PHYSICAL REVIEW B **79**, 245205 (2009)

First-principles calculations of elasticity, polarization-related properties, and nonlinear optical coefficients in Zn-IV-N_2 compounds

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(Received 11 March 2009; revised manuscript received 26 May 2009; published 18 June 2009)

Elastic stiffness and compliance tensor components, spontaneous polarization, piezoelectric constants, and second-order nonlinear optical coefficients in the static limit, including the strain-free (clamped) and stress-free (unclamped) electro-optic tensors, are calculated using the density functional perturbation theory approach for Zn-IV-N_2 compounds with IV=(Si,Ge,Sn) and compared with the corresponding values in III-N with III =(Al,Ga,In).

DOI: 10.1103/PhysRevB.79.245205 PACS number(s): 71.22.+i, 42.70.Nq, 71.20.Mq, 71.20.Nr

I. INTRODUCTION

The Zn-IV-N_2 compounds with the group-IV elements Si, Ge, and Sn are a series of promising wide-band-gap semiconductors with estimated band gaps ranging from about 1 to possibly as large as 5 eV.[1–3] As is the case for their III-N analogs, their relatively high ionicity implies that they are also potentially interesting piezoelectric materials and, according to their relatively low symmetry, should be pyroelectric, i.e., possess a nonzero spontaneous polarization. Their analogy with the II-IV-V_2 chalcopyrites suggests that they may also have interesting nonlinear optical properties. Although second-order nonlinear coefficients are known to decrease with increasing band gap, certain applications such as frequency doubling into the UV range require wide band gaps.

In a recent series of papers, we have studied the structural and phonon related properties of these materials.[3–6] These calculations were carried out using the linear response approach within the local density approximation (LDA) and a pseudopotential plane wave method.[7,8] This approach is based on density functional perturbation theory (DFPT). It allows one to calculate first-order corrections to the Kohn-Sham orbitals in response to perturbations, such as electric field and atomic displacements. The latter enter in the study of vibrational properties as reported earlier.[3] Here, we consider strain related properties, which correspond to perturbations of the unit cell lattice vectors. The consistent treatment of strains in DFPT is discussed by Hamann *et al.*[9] and Wu *et al.*[10] From the first-order corrected wave functions, one can obtain corrections to the total energy to third order.[11] Elastic constants are second derivatives of the total energy versus strain and are thus readily available in this formalism.

The other quantities we consider here are related to polarization, i.e., the derivative of the total energy versus a static electric field. The piezoelectric effect is the strain derivative of the polarization, i.e., a mixed second derivative of the total energy versus electric field and strain. Since piezoelectricity is closely related to spontaneous polarization, we also consider the Berry-phase calculation of the spontaneous polarization in the absence of strain. By combining these two quantities it is in principle possible to evaluate internal electric fields in quantum wells and surface charges induced on interfaces between the materials in heterojunctions for various strain states in which the latter may find themselves depending on film thickness and growth procedures.

Second-order derivatives of the total energy versus electric field give the electrical susceptibility or high-frequency dielectric constant and hence refractive index and were already presented in Ref. 3. Third-order derivatives of the energy versus electric field give second-order nonlinear optical response. Here, we consider only the "static" limit, i.e., optical frequencies well below the band gap, so we can take derivatives versus static electric fields. In other words, they do not include the region above the band gap where interband transition effects come into play but only adiabatic response to the electric field as can be obtained in a Berry-phase calculation. At the same time we here consider high frequencies with respect to vibrational frequencies so that the lattice can be kept static. In other words, this gives the second-order optical response as enters, for example, in second-harmonic generation or sum and difference frequency generation.

Another nonlinear optical property is the electro-optic or Pockel's effect. This gives the change in optical refractive index in a truly static electric field. In that case, the effect of lattice vibrations must be incorporated in the response. Even though atomic vibrations are included, one must still distinguish "clamped" and "unclamped" values. The former means a strain-free calculation in which the piezoelectric response to the electric field is not included and the latter means a stress-free situation in which the piezoresponse is included. For details of these definitions, see Ref. 11.

In this paper, we present the results of first-principles calculations of these properties using the method sketched above and compare them with the values for the III-N semiconductors. At present, none of these quantities have been measured for the Zn-IV-N_2 materials. $ZnSnN_2$ remains to be synthesized and only a handful of papers have appeared on the other two materials. The quantities calculated here may be useful to evaluate the potential of these materials for future applications and inspire renewed efforts for their crystal and thin film growth.

II. COMPUTATIONAL DETAILS

The details of the computational method are the same as in Ref. 3. All calculations are performed in the LDA. The

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DFPT in terms of electric field, strain, and internal atomic coordinate displacements is implemented in the open-source ABINIT package, which is used here. We use norm-conserving Fritz-Haber pseudopotential,[12] 200 Ry plane-wave energy cutoff, and $2\times2\times2$ sampling of the Brillouin zone. Zn $3d$ states are treated as valence electrons. Such a high cutoff is required for the convergence of the strain related derivatives, which is found to be more sensitive to convergence than the derivatives versus internal atomic displacements as calculated in our previous work.[3] Further for the Berry-phase calculation of spontaneous polarization we used a $4\times4\times4$ k-point sampling.

The unclamped electro-optic tensor involves various terms as discussed by Veithen *et al.*[11] Among these is a term corresponding to the derivative of the high-frequency dielectric constant with respect to strain, i.e., the part of the dielectric response not involving atomic displacements in the cell,

$$\left.\frac{d\varepsilon_{\alpha\gamma}(\mathbf{R},\eta)}{d\eta_{\mu,\nu}}\right|_{\mathbf{R}_0,\eta_0}. \tag{1}$$

Since the calculation of the latter by DFPT is not yet implemented in the ABINIT code, we calculate it by a numerical finite difference method. In other words, we simply evaluate the high-frequency dielectric constant for two finite but small strains to evaluate this derivative. This corresponds to a calculation with frozen internal coordinates. The terms which involve the relaxation of the internal coordinates were worked out by Veithen *et al.* in terms of the Raman tensor and the internal strain tensor and are all evaluated by DFPT in the ABINIT approach and simply assembled here as described by Veithen *et al.*[11] to give the final values of the Pockel's effect.

III. RESULTS

A. Elastic and compliance tensors

Following the notation convention of the papers by Wu *et al.*,[13] we use Roman indices $i,j,\ldots$ for Voigt notation indices ($i=1\ldots6$) commonly used for second rank tensors and Greek indices $\alpha,\beta,\ldots$ for Cartesian components of electric fields. The crystals we are studying have point group C_{2v} (or $mm2$ in international crystallography notation).

We start with the relaxed ion elastic stiffness tensor, given in Table I. These are calculated under the assumption of fixed (vanishing) electric field and give the stress (σ_i) response to an imposed strain (η_j),

$$\sigma_i = C_{ij}\eta_j, \tag{2}$$

using summation convention. The only nonzero components for the present symmetry are C_{ij}, $i=1,2,3$, and C_{ii}, $i=4,5,6$. The present elastic constants are calculated by obtaining the clamped ion strain derivatives first and are then corrected for the internal strain effects, i.e., the internal positions under strain are obtained by imposing zero force from the knowledge of the mixed second derivatives of energy versus strain and internal atomic coordinates, all of which are obtained from perturbation theory.

In order to compare these values with wurtzite III-N, we note that the same Cartesian axes apply with z along the **c** axis, x along the **a** axis of wurtzite or orthorhombic material, and y in the **c** plane and perpendicular to **a**. The only difference is that in hexagonal materials, $C_{11}=C_{22}$, $C_{44}=C_{55}$, and $C_{13}=C_{23}$, whereas no such symmetry restrictions hold in the orthorhombic system. We can indeed see that these relations still hold approximately for the current materials, indicating that their deviations from hexagonal wurtzite are relatively small. Compared to AlN, GaN, and InN the elastic constants are generally lower in $ZnSiN_2$ and $ZnGeN_2$ but higher in $ZnSnN_2$. We can also see that the differences between $ZnSiN_2$ and $ZnGeN_2$ elastic constants are smaller than their differences from $ZnSnN_2$, which is clearly significantly softer. This is also true for AlN and GaN compared to InN.

TABLE I. Elastic constants C_{ij} in Voigt notation in the units of 100 GPa=Mbar compared to the corresponding ones in the III-N.

Components	$ZnSiN_2$	$ZnGeN_2$	$ZnSnN_2$	AlN[a]	GaN	InN
C_{11}	3.83	3.41	2.72	3.96	3.67	2.23
C_{22}	4.08	3.58	2.90			
C_{33}	4.63	4.01	3.06	3.73	4.05	2.24
C_{44}	1.04	0.86	0.64	1.16	0.95	0.48
C_{55}	1.10	0.95	0.67			
C_{66}	1.24	1.05	0.74	1.29	1.16	0.54
C_{12}	1.46	1.36	1.28	1.37	1.35	1.15
C_{13}	1.17	1.03	1.00	1.08	1.03	0.92
C_{23}	1.05	0.98	1.05			

[a] Values for III-N are taken from Wright (Ref. 14).

The corresponding compliance tensor S gives the strain response to imposed stress again under fixed (vanishing) electric field boundary conditions, $\eta_i=S_{ij}\sigma_j$, and is listed in Table II.

First, we note that for an orthorhombic material, the bulk modulus $B=-dp/d\ln V=Vd^2E/dV^2$ can be expressed as

$$B=\tfrac{1}{9}[C_{11}+C_{22}+C_{33}+2C_{12}+2C_{13}+2C_{23}]. \tag{3}$$

This gives 221, 197, and 170 GPa for $ZnSiN_2$, $ZnGeN_2$, and $ZnSnN_2$. These values are in agreement with the values of 228, 197, and 184 GPa obtained by fitting an equation of state to the relaxed energy versus volume calculations.[3]

TABLE II. Relaxed ion compliance tensor S at fixed electric field boundary condition in Voigt notation in units of Mbar^{-1}.

Components	$ZnSiN_2$	$ZnGeN_2$	$ZnSnN_2$
S_{11}	0.32	0.26	0.49
S_{22}	0.29	0.23	0.46
S_{33}	0.24	0.22	0.39
S_{44}	0.96	0.89	1.56
S_{55}	0.90	0.85	1.50
S_{66}	0.80	0.62	1.34
S_{12}	−0.099	−0.054	−0.179
S_{13}	−0.057	−0.029	−0.099
S_{23}	−0.041	−0.023	−0.098

Single crystalline material is required to measure the elastic stiffness constants. For the materials under consideration here, only small crystals and polycrystalline material are presently available. It is thus of interest to estimate the bulk and shear moduli of polycrystalline forms of this material. Two estimates are widely used: the Voigt average[15] corresponding to the assumption that the internal strain of an isotropic aggregate of small crystals equals the externally imposed strain and the Reuss average[16] in which the internal stress is assumed to equal to externally imposed stress. The isotropic elastic moduli of the polycrystalline aggregate calculated from anisotropic single crystal elastic stiffness tensor in Voigt and Reuss approximations represent the theoretical maxima and minima.[17] In the case of orthorhombic materials, the Reuss shear and bulk moduli (G_R and B_R) and the Voigt shear and bulk moduli (G_V and B_V) can be written as

$$G_R = 15[4(S_{11}+S_{22}+S_{33}-S_{12}-S_{13}-S_{23}) + 3(S_{44}+S_{55}+S_{66})]^{-1}, \tag{4}$$

$$G_V = \tfrac{1}{15}(C_{11}+C_{22}+C_{33}-C_{12}-C_{13}-C_{23}) + \tfrac{1}{5}(C_{44}+C_{55}+C_{66}), \tag{5}$$

$$B_R = [(S_{11}+S_{22}+S_{33}) + 2(S_{12}+S_{13}+S_{23})]^{-1}, \tag{6}$$

$$B_V = \tfrac{1}{9}(C_{11}+C_{22}+C_{33}+2C_{12}+2C_{13}+2C_{23}). \tag{7}$$

Since the Voigt and Reuss isotropic averages of the bulk and shear moduli represent an upper and lower boundaries, Hill[18] suggested that the true value of the bulk and shear moduli of polycrystalline aggregates should be approximately the mathematical mean of the two values, $B=(B_R+B_V)/2$ and $G=(G_R+G_V)/2$. Note that the Voigt expression for the bulk modulus of an isotropic mixture is the same as we mentioned above for an orthorhombic crystal under isotropic strain and is thus in good agreement with direct calculations of the total energy versus volume. With this value of B and G, we can define the Young's modulus $Y=(9BG)/(3B+G)$ and the Poisson's ratio $\nu=(3B-2G)/(6B-2G)$. The ratio of B/G is also of interest since it gives a qualitative measure of ductility: low G means low resistance to shear, hence ductility, while low B means low resistance to fracture, hence brittleness. The critical value separating brittle from ductile materials is about 1.75.[17] These quantities are computed using the calculated elastic and compliance tensor and tabulated in Table III.

B. Spontaneous polarization and piezoelectric tensor

In this section we first present our results for the spontaneous polarization of these materials. By symmetry we expect the only nonzero component to be in the z direction because the system has mirror planes perpendicular to x and y but no symmetry relating $+z$ with $-z$ directions. Furthermore, we remind the reader that strictly speaking only changes in spontaneous polarization under adiabatic transformations are uniquely defined. Nonetheless it is possible to give a definition of spontaneous polarization as a bulk value for a crystal of the appropriate low enough symmetry using a Berry-phase calculation. The latter reduces to an integral over k points across the Brillouin zone only, without the need for an additional integral over the adiabatically varying parameter. The value of **P** obtained in this manner is defined only within a quantum $2e\mathbf{R}/\Omega$, where **R** is a lattice vector in the direction of the polarization, Ω is the unit cell volume, and the factor 2 is for spin degeneracy. Furthermore, as pointed out by Vanderbilt and King-Smith,[19] certain high-symmetry structures can give a nonzero value with this definition. Relatedly, we here point out that for the wurtzite, from which the present lattice structures are derived, there is a symmetry operation connecting the atoms in the $z=0$ and $z=c/2$ planes comprising the structure. As a result, the spontaneous polarization obtained by the Berry-phase formula may differ from its "effective value" given below by a vector $2e(n+1/4)c/\Omega$. This however plays no role in determining interface charges at in-plane lattice-matched heterojunctions because it only depends on the cross-sectional area $A=\Omega/c$.

TABLE III. Various polycrystalline elastic moduli in units of 100 GPa and dimensionless Poisson ratio and B/G ratio.

Components	$ZnSiN_2$	$ZnGeN_2$	$ZnSnN_2$
G_R	1.23	1.45	0.75
G_V	1.26	1.08	0.77
B_R	2.19	2.00	1.70
B_V	2.21	1.97	1.70
G	1.245	1.265	0.76
B	2.20	1.985	1.70
Y	3.14	3.08	1.97
ν	0.38	0.36	0.30
B/G	1.77	1.60	2.24

Suppose we wish to consider the surface charge at an interface between $ZnGeN_2$ and $ZnSiN_2$. In general, the strain state of either of the materials will depend on the layer thicknesses, the substrate they are grown on, and eventually even the growth conditions. In the pseudomorphic case, for very thin layers, it can in principle be determined by minimizing the strain energy using the elastic constants but, in general, misfit dislocations may relax the strain at high temperature and the subsequent residual strain will then depend on the thermal expansion coefficient differences. In any case, we may first consider a lattice-matched junction and calculate the polarization in each part as a sum of the spontaneous polarizations for the unstrained crystal plus some piezoelectric contribution. The charge at the interface is given by $\sigma = \hat{n}\cdot\Delta\mathbf{P}$ with $\hat{n}$ as the unit vector normal to the interface and $\Delta\mathbf{P}$ as the change in polarization. The spontaneous polarization here can omit any quanta related to e/A since the area is the same on both sides and cancels out. Afterward, any further strain changes related to misfit dislocation formation or other strain relaxation can still be added by means of an additional piezoelectric contribution. The values obtained for the "effective spontaneous polarization" defined in this way are given in Table IV in comparison with those in the III-N materials as calculated by Bernardini *et al.*[20]

TABLE IV. Spontaneous polarizations in Zn-IV-N_2 and III-N materials in C/m^2.

$ZnSiN_2$	$ZnGeN_2$	$ZnSnN_2$
−0.022	−0.023	−0.029
AlN	GaN	InN[a]
−0.090	−0.029	−0.042

[a] Values for III-N are taken from Bernardini *et al.* (Ref. 20).

We note that the values for the Zn-IV-N_2 materials are much closer to each other than those of the III-N values. In fact, they are all close to the value for GaN. This implies that, as long as piezoelectric polarization contributions also stay small, one may expect smaller induced interface charges at their polar heterojunctions and hence much smaller internal electric fields in quantum wells. This is potentially an advantage of the class of materials considered here for electro-optic applications since such fields separate electron and hole states at opposite ends of a quantum well and hence lower optical matrix elements. The fact that the systems are also closer lattice matched to each other means that also the piezoelectric contributions to polarization will be smaller. These smaller values of the polarization differences are probably simply related to the fact that only one of the cation sublattices is subject to change, namely, the IV sublattice, whereas the Zn sublattice remains unchanged. One thus expects smaller dipole changes.

Next we present the piezoelectric constants. The (relaxed) piezoelectric tensor is defined by

$$e_{\alpha j} = \left.\frac{\partial P_\alpha}{\partial \eta_j}\right|_{\mathcal{E}} = -\left.\frac{\partial \sigma_j}{\partial \mathcal{E}_\alpha}\right|_{\eta}. \quad (8)$$

As explained by Wu *et al.*,[10] the electric polarization P_α and electric field $\mathcal{E}_\alpha$ here are to be interpreted as "reduced" quantities in order to give the "proper" piezoelectric tensor. The results are given in Table V.

TABLE V. Relaxed ion piezoelectric tensor $e_{\alpha j}$ in C/m^2 for Zn-IV-N_2 and III-N materials.

Components	$ZnSiN_2$	$ZnGeN_2$	$ZnSnN_2$
e_{15}	−0.31	−0.27	−0.41
e_{24}	−0.30	−0.35	−0.44
e_{31}	−0.45	−0.43	−0.59
e_{32}	−0.44	−0.49	−0.59
e_{33}	0.80	0.73	1.09
	AlN	GaN	InN[a]
e_{33}	1.46	0.73	0.97
e_{31}	−0.60	−0.49	−0.57

[a] The values for III-N are from Bernardini *et al.* (Ref. 20).

Comparing again to the hexagonal wurtzite system with symmetry 6*mm*, we note that in that symmetry, $e_{15}=e_{24}$ and $e_{31}=e_{32}$. We may notice the same trend for Zn-IV-N_2 as for III-N: the values decrease in the order AlN, InN, and GaN and in the order $ZnSnN_2$, $ZnSiN_2$, and $ZnGeN_2$. This is indicative of the ionicity decreasing in this order. The same order is, for example, found for the Born effective charges.[3]

Experimental values[21] for bulk GaN are $e_{33}=1.12\ \mathrm{C\,m^{-2}}$ and $e_{31}=-0.55\ \mathrm{C\,m^{-2}}$, while for AlN they are 1.5 and −0.6 C/m_2. Experimentally, one often prefers to measure the $d_{\alpha j}$ coefficients, which give the response to stress rather than to strain. The two are related by $e_{\alpha j}=d_{\alpha i}C_{i,j}$. Specifically, we have $e_{15}=d_{15}C_{44}$ in wurtzite. Experimental data are available for d_{15} in GaN and AlN by Muensit *et al.*[22] and using the elastic constants from Wright[14] convert to $|e_{15}|=0.29\ \mathrm{C\,m^{-2}}$ for GaN and $0.42\ \mathrm{C\,m^{-2}}$ for AlN. This value for GaN is close to our calculated value for $ZnGeN_2$ as expected. The sign of these coefficients depends on how the Cartesian axes are oriented versus the crystal structure polarity (positive from anion to cation along its axial bond) and it is not clear from the experimental data if the sign was actually determined. Overall, we can see that the values for the Zn-IV-N_2 compounds are comparable to the corresponding III-N, in particular, for $ZnGeN_2$ and GaN. Although the values for $ZnSiN_2$ are smaller than those in AlN, AlN has been considered for surface-acoustic-wave applications because of its high piezoelectric constants. From another point of view, since the crystals are also closer lattice matched than in the III-N compounds, we expect that piezo as well as spontaneous polarization induced effects in heterojunctions in this class of materials will be markedly reduced compared to those in III-N materials.

C. Nonlinear optical tensor

Next, we turn to nonlinear optical properties. For an insulator the polarization can be expanded as

$$P_\alpha = P_0 + \chi^{(1)}_{\alpha\beta}\mathcal{E}_\beta + \chi^{(2)}_{\alpha\beta\gamma}\mathcal{E}_\beta\mathcal{E}_\gamma + \cdots. \quad (9)$$

We are here concerned with the third rank tensor $\chi^{(2)}_{\alpha\beta\gamma}=\chi^{(2)}_{\alpha j}$, where the last notation converts the two indices of the input electric fields to Voigt second rank tensor notation. This tensor determines second-harmonic generation and other sum or difference frequency generation efficiencies. As already mentioned in Sec. I, we consider only frequencies of the electric field small compared to electronic excitations, i.e., well below band gap, but high compared to any phonons, so that the ions are clamped in response to the electric field. Since the polarization is a first derivative of the total energy versus electric field, the quantity of interest here is a third derivative versus three electric fields. In the static limit, the Kleinman symmetry is obeyed, meaning that the indices can be cyclically permuted. In this limit, the indices for which the components are nonzero are the same as for the piezoelectric tensor but two additional equalities hold because here all derivatives refer to electric field. It is important to note that wavelength dispersion is not included in these calculations. On the other hand, the polarization is calculated using Berry-phase methods, which does not require the ran-

TABLE VI. Second-order nonlinear optical tensor coefficients $\mathbf{d}_{\alpha j}=\frac{1}{2}\chi^{(2)}_{\alpha j}$ in pm/V and LDA band gaps (in eV) calculated using the PW-pseudopotential approach.

Components	$ZnSiN_2$	$ZnGeN_2$	$ZnSnN_2$
$\mathbf{d}_{15}=\mathbf{d}_{31}$	−2.19	−2.63	−0.99
$\mathbf{d}_{24}=\mathbf{d}_{32}$	−2.09	−3.17	−2.96
$\mathbf{d}_{33}$	5.60	6.98	9.27
E_g	3.96	2.37	0.70

TABLE VII. Clamped (A) and unclamped (B) linear electro-optical coefficients (pm/V).

	$ZnSiN_2$		$ZnGeN_2$		$ZnSnN_2$	
Components	A	B	A	B	A	B
r_{15}	0.40	0.40	0.45	0.48	0.25	0.25
r_{24}	0.31	0.31	0.52	0.46	0.50	0.50
r_{31}	0.17	0.18	0.20	0.47	−0.16	−0.15
r_{32}	0.12	0.21	0.09	0.12	−0.14	0.09
r_{33}	−0.66	−0.59	−0.77	−1.15	−0.77	−0.60

dom phase approximation and thus includes local field effects properly. The resulting nonlinear optical coefficients are given in Table VI. As is customary, we give $\mathbf{d}_{\alpha j}=\frac{1}{2}\chi^{(2)}_{\alpha j}$. The standard notation $\mathbf{d}$ is used here and should not be confused with the piezoelectric coefficient at given stress which unfortunately is usually given by the same symbol. We use a different font to distinguish the two.

The value for $\mathbf{d}_{33}$ for $ZnGeN_2$ is reasonably close to that in GaN of 5.76 pm/V as obtained by a "sum-over-states" calculation in LDA and including local field effects by Chen *et al.*[23] The values obtained by Rashkeev *et al.*[24] (2.8–4.4 depending on whether or not a scissor correction was included) differ by almost a factor of 2 because they do not include local field effects. The only experimental value available by Miragliotta *et al.*[25] is 5.35 pm/V. For AlN, Chen *et al.*[23] obtained 4.61 and the experimental value is 6.3.[26] The values given here are LDA values. One expects that the underestimate gap would overestimate the $\chi^{(2)}$. Consistent with the expected trend with LDA gap, also given in Table VI, the values increase from $ZnSiN_2$ to $ZnGeN_2$ to $ZnSnN_2$. The values appear to be comparable to those in the III nitrides as far as data are available on those. The value in $ZnSnN_2$ is still rather small compared to that in chalcopyrite semiconductors, given its relatively small band gap, in particular in the LDA, where it is 0.7 eV. However, one should recall that the $\chi^{(2)}$ components depend on the average gap over the whole Brillouin zone rather than the minimum gap. In $ZnSnN_2$, the lowest conduction bands have a very large dispersion so that the average gap is significantly larger than the minimum gap at Γ.

The ratio $\chi^{(2)}_{31}/\chi^{(2)}_{33}\approx -1/2$ is expected on the basis of the relation between zinc blende and wurtzite. Furthermore one expects $\chi^{(2)}_{31}\approx\chi^{(2)}_{32}$ based on the relation between the orthorhombic $ZnGeN_2$ structure and wurtzite. The actual ratios $\chi^{(2)}_{31}/\chi^{(2)}_{33}$ are −0.39, −0.38, and −0.10 for $ZnSiN_2$, $ZnGeN_2$, and $ZnSnN_2$, respectively. The $\chi^{(2)}_{32}/\chi^{(2)}_{33}$ ratios are −0.37, −0.45, and −0.31. Thus the structural deviations of the orthorhombic from wurtzite and nonideal wurtzite relative to cubic material significantly affect these ratios.

D. Pockel's coefficient

Closely related to the nonlinear optical coefficient is the electro-optic tensor. The linear electro-optic coefficient or Pockel's coefficient corresponds to the change in index of refraction in the presence of a static electric field. More specifically, it is given by

$$\Delta(\varepsilon^{-1})_{\alpha\beta}=r_{\alpha\beta\lambda}\mathcal{E}_{\lambda}, \tag{10}$$

in which we use summation convention as usual but additionally use indices λ for the static field and α,β for the optic frequency electric fields. Depending on the mechanical boundary conditions, it may contain three contributions, a purely electronic one, which is directly related to the nonlinear optic coefficient, an ionic contribution, and a piezoelectric contribution. For details, we refer the reader to Veithen *et al.*[11] The clamped value refers to the value measured under strain-free conditions and includes the electronic and ionic contribution but not the piezoelectric contribution. The unclamped value refers to the value measured under stress-free conditions and includes the additional piezoelectric contribution arising from the changes in the unit cell shape in response to the electric field. The ionic contribution is calculated in terms of the Raman tensor and the mode "polarities," closely related to the oscillator strength of the mode, summed over all the vibrational modes at $\mathbf{q}=0$. The values for the clamped and unclamped electro-optic tensor are given in Table VII.

No experimental data on these coefficients are available in Zn-IV-N_2 or III-N materials to the best of our knowledge.

E. Summary

In summary, we here presented results for the following: (1) the elastic constants and compliances and related polycrystalline elastic constants, (2) the piezoelectric tensor and spontaneous polarization, and (3) the nonlinear optical and (clamped) linear electro-optic coefficients for the Zn-IV-N_2 materials. Where possible, comparisons were made with the corresponding quantities in III-N materials AlN, GaN, and InN. The elastic constants and piezoelectric coefficients are found to be comparable in magnitude to those in III-N materials, which should make them suitable for some practical applications. The spontaneous polarization differences were found to be markedly smaller between members of this class of compounds than in the class of III-N compounds. Along with the better lattice match among them this suggests that polar interface electric field effects will be markedly suppressed in these compounds, which can be considered as an advantage for electro-optical applications relying on strong optical transitions. The piezoelectric constants are strongest for the Si and Sn based compounds, which are related to the higher ionicity in these materials. The nonlinear optical coefficients are also comparable to those in III-N materials and are as expected rather small because of the large "average" gaps across the Brillouin zone.

ACKNOWLEDGMENTS

It is a pleasure to thank David Vanderbilt for helpful discussions on spontaneous polarization. This work was supported by the (U.S.) Army Research Office under Grant No. W911NF-06-1-0476. The calculations were performed at the Core Facility in Advanced Research Computing of CWRU.

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