, 0.3750	Si	Al	Si	Al	Al
12	0.3750, 0.3750, 0.6250	Si	Al	Si	Al	Al
13	0.8750, 0.8750, 0.6250	Si	Si	Si	Si	Al
14	0.6250, 0.8750, 0.8750	Si	Si	Si	Si	Al
15	0.8750, 0.6250, 0.8750	Si	Si	Si	Si	Al
16	0.6250, 0.1250, 0.1250	Si	Si	Si	Si	Al
17	0.8750, 0.3750, 0.1250	Si	Si	Si	Si	Al
18	0.8750, 0.1250, 0.3750	Si	Si	Si	Si	Al
19	0.1250, 0.6250, 0.1250	Si	Si	Si	Si	Al
20	0.3750, 0.8750, 0.1250	Si	Si	Si	Si	Al
21	0.1250, 0.8750, 0.3750	Si	Si	Si	Si	Al
22	0.1250, 0.1250, 0.6250	Si	Si	Si	Si	Al
23	0.1250, 0.3750, 0.8750	Si	Si	Si	Si	Al
24	0.3750, 0.1250, 0.8750	Si	Si	Si	Si	Al
25	0.8670, 0.8670, 0.8670	N	N	O	O	O
26	0.8670, 0.1330, 0.1330	N	N	O	O	O
27	0.1330, 0.8670, 0.1330	N	N	O	O	O
28	0.1330, 0.1330, 0.8670	N	N	O	O	O
29	0.6329, 0.6329, 0.8670	N	N	N	N	O
30	0.8670, 0.6329, 0.6329	N	N	N	N	O
31	0.6329, 0.8670, 0.6329	N	N	N	N	O
32	0.8670, 0.3671, 0.3671	N	N	N	N	O
33	0.6329, 0.1330, 0.3671	N	N	N	N	O
34	0.6329, 0.3671, 0.1330	N	N	N	N	O
35	0.3671, 0.8670, 0.3671	N	N	N	N	O
36	0.1330, 0.6329, 0.3671	N	N	N	N	O
37	0.1170, 0.6170, 0.8830	N	N	N	N	N
38	0.1170, 0.8830, 0.6170	N	N	N	N	N
39	0.6170, 0.1170, 0.8830	N	N	N	N	N
40	0.8830, 0.1170, 0.6170	N	N	N	N	N
41	0.3671, 0.6329, 0.1330	N	N	N	N	O
42	0.3671, 0.3671, 0.8670	N	N	N	N	O
43	0.3671, 0.1330, 0.6329	N	N	N	N	O
44	0.1330, 0.3671, 0.6329	N	N	N	N	O
45	0.6170, 0.8830, 0.1170	N	N	N	N	N
46	0.8830, 0.6170, 0.1170	N	N	N	N	N
47	0.1170, 0.1170, 0.3830	N	N	N	N	N
48	0.8830, 0.8830, 0.3830	N	N	N	N	N
49	0.1170, 0.3830, 0.1170	N	N	N	N	N
50	0.8830, 0.3830, 0.8830	N	N	N	N	N
51	0.3830, 0.1170, 0.1170	N	N	N	N	N
52	0.3830, 0.8830, 0.8830	N	N	N	N	N
53	0.6171, 0.3829, 0.6171	N	O	O	O	N
54	0.3829, 0.6171, 0.6171	N	O	O	O	N
55	0.3829, 0.3829, 0.3829	N	O	O	O	N
56	0.6171, 0.6171, 0.3829	N	O	O	O	N

Overall the cubic spinel system has space group $Fd3m$. As seen from site occupancy, a four-fold symmetry is still retained in the system for the various stoichiometries of $\text{Si}_{6-z}\text{Al}_z\text{O}_2\text{N}_{8-z}$ spinels considered here.

Table 3
Calculation properties of two phases of spinel Si_2AlON_3

	a_0	B (GPa), B'	E_{coh} (eV)
Si_2AlON_3 —normal	7.824	260, 4.80	−365.24(24)
Si_2AlON_3 —inversed	7.806	271, 4.23	−365.25(18)

B and B' are the bulk modulus and pressure derivative, E_{coh} the cohesive energy per 56-atom unit cell. The observed lattice parameter is $a_0 = 7.823 \text{ \AA}$.

is quite consistent with other calculations [20] for SiAlON s of similar stoichiometry. For both structures, there is negligible difference both in the unit-cell length and the cohesive properties as measured by the bulk modulus albeit the inversed structure appears possibly less compressible with higher bulk modulus. The significance of this result is that the overall material refractory and structural characteristics of quaternary spinel SiAlON unlike their ternary-based metal oxide counterparts, display very little dependence on the relative cation occupancy of the tetrahedral or octahedral sites. In many ways this is not unlike the behavior of the refractory material B_4C where similar ab initio total energy calculations [21] indicate a very slight preference for one possible site for C occupancy over another possible site yet at the same time both possible configurations have similar structural and elastic characteristics.

The calculated nearest neighbor distances in each of the structures are now shown in Table 4. It is clear from these values that the inversed structure allows for slightly shorter bond lengths throughout—and this feature possibly accounts for the slightly larger value of the bulk modulus in this phase. Notably, we see that the inversed spinel structure has lowest value of the Si–O bond.

The results for all structures are presented in Table 5 and where comparison is made with Si_3N_4 which corresponds, of course, to the trivial $z = 0$ case in the SiAlON family.

Specifying a bond length to be a bond distance of 2 \AA or less, we can make count of the number of bonds for each of the four types namely Si–O, Al–O, Si–N and Al–N. There is no correlation between the calculated bulk modulus and the number of Si–O or even Al–O bonds. To the contrary as shown in Fig. 5 there is a weak correlation of the bulk modulus with number of Al–N bonds and a very strong correlation with the number of Si–N bonds. We hasten to add for that the lengths of the Si–N bonds is somewhat constant only slightly varying between about 1.78 and 1.92 \AA structures for all structures investigated.

Quite clearly a trend is seen to emerge. First the concentration of O increases the size of the unit cell, and with this increase in volume there is a lowering of the bulk modulus. N-rich SiAlON s, therefore, are predicted

Table 4
Smallest interatomic cation–anion calculated spacings (\AA) in the two spinel structures considered in this work

	$d_{\text{Si-O}}$	$d_{\text{Si-N}}$	$d_{\text{Al-O}}$	$d_{\text{Al-N}}$
Si_2AlON_3 —normal	1.92	1.78	1.93	1.81
Si_2AlON_3 —inversed	1.78	1.79	1.89	1.78

Table 5
Calculated structural, elastic and cohesive properties of some $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ spinels

z	Spinel	a (\AA)	B (GPa), B'	E_{coh} (eV/atom)
0	Si_3N_4	7.74	302, 3.81	−7.113
1	Si_5AlON_7	7.73	299, 4.37	−6.838
2	Si_2AlON_3	7.80	260, 4.00	−6.522
4	$\text{SiAl}_2\text{O}_2\text{N}_2$	7.86	257, 3.81	−5.945

The observed lattice parameter of Si_3N_4 is 7.80 ± 0.03 and 7.823 \AA in Si_2AlON_3 .

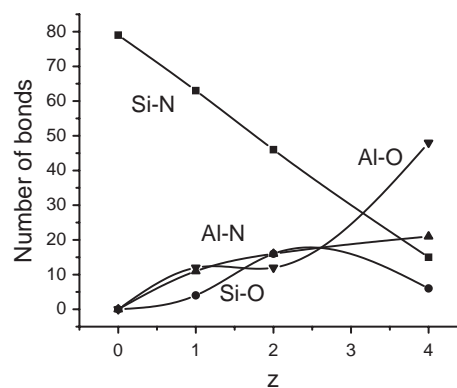


Fig. 5. Number of Si–N and Al–N bonds for $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ spinels. As discussed in the text the criteria is that such bonds have length less than 2 \AA .

to have the higher bulk modulus and possibly higher hardness, although shear-modulus calculations would confirm this trend. But the O-rich SiAlON s are also the least stable as indicated from the steady reduction in cohesive energy. Once again this suggests that N-rich SiAlON s are likely to be slightly more stable than SiAlON s that are O-rich.

3.2. Electronic band structure

In Fig. 6, we show part of the electronic energy band structure for the various spinels that we have considered. We bear in mind that the LDA formalism we have employed is not really that good for quantitative prediction of energy band gaps yet we expect that trends will be accurately suggested. First is the case of Si_3N_4 , that calculated energy gap is 3.63 eV and is a

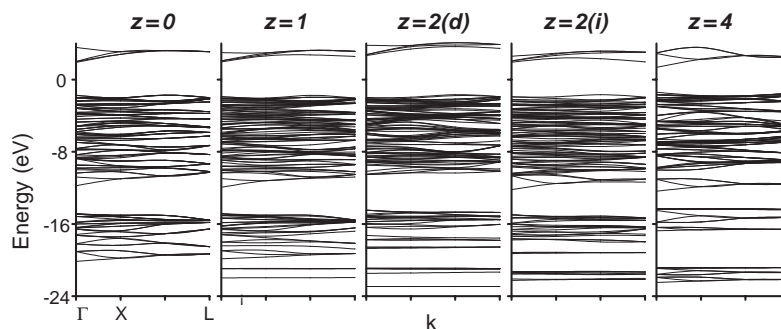


Fig. 6. Electronic band structure of $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ spinels along the Γ - X - L direction. The Fermi energy is at the zero of energy in all cases. Γ is the point (0,0,0), X (1,0,0) and L (1,1,1) in the cubic 56-atom cell.

direct gap which is in good agreement with an earlier calculation of 3.45 eV [7] using an electron-orbital rather than plane wave approach as here. The direct nature of the energy gap is retained with increasing O content and even increasing to about 4 eV for the $z = 2$ SiAlONs. With higher O-concentration, however, the gap decreases to about 3.1 eV in the case of the $z = 4$ SiAlON. For all SiAlONs, the upper levels of the valence band are quite flat—consistent with all spinel structures, but the conduction band structure shows a marked dependence on O concentration. This point merits further investigation.

4. Conclusion

In summary, various $\text{Si}_{6-z}\text{Al}_z\text{O}_z\text{N}_{8-z}$ SiAlONs with the spinel structure have been examined over the range $z = 1, 2$, and 4 using soft Troullier Martins pseudopotentials and a plane wave basis. The recently synthesized spinel SiAlON material in the stoichiometry Si_2AlON_3 —corresponding to $z = 2$ was examined through electronic structure calculations. The calculated unit-cell parameter is in excellent agreement with experiment, pointing to the good accuracy of the pseudopotentials used in the present work. A mixed occupancy of the cation sites is determined from the electronic structure calculations, with the inversed spinel structure only being very slightly favored. Yet the energy differences between the two possible spinel structures for the same stoichiometry is very small and both have similar compressibility. This suggests that a mixed random atomic structure is very likely for the Si_2AlON_3 spinels and which is a promising new candidate material for novel refractory applications. The modelling has also been extended to two other structures representative of $z = 1$ and $z = 2$ SiAlONs and comparison made with spinel Si_3N_4 ($z = 0$). It is shown that there are steady changes in the behavior of these SiAlONs with z and it is predicted that SiAlONs that are essentially nitrogen rich in character would have

the optimum cohesive character. We have also concluded that SiAlONs are likely to exhibit semiconducting behavior with energy gaps in the region 3–4 eV. Whilst there are little differences in the structure at the top of the valence bands, the effect of O on properties of the lower conduction bands merits further investigation.

Acknowledgments

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References

- [1] J.E. Lowther, in: P. Deak, Th. Fraueheim, M.R. Pederson (Eds.), *Simulation of Materials at Atomic Level*, Wiley-VCH, Berlin, 2001, p. 533.
- [2] J.E. Lowther, *Mater. Res. Sci. Bull.* 28 (2003) 189.
- [3] M. Schwarz, G. Miehe, A. Zerr, E. Kroke, M. Heck, B. Thybusch, B.T. Poe, I-Wei Chen, R. Riedel, *Angew. Chem. Int. Ed.* 41 (2001) 789.
- [4] A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fueß, P. Kröll, R. Boehler, *Nature* 400 (1999) 340.
- [5] G. Serghiou, G. Miehe, O. Tschauener, A. Zerr, R. Boehler, *J. Chem. Phys.* 11 (1999) 4659.
- [6] E. Soignard, M. Somayazulu, H.K. Mao, J.J. Dong, O.F. Sankey, P.F. McMillan, *Solid State Commun.* 120 (2001) 237.
- [7] W.Y. Ching, Shang-Di Mo, Isao Tanaka, Masato Yoshiya, *Phys. Rev. B* 63 (2001) 064102.
- [8] J.E. Lowther, *Phys. Rev. B* 60 (1999) 11943.
- [9] Shang-Di Mo, Lizhi Ouyang, W.Y. Ching, I. Tanaka, R. Riedel, *Phys. Rev. Lett.* 83 (1999) 5046.
- [10] J.M. Recio, R. Franco, A. Mart3n Pendas, M.A. Blanco, L. Pueyo, R. Pandey, *Phys. Rev. B* 63 (2001) 184101.
- [11] K.E. Sickafus, J.M. Wills, N.W. Grimes, *J. Am. Ceram. Soc.* 82 (1999) 3279.
- [12] E.J.W. Verwey, E.L. Heilman, *J. Chem. Phys.* 15 (1947) 174.

- [13] D.J. Singh, M. Gupta, F.R. Gupta, *Phys. Rev. B* 63 (2000) 205102.
- [14] M. Haviar, Z. Lences, H. Herbertsson, *J. Mater. Sci. Lett.* 16 (1997) 236.
- [15] T. Sekine, H. He, T. Kobayashi, M. Tansho, K. Kimoto, *Chem. Phys. Lett.* 344 (2001) 395.
- [16] K. Tatsumi, I. Tanaka, H. Adachi, M. Yoshiya, *Phys. Rev. B* 66 (2002) 165210.
- [17] N. Troullier, J.L. Martins, *Phys. Rev. B* 43 (1991) 1993.
- [18] M. Bockstedte, A. Kley, J. Neugebauer, M. Scheffler, *Comp. Phys. Commun.* 107 (1997) 187.
- [19] F. Birch, *Phys. Rev.* 71 (1947) 908.
- [20] L. Ouyang, W.Y. Ching, *Appl. Phys. Lett.* 81 (2002) 229.
- [21] R. Lazzari, N. Vast, J.M. Besson, S. Baroni, A. Dal Corso, *Phys. Rev. B* 83 (1999) 3230.