

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/232906948>

# Structural, electronic and optical properties of II–IV–N<sub>2</sub> compounds (II=Be, Zn; IV=Si, Ge)

ARTICLE in PHYSICA STATUS SOLIDI (B) · JANUARY 2008

Impact Factor: 1.49 · DOI: 10.1002/pssb.200743400

CITATIONS

11

READS

40

5 AUTHORS, INCLUDING:



[Victor L. Shaposhnikov](#)

Belarusian State University of Informatics a...

81 PUBLICATIONS 731 CITATIONS

SEE PROFILE



[A. V. Krivosheeva](#)

Belarusian State University of Informatics a...

30 PUBLICATIONS 191 CITATIONS

SEE PROFILE



[Francois ARNAUD d'AVITAYA](#)

CINaM - Centre Interdisciplinaire de Nanosc...

119 PUBLICATIONS 1,066 CITATIONS

SEE PROFILE



[Jean-Louis Lazzari](#)

CNRS -- Aix-Marseille Université, Marseille, ...

106 PUBLICATIONS 494 CITATIONS

SEE PROFILE

# Structural, electronic and optical properties of II–IV–N<sub>2</sub> compounds (II = Be, Zn; IV = Si, Ge)

V. L. Shaposhnikov<sup>\*1</sup>, A. V. Krivosheeva<sup>1,2</sup>, F. Arnaud D'Avitaya<sup>2</sup>, J.-L. Lazzari<sup>2</sup>, and V. E. Borisenko<sup>1</sup>

<sup>1</sup> Belarusian State University of Informatics and Radioelectronics, P. Browka 6, 220013 Minsk, Belarus

<sup>2</sup> Centre de Recherche en Matière Condensée et Nanosciences, CRMC-N<sup>\*\*</sup>, UPR-CNRS 7251, Campus de Luminy, Case 913, 13288 Marseille cedex 9, France

Received 27 September 2007, revised 18 October 2007, accepted 25 October 2007

Published online 13 December 2007

PACS 71.15.Mb, 71.20.Nr, 78.20.Bh

\* Corresponding author: e-mail shaposhnikov@nano.bsuir.edu.by, Phone: +375 172 938 869

\*\* Laboratory associated with the Université de la Méditerranée and the Université Paul Cézanne, Aix Marseille II & III, France

A detailed study of structural, electronic and optical properties of II–IV–N<sub>2</sub> ternary compounds (II = Be, Zn; IV = Si, Ge) has been performed by means of *ab initio* density functional theory calculations. The germanium containing compounds were found to be direct-gap semiconductors with gaps of 3.37 eV and 1.67 eV for BeGeN<sub>2</sub> and ZnGeN<sub>2</sub>, respec-

tively, with oscillator strength of direct transition comparable to GaN. Two other silicon containing compounds are characterized by indirect gaps of 5.19 (3.32) eV for BeSiN<sub>2</sub> (ZnSiN<sub>2</sub>). Crystal structure being orthorhombic and lattice parameters for BeSiN<sub>2</sub> and ZnSiN<sub>2</sub> are in good agreement with the available experimental data.

© 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1 Introduction** Last years much attention was paid to II–IV–V<sub>2</sub> semiconducting compounds due to their interesting optical, transport and structural properties [1]. Magnetic properties of doped materials are intensively studied [2, 3] for their potential applications in spintronics. Room-temperature ferromagnetism has been experimentally observed in Mn-doped ternaries, such as ZnGeP<sub>2</sub>, CdGeP<sub>2</sub> and CdGeAs<sub>2</sub> [4–6]. While II–IV–As<sub>2</sub> and II–IV–P<sub>2</sub> arsenide and phosphide compounds are rather well studied both theoretically and experimentally, nitrogen-containing materials are less investigated.

The II–IV–V<sub>2</sub> compounds are ternary analogs of III–V binaries, in which the group III element is replaced by the elements of groups II and IV. In most III–V semiconductors such replacement leads to a distorted 1 × 1 × 2 supercell of the sphalerite structure, known as chalcopyrite structure, with *c/a* lattice parameters ratio usually not equal to 2. That may provide new electronic, transport and optical properties of the materials because of the symmetry lowering. However, in the case of III–N semiconductors their stable crystal structure is hexagonal (due to the higher ionicity), thus II–IV–N<sub>2</sub> ternaries may have wurtzite-like

structure. Some of the compounds have already been synthesized and their crystal structure was characterized being orthorhombic derived from wurtzite [7–9].

Another interest to II–IV–N<sub>2</sub> is associated with their possible non-linear optical properties, since some of their binary analogs, such as AlN and GaN, are already being used in optoelectronics. In order to form optoelectronic devices based on nitrides, the lattice constants of II–IV–N<sub>2</sub> compounds should have a small mismatch with host substrates. Only few experimental papers are available for II–IV–N<sub>2</sub> compounds [7–10], mostly focused on their structures, but not on electronic and optical properties. While several theoretical studies of Zn–IV–N<sub>2</sub> and Mg–IV–N<sub>2</sub> ternaries have already been done [11–13], Be–IV–N<sub>2</sub> compounds remain unexplored.

The crystals of BeSiN<sub>2</sub> has been synthesized early by von Eckerlin [7]. An orthorhombic unit cell of space group Pna2<sub>1</sub> containing four formula units with lattice constants *a* = 4.977 Å, *b* = 5.747 Å, and *c* = 4.674 Å has been identified. ZnGeN<sub>2</sub> has been firstly reported to have a monoclinic structure with *a* = *b* = 3.167 Å, *c* = 5.194 Å and an angle *γ* = 118°53' [14]. Subsequently, its crystal structure

has been also determined as orthorhombic  $\text{Pna}2_1$  with  $a = 6.441 \text{ \AA}$ ,  $b = 5.454 \text{ \AA}$ , and  $c = 5.194 \text{ \AA}$  [8]. Further, the orthorhombic  $\text{ZnGeN}_2$  has been also formed in other experiments [10, 15, 16]. This compound has been characterized as a direct-gap semiconductor with the band gap of 2.67 eV [17]. Only few experiments were performed with  $\text{ZnSiN}_2$  [9, 18, 19]. Single crystalline epitaxial  $\text{ZnSiN}_2$  layers were obtained on nitridated sapphire substrates with the lattice parameters  $a = 5.34 \text{ \AA}$ ,  $b = 6.17 \text{ \AA}$ , and  $c = 5.04 \text{ \AA}$  [9]. An indirect band-gap of 3.64 eV has been reported in [18]. Up to now no experimental information is available for  $\text{BeGeN}_2$ .

First principle simulation is a powerful tool to search for materials with specified properties, satisfying the requirements of modern technology, when it is difficult to synthesize and investigate all kinds of compounds experimentally. The aim of our work is *ab initio* calculations of structural, electronic and optical properties of the  $\text{Be-IV-N}_2$  and  $\text{Zn-IV-N}_2$  ( $\text{IV} = \text{Si, Ge}$ ) ternary compounds, and to estimate their prospects for applications.

**2 Computational details** The computer simulations performed included analysis and optimization of atomic arrangement in the materials under consideration with subsequent calculation of their electronic and optical properties.

**2.1 Crystal structure** According to the experimental data,  $\text{II-IV-V}_2$  ternary compounds may be formed in different phases. We considered three of them: (i) the face centered cubic (fcc) zincblende structure (space group  $F\bar{4}3m$ ); (ii) the body centered tetragonal (bct) chalcopyrite structure (space group  $I4_2d$ ), which is a doubled zincblende, but with a different arrangements of cations; and (iii) the simple orthorhombic (so) structure (space group  $\text{Pna}2_1$ ), which is a slightly modified from the wurtzite structure. Thus, the unit cells of fcc, bct and so phases contain 8, 8 and 16 atoms, respectively.

The lattice constants together with the appropriate atomic positions were optimized in the relaxation process and the resulting equilibrium structural parameters were obtained. In order to estimate the phase stability, we have computed the total energy ( $E_{\text{tot}}$ ) as a function of unit cell volume ( $V$ ) for three phases at several different volumes and then fit the obtained values to the Murnaghan's equation of state [20]. From these fits the equilibrium volume  $V_0$  and bulk modulus ( $B_0$ ) have been estimated.

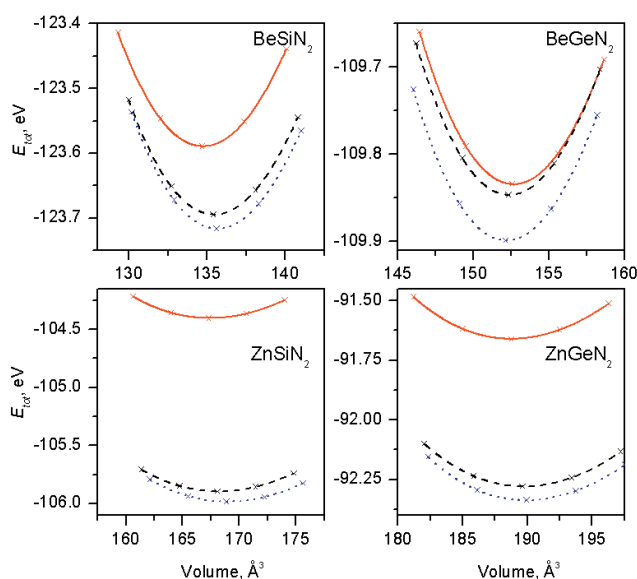
We also calculated the enthalpy of formation as the difference of the compound's total energy and the total energy of the ground-state elemental phases:  $\Delta H_f(\text{II-IV-N}_2) = E(\text{II-IV-N}_2) - E(\text{II}) - E(\text{IV}) - 2E(\text{N})$ . The hexagonal close-packed, diamond and molecular dimer structures were considered for II group metals (Be, Zn), IV group semiconductors (Si, Ge) and nitrogen, respectively. To compare phases with different number of atoms, the resulting total energies and equilibrium volumes for fcc and bct crystal lattices were renormalized. Thus, the fcc lattice has been doubled in  $c$ -direction.

**2.2 Structural optimization** The full structural optimizations as well as the total energy calculations were performed using the Vienna *ab initio* simulation package (VASP) [21, 22] with a plane-wave basis-set and using the projector-augmented wave (PAW) method [23]. Exchange and correlation potentials were included using either the local density approximation (LDA) of Ceperly and Alder [24] by the parameterization of Perdew and Zunger [25], or the generalized gradient approximation (GGA) of Perdew and Wang [26]. Semicore 3d states of Zn and Ge were treated as valence states. Total energy minimization was obtained by calculating of Hellmann–Feynman forces and the stress tensor.

The optimization of lattice parameters and the relaxation of atomic positions has been done by the conjugate gradient method. The atomic relaxation was stopped when forces on atoms were less than 0.01 eV/Å. The Brillouin zone integration has been performed by the linear tetrahedron method with Blöchl corrections [27]. In order to compare the total energies for different phases, the same energy cutoff of 550 eV was applied, while the  $9 \times 9 \times 9$ ,  $12 \times 12 \times 6$  and  $8 \times 7 \times 9$  grids of Monkhorst–Pack points were used for fcc, bct and so lattices, respectively. The convergence in the total energy of the unit cell was better than 1 meV/atom for all phases considered.

**2.3 Electronic and optical properties** Band structures and optical properties of  $\text{II-IV-N}_2$  compounds were calculated only for the most stable so phase by the full-potential linearized augmented plane wave (FLAPW) method (package WIEN2K) [28]. The structural parameters of these compounds fully optimized by VASP (both for LDA and GGA) have been used. The exchange-correlation potentials were applied using the same parametrization as in VASP, e.g. the one by Ceperly and Alder for LDA [24, 25] or Perdew and Wang for GGA [26]. The corresponding plane-wave cutoff  $R_{\text{MT}} \cdot K_{\text{max}}$  was kept equal to 8 for all cases considered. The self-consistent procedure was performed on the grid of 180  $k$ -points uniformly distributed in the irreducible part of the orthorhombic BZ. Further increase in the cutoff value and  $k$ -point number did not lead to any noticeable changes in the eigenvalues. The self-consistent procedure was continued until the difference between the total energies in two successive iterations was less than 1 meV/atom. For the band structure representation we have chosen up to 30  $k$ -points for each segment along the high-symmetry directions. A dense mesh of 448  $k$ -points was used to compute the dipole matrix elements. The interband contribution to the imaginary part of the dielectric function ( $\epsilon_2$ ) has been computed within the random-phase approximation, neglecting local-field and finite-lifetime effects. The Kramers–Kronig relation has been applied to obtain the corresponding real part ( $\epsilon_1$ ).

**3 Results and discussion** Structural properties and the fundamental electronic and optical properties of the  $\text{II-IV-N}_2$  compounds are presented in this section.



**Figure 1** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Total energy versus unit cell volume for three phases: fcc (solid line), bct (dashed line) and so (dotted line).

**3.1 Structural properties** Figure 1 presents the total energy as a function of unit cell volume for the three phases of the ternary compounds considered. From the

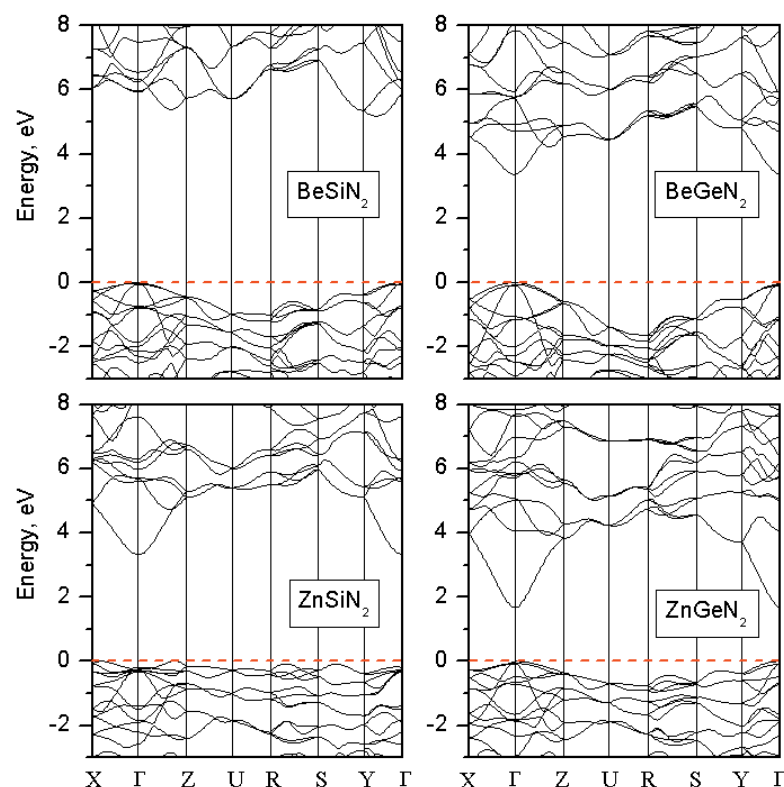
crystal structure optimization and total energy calculations the equilibrium lattice constants, unit cell volume, bulk modulus and enthalpy of formation are collected in Table 1, together with available experimental information.

The examined simple orthorhombic phase appeared to be energetically more favorable with respect to the bct and fcc phases. Thus, further investigations in the present work were done mainly for that phase. The negative  $\Delta H_f$  values for all phases indicate that they all are thermodynamically stable. The results showed that the fcc structure transforms to the face centered tetragonal with a small distortion (less than 1%) from the cubic lattice. This can be explained by the fact, that the anion (nitrogen) forms bonds of different lengths with the two types of cations (II and IV group elements) and thus is displaced off-center from the cation tetrahedron surrounding it.

In order to compare the computed lattice constants to the experimentally determined ones the corresponding thermal expansion coefficient should be taken into account because the experiments have been carried out at room temperature ( $\sim 300$  K) whereas the *ab initio* calculations for 0 K. Unfortunately, for II–IV–N<sub>2</sub> compounds these coefficients are unknown. Usually GGA overestimates the unit cell volume and lattice constants and under estimates the bulk modulus, while LDA shows opposite tendency. It is clearly seen, that our GGA-calculated lattice param-

**Table 1** Equilibrium lattice constants, unit cell volume ( $V_0$ ), bulk modulus ( $B_0$ ) and enthalpy of formation ( $\Delta H_f$ ) together with experimental data for II–IV–N<sub>2</sub> compounds.

	type	$a$ (Å)	$b$ (Å)	$c$ (Å)	$c/a$	$V_0$ (Å <sup>3</sup> )	$\Delta H_f$ (eV)	$B_0$ (GPa)
<b>BeSiN<sub>2</sub></b>								
	fcc	4.080	4.080	8.092	1.983	134.7	−5.06	241.91
	bct	4.073	4.073	8.164	2.005	135.4	−5.09	241.58
GGA	so	4.999	5.772	4.699	0.940	135.6	−5.09	243.18
LDA	so	4.939	5.697	4.639	0.940	130.5	−6.34	263.70
exp. [7]	so	4.977	5.747	4.674	0.939	133.7	–	–
<b>BeGeN<sub>2</sub></b>								
	fcc	4.271	4.271	8.361	1.958	152.5	−2.54	207.62
	bct	4.225	4.225	8.531	2.019	152.3	−2.54	207.76
GGA	so	5.204	5.972	4.894	0.940	152.1	−2.55	207.53
LDA	so	5.105	5.856	4.803	0.941	143.6	−3.75	233.54
<b>ZnSiN<sub>2</sub></b>								
	fcc	4.257	4.256	9.236	2.170	167.3	−2.88	204.95
	bct	4.479	4.479	8.378	1.871	168.1	−3.25	204.56
GGA	so	5.279	6.307	5.071	0.961	168.9	−3.27	206.13
LDA	so	5.199	6.182	4.989	0.960	160.3	−4.54	233.16
exp. [9]	so	5.340	6.170	5.040	0.944	166.1	–	–
<b>ZnGeN<sub>2</sub></b>								
	fcc	4.474	4.474	9.430	2.108	188.7	−0.60	171.84
	bct	4.615	4.615	8.902	1.929	189.6	−0.76	170.71
GGA	so	5.535	6.513	5.269	0.952	189.9	−0.77	172.36
LDA	so	5.402	6.351	5.149	0.953	176.7	−1.95	200.18
exp. [15]	so	5.518	6.372	5.174	0.938	181.9	–	–
exp. [10]	so	5.500	6.440	5.140	0.935	182.1	–	–
exp. [8]	so	5.454	6.441	5.194	0.952	182.5	–	–
exp. [14]	so	5.565	6.426	5.191	0.933	185.6	–	–



**Figure 2** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Band structures of II–IV–N<sub>2</sub> compounds along some high-symmetry directions of the orthorhombic Brillouin zone as calculated by the FLAPW method with GGA. The zero level corresponds to the Fermi energy.

eters for BeSiN<sub>2</sub> and ZnSiN<sub>2</sub> are in good agreement with the available experimental data, while LDA sizably underestimates the lattice constants. Unfortunately, no experimental lattice parameters are available for BeGeN<sub>2</sub> while a deviation in the experimental structural data occurs for ZnGeN<sub>2</sub>. Nevertheless, the lattice constants for that compound obtained by GGA are closer to experimental values than those computed by LDA.

**3.2 Band structure** The electronic band spectra for isostructural ternary compounds calculated within GGA along some high-symmetry directions of the simple orthorhombic Brillouin zone are shown in Fig. 2 demonstrating all compounds to be semiconductors. The semiconductor nature as well as the band topology near the Fermi level remains unchanged when LDA is used instead of GGA.

BeGeN<sub>2</sub> and ZnGeN<sub>2</sub> are found to be direct-gap semiconductors with one well-resolved valence band maximum (VBM) and conduction band minimum (CBM) both located at the  $\Gamma$ -point. The band gaps are estimated to be 3.37 (3.69) eV and 1.67 (2.04) eV for BeGeN<sub>2</sub> and ZnGeN<sub>2</sub> calculated within GGA (LDA), respectively. Qualitatively the band spectrum and the LDA band gap of ZnGeN<sub>2</sub> is in good agreement with results obtained by previous LDA calculations [13] ( $E_g = 1.98$  eV), while a certain underestimation of  $E_g$  is observed in comparison with the experimental value of 2.67 eV [17] and the theoretical value of 2.65 eV [11]. The interesting feature of band spectra obtained is three upper valence bands with energy difference at the  $\Gamma$ -point of some meV.

Indirect band-gap semiconducting BeSiN<sub>2</sub> is characterized by almost the same topology of the valence bands near the Fermi level as for BeGeN<sub>2</sub> and ZnGeN<sub>2</sub> with the VBM located at the  $\Gamma$ -point, while the CBM is shifted from the  $\Gamma$ -point in the  $\Gamma$ –Z-direction ( $0.7 \times \Gamma$ –Z). Thus, the lowest band gap is 5.19 (4.95) eV while the direct gap in the  $\Gamma$ -point is 5.93 (5.82) eV for GGA (LDA) calculations.

The ZnSiN<sub>2</sub> material has a more complicated band structure. Its first conduction band has one well pronounced minimum at the  $\Gamma$ -point while the upper valence band has a local minimum instead of a maximum at this point (located at 0.18 eV below the Fermi level). There are two main VBM at the  $0.2 \times X$ – $\Gamma$  and  $0.8 \times \Gamma$ –Z while similar maxima located at  $0.3 \times R$ –S and  $0.4 \times S$ –Y are shifted down to 0.08 eV. That band structure behavior does not change when the LDA approach has been used instead of GGA. Our indirect band gap value of 3.32 eV agrees well with the experimentally obtained 3.64 eV [18], but is smaller than  $E_g$  of 4.01 eV calculated in [11].

In our study we have not used the computationally expensive GW approximation for the electronic self-energy and we are aware that the calculated values of the band gaps are sizably underestimated with respect to the experimentally measured ones. For example, the band gap of GaN calculated within the same GGA (LDA) approach was estimated to be 1.72 (2.10) eV while experimental value is 3.44 eV [29]. However, we believe that the dispersion of the bands close to the gap region is well reproduced by the methods we used and our predictions of the nature of the gaps are reasonable.

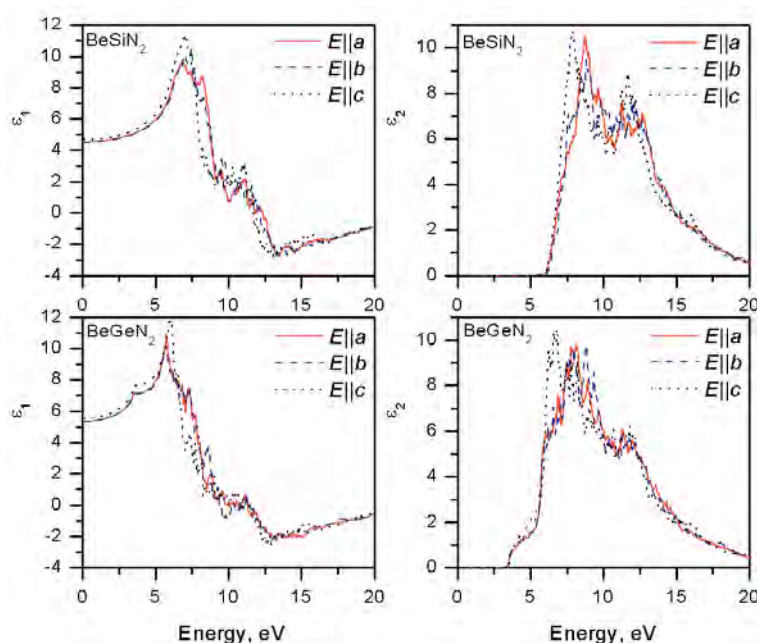


**Table 2** Orbital composition of the three upper valence bands and one conduction band eigenstates (the appropriate occupancies in % are in brackets) at the  $\Gamma$ -point for II–IV–N<sub>2</sub> compounds compared to GaN. In case of GaN II and IV sites are occupied by Ga atoms. Insignificant contributions (less than 2%) are not shown. Three squared values of the dipole matrix elements ( $M^2$ ) correspond to direct transitions from upper valence bands to conduction band.

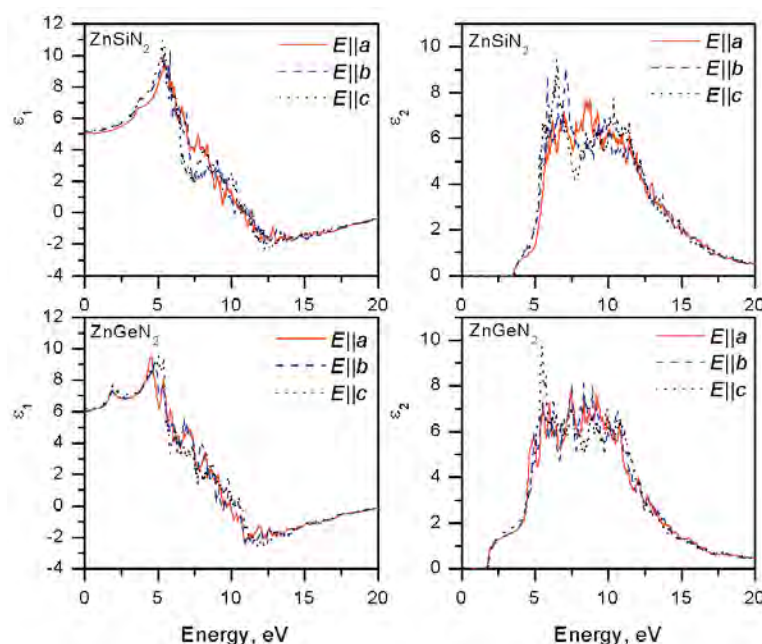
site	band	BeSiN <sub>2</sub>	BeGeN <sub>2</sub>	ZnSiN <sub>2</sub>	ZnGeN <sub>2</sub>	GaN
energy (eV)	VBM-2	−0.05	−0.08	−0.27	−0.09	−0.03
	VBM-1	−0.01	−0.05	−0.25	−0.06	0.0
	VBM	0.0	0.0	−0.18	0.0	0.0
	CBM	5.93	3.37	3.32	1.67	1.72
II	s CBM	0	2	11	9	8
	d VBM-2	0	0	0	$3z^2-r^2$ (10)	0
	d VBM-1	0	0	$xy$ (7)	$xy$ (7)	0
	d VBM	0	0	$x^2-y^2$ (5)	$x^2-y^2$ (7)	0
IV	s CBM	0	10	3	9	8
N1	s CBM	6	15	17	18	19
	p VBM-2	$x$ (33)	$z$ (31)	$x$ (22), $z$ (20)	$z$ (33)	$z$ (37)
	p VBM-1	$y$ (34)	$x$ (39)	$y$ (26), $z$ (10)	$y$ (32)	$x$ (38)
	p VBM	$z$ (34)	$y$ (34)	$x$ (16)	$x$ (32)	$y$ (38)
N2	s CBM	7	15	17	19	19
	p VBM-2	$x$ (35)	$z$ (39)	$x$ (4), $z$ (10)	$z$ (33)	$z$ (37)
	p VBM-1	$y$ (35)	$x$ (31)	$y$ (13), $z$ (7)	$y$ (33)	$x$ (38)
	p VBM	$z$ (34)	$y$ (37)	$x$ (36), $y$ (5)	$x$ (33)	$y$ (38)
	p CBM	0	$y$ (4)	0	0	0
$M^2$	VBM-2	$x$ (0.106)	$z$ (0.206)	$x$ (0.090)	$z$ (0.181)	$z$ (0.206)
	VBM-1	$y$ (0.080)	$x$ (0.167)	0.000	$y$ (0.153)	$x$ (0.178)
	VBM	$z$ (0.104)	$y$ (0.164)	$z$ (0.114)	$x$ (0.155)	$y$ (0.178)

In order to analyze the orbital angular character of the states forming the band gap and to understand optical properties, the orbital composition and dipole matrix elements of interband transitions in comparison with GaN are summarized in Table 2. As it was mentioned above, there are three upper valence bands with energy values at the  $\Gamma$ -point close to each other, thus we took into consideration

these three bands together with the lowest conduction band. Here one should take into account that VBM and especially CBM states are highly delocalized: about 30% (50%) of charge is located in the interstitial region for VBM (CBM), respectively. The contributions of p-electrons of Be and Zn as well as p- and d-electrons of group IV elements are negligible.



**Figure 3** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric function versus photon energy of orthorhombic BeSiN<sub>2</sub> and BeGeN<sub>2</sub> for different light polarizations as calculated by FLAPW with GGA.



**Figure 4** (online colour at: [www.pss-b.com](http://www.pss-b.com)) Real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) parts of the dielectric function versus photon energy of orthorhombic  $\text{ZnSiN}_2$  and  $\text{ZnGeN}_2$  for different light polarizations as calculated by FLAPW with GGA.

It is evident that all three upper valence bands are characterized mainly by p-electrons of nitrogen with some admixture of other electronic states while CBM is composed of s-electrons of nitrogen together with s-electrons of group II and IV elements. Thus one can suppose the direct across-gap transitions from three upper valence bands to lower conduction band to be allowed in the dipole approximation. The squared values of the dipole matrix elements ( $M^2$ ) are of the same order as for GaN. It is obvious, that the non-zero  $M$  component is defined by the polarization of p-orbital of nitrogen.

**3.3 Optical properties** The real and imaginary parts of the dielectric function calculated within GGA in the energy region 0–20 eV along three main crystallographic directions are presented in Figs. 3 and 4. Some anisotropy effects in the optical properties are evident for  $\text{BeSiN}_2$ . The compound is characterized by almost the same shape of the  $\epsilon_2$  curves for  $E \parallel a$  and  $E \parallel b$  whereas some differences can be found in case of  $E \parallel c$ . The region of  $\epsilon_2$  growth can be traced from 5.7 eV. The main maxima in the curves are at 8.71 eV, 8.70 eV and 7.84 eV for  $E \parallel a$ ,  $E \parallel b$ ,  $E \parallel c$ , respectively. A  $\text{ZnSiN}_2$  has similar behavior of the dielectric function, but more pronounced anisotropy can be found between all three directions of light polarization. However, one can observe rapid increase of  $\epsilon_2$  at 3.5 eV that may be induced by the large dipole matrix element components of direct transitions at the  $\Gamma$ -point.

Both Ge containing materials are found to be direct-gap semiconductors with similar shape of optical spectra. Anisotropy of  $\epsilon_2$  curves for  $E \parallel a$  and  $E \parallel b$  in comparison with  $E \parallel c$  is observed, indicating different location of the main peaks. The  $\epsilon_2$  spectra of  $\text{BeGeN}_2$  and  $\text{ZnGeN}_2$  are characterized by abrupt threshold and strong increase of  $\epsilon_2$

curves for all light polarizations at 3.45 eV and 1.74 eV, respectively. That occurs due to large (comparable to the GaN compound) dipole matrix elements of the inter-band direct transitions between three upper valence bands to the lower conduction band at the  $\Gamma$ -point. That explains the practically equal starts of  $\epsilon_2$  curves for different light polarizations. The  $\epsilon_2$  spectra calculated for  $\text{ZnGeN}_2$  correlates well with the theoretical results of [13]. A similar situation with optical properties has been observed for  $\text{BaSi}_2$  [30] and  $\text{Ca}_2\text{Si}$  [31], where high values of dipole matrix elements of across-gap transitions were defined by Ba-pd and Si-spd ( $\text{BaSi}_2$ ) or Ca-pd and Si-pd ( $\text{Ca}_2\text{Si}$ ) whereas for transition-metal silicides in which the metal d-like character dominates in the gap region low oscillator strength has been found [32]. Such interesting optical properties obtained for  $\text{BeGeN}_2$  and  $\text{ZnGeN}_2$  make these compounds promising for optoelectronic applications.

**4 Conclusions** The theoretical study of structural, electronic and optical properties of II–IV– $\text{N}_2$  ternary compounds (II = Be, Zn; IV = Si, Ge) has shown that the orthorhombic structure is an energetically favorable phase. In that phase,  $\text{BeGeN}_2$  and  $\text{ZnGeN}_2$  were found to be direct gap semiconductors with gaps of 3.37 eV and 1.67 eV, respectively. The first direct transitions at the  $\Gamma$ -point possess high values of the dipole matrix element. Two other compounds ( $\text{BeSiN}_2$  and  $\text{ZnSiN}_2$ ) were found to be indirect gap semiconductors with  $E_g$  of 5.19 eV and 3.32 eV, respectively. Anisotropy of the optical functions for different light polarizations together with high oscillator strength comparable to GaN opens possibilities for applications of II–Ge– $\text{N}_2$  materials in optoelectronics.

**Acknowledgements** This work was partially supported by the French Ministry of Foreign Affairs within the 2006–2007 ECO-NET Program (No. 12583ZM) of EGIDE association. The authors would like to thank Dr. D. B. Migas for fruitful discussion of the results obtained.

## References

- [1] S. Siebentritt and U. Rau (eds.), *Wide-Gap Chalcopyrites* (Springer, Berlin, 2006).
- [2] S. C. Erwin and I. Žutić, *Nature Mater.* **3**, 410 (2004).
- [3] S. Picozzi, *Nature Mater.* **3**, 349 (2004).
- [4] S. Cho, S. Choi, G.-B. Cha, S. C. Hong, Y. Kim, Y.-J. Zhao, A. J. Freeman, J. B. Ketterson, B. J. Kim, Y. C. Kim, and B.-C. Choi, *Phys. Rev. Lett.* **88**, 257203 (2002).
- [5] G. A. Medvedkin, K. Hirose, T. Ishibashi, T. Nishi, V. G. Voevodin, and K. Sato, *J. Cryst. Growth* **236**, 609 (2002).
- [6] R. V. Demin, L. I. Koroleva, S. F. Marenkin, S. G. Mikhailov, V. M. Novotortsev, V. T. Kalinnikov, T. G. Aminov, R. Szymczak, H. Szymczak, and M. Baran, *Tech. Phys. Lett.* **30**, 924 (2004).
- [7] P. Eckerlin, *Z. Anorg. Allg. Chem.* **533**, 225 (1967).
- [8] M. Wintenberger, M. Maunaye, and Y. Laurent, *Mater. Res. Bull.* **8**, 1049 (1973).
- [9] T. Cloitre, A. Sere, and R. L. Aulombard, *Superlattices Microstruct.* **36**, 377 (2004).
- [10] T. Misaki, A. Wakahara, H. Okada, and A. Yoshida, *J. Cryst. Growth* **260**, 125 (2004).
- [11] T. Misaki, X. Wu, A. Wakahara, and A. Yoshida, *IPAP Conf. Ser. (Tokyo)* **1**, 685–688 (2000).
- [12] W. R. L. Lambrecht, E. Alldredge, and K. Kim, *Phys. Rev. B* **72**, 155202 (2005).
- [13] S. Limpijumnong, S. N. Rashkeev, and W. R. L. Lambrecht, *MRS Internet J. Nitride Semicond. Res.* **4S1**, G6.11 (1999).
- [14] M. Maunaye and J. Lang, *Mater. Res. Bull.* **5**, 793 (1970).
- [15] L. D. Zhu, P. H. Maruska, P. E. Norris, P. W. Yip, and L. O. Bouthillette, *MRS Internet J. Nitride Semicond. Res.* **4S1**, G3.8 (1999).
- [16] S. Kikkawa and H. Morisaka, *Solid State Commun.* **112**, 513 (1999).
- [17] W. L. Larson, H. P. Maruska, and A. Stevenson, *J. Electrochem. Soc.* **121**, 1673 (1974).
- [18] T. Endo, Y. Sato, H. Takizawa, and M. Shimada, *J. Mater. Sci. Lett.* **11**, 424 (1992).
- [19] J. Muth, A. Cai, A. Osinsky, H. Everitt, B. Cook, and I. Avrutsky, *MRS Symp. Proc.* **831**, E11.45.1 (2005).
- [20] F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* **30**, 244 (1944).
- [21] G. Kresse and J. Hafner, *Phys. Rev. B* **49**, 14251 (1994).
- [22] G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996); *Phys. Rev. B* **54**, 11169 (1996).
- [23] G. Kresse and J. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- [24] D. M. Ceperly and B. J. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- [25] J. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- [26] J. Perdew and Y. Wang, *Phys. Rev. B* **45**, 13244 (1992).
- [27] P. Blöchl, O. Jepsen, and O. K. Andersen, *Phys. Rev. B* **49**, 16223 (1994).
- [28] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universität Wien, Austria, 2001), ISBN 3-9501031-1-2.
- [29] B. Monemar, *Phys. Rev. B* **10**, 676 (1974).
- [30] D. B. Migas, V. L. Shaposhnikov, and V. E. Borisenko, *phys. stat. sol. (b)* **244**, 2611 (2007).
- [31] D. B. Migas, L. Miglio, V. L. Shaposhnikov, and V. E. Borisenko, *Phys. Rev. B* **67**, 205203 (2003).
- [32] V. E. Borisenko (ed.), *Semiconducting Silicides* (Springer, Berlin, 2000).