ELECTRONIC STRUCTURE AND OPTICAL PROPERTIES OF $ZnGeN_2$

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ABSTRACT

The electronic band structure, structural and bonding, and some linear and nonlinear optical properties are calculated for a new ternary nitride compound $ZnGeN_2$ using first-principles methods. Good agreement is obtained with crystallographic data and with absorption data on the band gap. The prospects for use as nonlinear optical material are discussed.

INTRODUCTION

The most common way to achieve band-structure engineering of semiconductor compounds is to make alloys using cations or anions from the same column of the parent compound. For example, GaN can be modified by making $In_xGa_{1-x}N$ alloys, i.e. replacing Ga by another group III element In. On the other hand, one may also replace every other group-III element by a group II and a group IV element. This will lead to a new kind of ternary compounds $II-IV-N_2$, such as, e.g. $ZnGeN_2$. This kind of chemical substitution is well known in more traditional III-V compounds: e.g. GaP $\rightarrow ZnGeP_2$. Typically because the replacement of a group III by a group II and IV element leads to stringent conditions on local charge neutrality, this leads to a well defined cation-ordered crystal structure rather than a disordered alloy. This may avoid the disadvantages of alloy disorder scattering in the transport. In addition, most semiconductor alloys are in principle only metastable and some (like $In_xGa_{1-x}N$ alloys) suffer from rather severe phase segregation problems. In most III-V semiconductors the III$\rightarrow$(II,IV) replacement leads to a superstructure of the zincblende structure, known as the chalcopyrite structure. The ordering is also typically accompanied by a local structural distortion of the tetrahedral first nearest neighbor environment. In other words, the anion makes different bond lengths with each of the two cations and thus is displaced off-center from the cation tetrahedron surrounding it. The latter may in addition slightly distort from the regular tetrahedron shape. This leads to an overall c/a distortion of the tetragonal lattice. These anisotropies in the structure translate in anisotropies in the electronic and optical properties. Among others, this makes the chalcopyrites suitable for second order nonlinear optics: the anisotropy in index of refraction leads to the possibility of phase matching light beams of different frequencies that can be generated by second-order nonlinear optical susceptibilities because the structure is noncentrosymmetric. It also splits certain degeneracies in the band structure and thus plays a similar role as strain in strained superlattices which is well known to be an efficient way to tailor the band structure of semiconductors. The difference is that in $II-IV-V_2$ compounds, this can be done in the bulk semiconductor instead of only in thin films.

In the case of nitrides, a similar family of compounds may be conceived but because the natural stacking favored by nitrides is hexagonal (because of the higher ionicity), we now

have to think of structures derived from wurtzite by cation ordering. It turns out that a well-defined ordering also exists and has been found in a number of II-IV-N_2 compounds.[1-4] The same cation ordering is also found in $LiGaO_2$ [5], which can be thought of as a I-III-VI_2 analog of ZnO. As a starting point for studying the properties of this family of materials we here present computational results for $ZnGeN_2$. $ZnGeN_2$ can be synthesized in bulk form by reacting Zn or Zn_3N_2 with Ge_3N_4 powders [1,2] or in polycrystalline thin film form by a $HCl + NH_3$ based process similar to the one used for GaN synthesis [6] and more recently has been grown epitaxially by MOCVD [7]. Its crystal structure was determined by neutron diffraction [8]. Here we present the first electronic structure study of this material to the best of our knowledge.

METHOD OF COMPUTATION

The density functional method is used in the local density approximation and solved using the full-potential linearized muffin-tin orbital method [9]. Care must be taken to treat the Zn 3d bands which are overlapping with the bottom of the N2p valence band. In order to also treat the higher lying 4d like atomic wave function character mixed in with the valence and conduction band states a so-called coupled panel calculations [10,11] is used. Because the interatomic spacings in the nitrides is unusually small, and the structure is open because of the tetrahedral bonding, fairly small Ge and Zn spheres have to be used. This means that it becomes advisable to treat even rather deep semicore levels such as Ge3d as bands, which was thus done here.
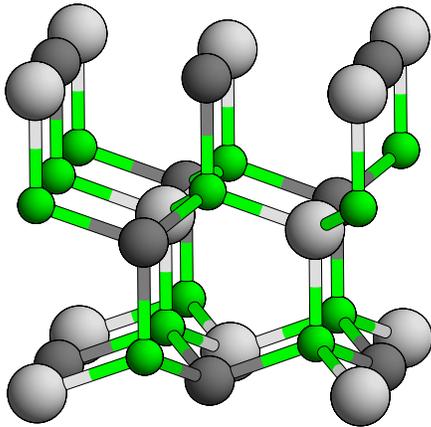
Figure 1: Crystal structure of $ZnGeN_2$: small spheres N, dark medium spheres Zn, light large spheres Ge.
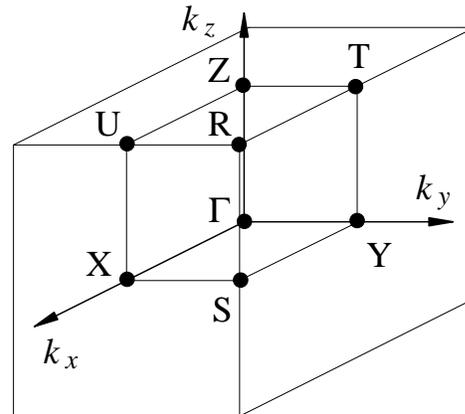
Figure 2: Brillouin zone of $ZnGeN_2$. X, Y, Z correspond to a, b, c with a horizontal, b normal to the page, and c vertical in Fig.1 .

As far as structures are concerned, we consider an idealized GaN wurtzite derived structure with the proper cation ordering but without bond relaxation, a structure in which the anion position is relaxed inside its nearest neighbor tetrahedron without cation sublattice distortions and finally, the actual experimental crystal structure. The latter is orthorombic with space group $Pna2_1$. Its relation to the wurtzite can be described as follows. The **a**-axis of the orthorhombic structure is along the [01-10] axis (or $\mathbf{a}_2$-$\mathbf{a}_3$) of wurtzite and the unit cell is double the lattice spacing of wurtzite in that direction, i.e.

approximately $a_{wz}\sqrt{3}$ with a_{wz} the wurtzite a-lattice constant, the **b**-axis is along the wurtzite [1000] direction (or **a**$_1$) and also takes a doubled lattice spacing, and the **c**-axis is along **c** of wurtzite and takes the same lattice spacing as wurtzite. The actual lattice parameters are a=0.545 nm, b=0.6441 nm and c=0.5194 nm, which is close to a=0.5524 nm, b=0.6378 nm and c=0.5185 nm which one would obtain from GaN lattice constants in the above described way. The crystal structure is shown in Fig. 1 and the corresponding Brillouin zone is shown in Fig. 2.

For calculating the optical properties we use an atomic sphere approximation to the linear muffin-tin orbital method. The calculation of the imaginary part of the dielectric constant $\varepsilon_2(\omega)$ is done in the usual independent particle approximation without including local field effects. From it the index of refraction tensor and hence the birefringence is obtained in the usual manner by calculating first the real part of the dielectric function by Kramers-Kronig transformation and then taking the complex square root. The method for the second harmonic generation coefficient calculations is described elsewhere [12].

RESULTS

Structure and binding energy

The results of the total energy calculations are summarized in Table I. The bond lengths calculated in the model in which only the anion sublattice relaxes with respect to a fixed and undistorted cation lattice is relaxed are close to the average values obtained in the actual experimentally determined structure. This indicates that this is the most important factor in the relaxation. In fact, we find the cohesive energy calculated at the experimental lattice constant differs by less than 0.1 eV from it. The value for the bulk modulus is close to that of GaN. As usual for LDA, the volume per unit cell is slightly underestimated.

Table I: Structural and total energy properties of $ZnGeN_2$.

	Expt structure	Ideal structure	Anion relaxed Structure
Average Zn-N bond length (nm)	0.2019[a]	0.193	0.2014
Average Ge-N bond length (nm)	0.1885[b]	0.193	0.1857
Unit cell volume (nm^3)	0.182	0.177	0.178
Bulk modulus (Gpa)		187	189
Cohesive energy (eV/atom)	19.02	18.66	19.08
Formation enthalpy (kcal/mol)	-36		-36
LDA band gap (eV)	1.77	1.38	1.98
$a_g=dE_g/d\ln V$ (eV)			-6.3

a. Actual bonds vary from 0.2005 to 0.2026 nm
b. Actual bonds vary from 0.1857 to 0.1898 nm

We also calculated the enthalpy of formation from the elements in their standard state, i.e. the reaction energy:

$$Zn(s)+Ge(s)+N_2(g)\rightarrow ZnGeN_2. \qquad (1)$$
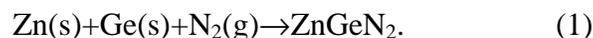
In order to obtain adequate cancellation of the typical overbinding energies of LDA, the cohesive energies of Zn and Ge in their standard solid forms (hcp and diamond structure, respectively) were calculated at the same LDA level as the right hand side of the

equation. The LDA binding energy of the N_2 molecule was taken from Jones and Gunnarsson [13]. The negative number indicates that it is thermodynamically favorable to form the compound. Using the experimental enthalpy of Ge_3N_4, we can conclude that also the reaction

$$3Zn(s) + Ge_3N_4(s) + N_2 \rightarrow 3ZnGeN_2, \qquad (2)$$
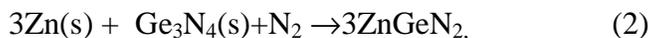
 is exothermic with enthalpy 30 kcal/mol.

Electronic properties

The band gaps are rather sensitive to the structure and are as usual severely underestimated by the LDA. One may expect a gap correction similar to that of GaN, i.e. about 1 eV. This would then lead to a predicted band gap of about 2.8 eV, in fair agreement with the value 2.7 eV obtained by optical absorption by Larson et al. [6]. This corresponds to the middle of the blue region of the spectrum. The band gap is found to be direct. The band structure is shown in Fig. 3 compared to that of GaN with the latter presented in the same Brillouin zone as $ZnGeN_2$ to facilitate the comparison.

The conduction band mass is found to be 0.23 along c, 0.25 along a and 0.26 along b, implying a slightly larger mass in-plane than perpendicular to the c-plane of the wurtzitic structure, similar to GaN [11].
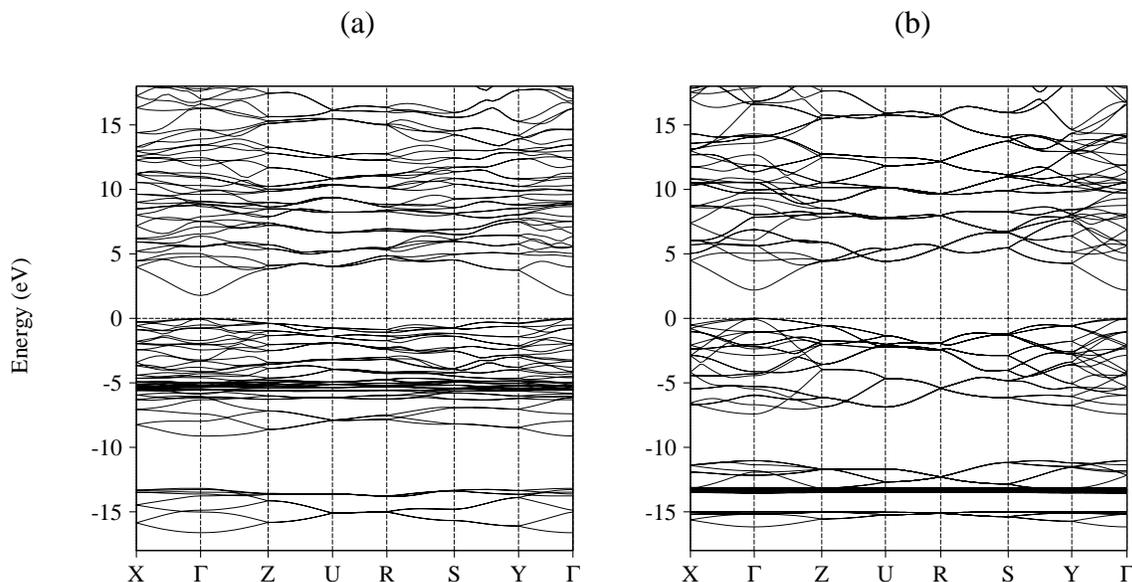
Figure 3: LDA band structures of $ZnGeN_2$ (a), and GaN (b) in the same Brillouin zone.

Optical properties

Fig. 4 shows the calculated imaginary parts of the dielectric function. Clearly, they exhibit anisotropy in all three directions. An analysis in terms of interband transitions will be presented elsewhere. Overall, the shape of the optical response is similar to that of GaN with a relatively flat region above the minimum direct band gap and an onset of the E1, E2 type transitions at about 6-7 eV. On the other hand, the indices of refraction shown in Fig. 5 derived from these show an almost uniaxial rather than biaxial behavior. The y and z components are quite close while the x component is different. The
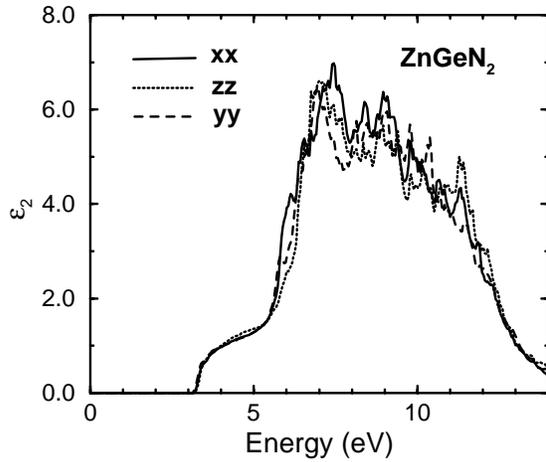
Figure 4: Imaginary part of the dielectric tensor of ZnGeN$_2$
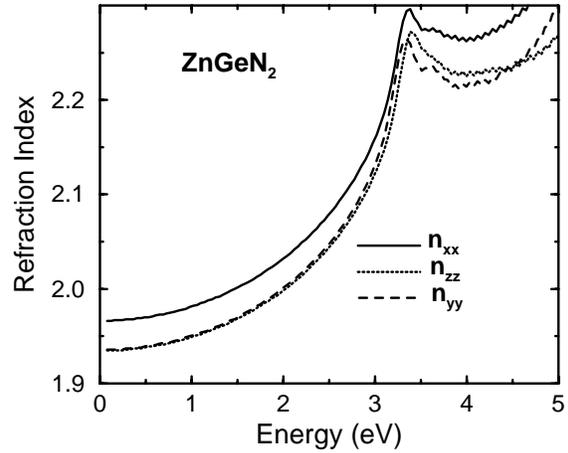
Figure 5: Indices of refraction of ZnGeN$_2$

birefringence is about 0.03 in the static limit (i.e. for low frequency compared to the gap but still only containing electronic contributions.) Viewed in this way as approximately uniaxial, it is a positive uniaxial crystal because the index of refraction along the axis which most differs from the other two is larger than the other two. Thus, it is possible to do type I (eeo) phasematching for second harmonic or sum frequency generation. It is of interest to compare this with GaN for which the birefringence is similar, also about 0.03 and also positive uniaxial, but now with the c-axis as the optical axis.[14] In GaN only type II (oeo) phase matching using the xzx component is possible because the xzz component of $\chi^{(2)}$ vanishes by symmetry. Note that in the usual notation the first component in xzx indicates the sum frequency or doubled frequency, while the last two indicate the fundamental. In the notation for phase matching however, it is the last index that indicates the sum frequency. In the oeo SHG phase matched process $[n_e(\omega)+n_o(\omega)]/2=n_o(2\omega)$, so only half the birefringence is effectively usable, meaning that the maximum frequency for which SHG is possible is smaller than for the eeo process. The calculated second harmonic generation coefficients of ZnGeN$_2$ in the static limit are given in Table II. The optimal coefficient that is phase matchable is the zxx component. Surprisingly, these SHG coeficients are smaller than in GaN by an order of magnitude [12]. The reason for this is not entirely clear but it appears to be a result of a large degree of cancellation between the so-called pure interband and mixed inter- and intraband contributions. This is illustrated in Fig. 6 for one of the components of the imaginary part of the SHG susceptibility.

Table II: SHG coefficients in ZnGeN$_2$ in the static limit (in pm/V)

zzz	zyy	zxx
-0.800	-0.293	-0.682
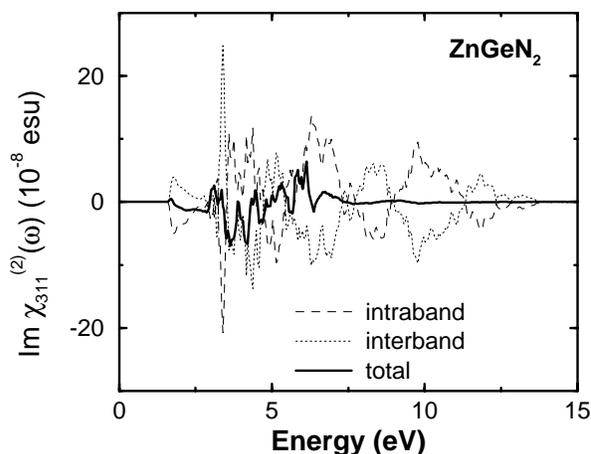
Figure 6: Imaginary part of $\chi_{zxx}^{(2)}(-2\omega,\omega,\omega)$ in ZnGeN$_2$ and its decomposition in intra- and interband components.

CONCLUSIONS

ZnGeN$_2$ is found to be a direct band gap semiconductor with a band gap corresponding to blue light and is a thermodynamically stable compound in contrast to In$_x$Ga$_{1-x}$N alloys. We found that the relaxations from the idealized wurtzite structure with ordered cations is dominated by a relative displacement of the anion versus the cation sublattice so as to accommodate the different bond lengths of Zn-N and Ge-N. A model which includes only this relaxation gives results for total energy, unit cell volume and average bond-lenghts of each type in good agreement with the experimentally determined structure.

Since this material has recently been grown in epitaxial thin film form, it would seem of interest to further study it for optoelectronic applications. Supported by Ballistic Missile Defense Organization Science and Technology through a STTR contract with NZ-Applied Technologies.

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