Vibrational modes in the $\text{Pmc}2_1$ structure of ZnGeN_2

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Abstract

Vibrational normal modes at the Brillouin zone center and related Raman and infrared spectra are calculated from first-principles density functional perturbation theory for the until now hypothetical $\text{Pmc}2_1$ structure of ZnGeN_2 and are compared with those in the known $\text{Pnb}2_1$ structure. Although there are great similarities in phonon spectra, we show that the distinctions are specific enough to experimentally distinguish the two crystal structures.

1. Introduction

ZnGeN_2 is a heterovalent ternary semiconductor closely related to GaN. It is derived from it conceptually by replacing the four nearest neighbor Ga around each N in the wurtzite structure by two Zn and two Ge atoms. This ensures the local charge neutrality since each Zn is divalent, each Ge is four-valent and Ga is three valent. While the known crystal structure of ZnGeN_2 and other II-IV-Nitrides has a 16 atom cell with space group $\text{Pna}2_1$, [1, 2] it was recently suggested that another crystal structure with spacegroup $\text{Pmc}2_1$ could have very close energy to this structure.[3] More precisely this structure was suggested for ZnSnN_2 and in that work found to have the same energy as $\text{Pna}2_1$ within the precision of the calculations.

Subsequently, it was shown by Quayle *et al.* [4] that disordered forms of both ZnGeN_2 and ZnSnN_2 could be viewed as a mixture at the atomic scale of these two crystal structures. They both contain rows of atoms in the basal plane which have alternating Zn and Ge atoms but are simply stacked slightly differently. As a result, a one dimensional type of disorder can result by randomly changing the stacking. It is important to note that both structures obey the octet rule locally. That is, each tetrahedron has two Zn and two Ge instead of for instance one Zn and three Ge or vice versa. Structures which contains such octetrule violating local environments were found to have significantly higher energy.

The two crystal structures are shown in Fig.1. The difference in structure between $\text{Pmc}2_1$ and $\text{Pna}2_1$, shown in Fig.1 is rather subtle. First note that with our chosen setting of the axes, we should really label the space group $\text{Pnb}2_1$. The $\text{Pmc}2_1$ structure has an ordinary mirror plane (labeled m corresponding to the $bc = yz$ plane in our choice of axes) instead of a glide mirror plane (labeled b

Figure 1: Crystal structures of $Pnb2_1$ (left) and $Pmc2_1$ (right).

corresponding to translation $\mathbf{b}/2$ in the plane) and one glide mirror-plane c with translation in only one crystallographic direction (lying the in $ac = xz$ plane with translation $\mathbf{c}/2$) instead of a diagonal glide mirror-plane (n with translation $(\mathbf{a} + \mathbf{c})/2$). Both spacegroups have twofold screw axes but in $Pmc2_1$ they are located at the intersection of the mirror planes, while in $Pnb2_1$ they lie halfway in between them. The unit cell has only 8 atoms. The two structures correspond simply to a $1 \times \sqrt{3}$ and $2 \times \sqrt{3}$ superlattice of the wurtzite lattice along so-called ortho-hexagonal axes. Both structures are orthorhombic. In Quale *et al.* [4] it was shown that for $ZnGeN_2$ the energy difference between the two structures is slightly larger than for $ZnSnN_2$. Although thus far only the $Pnb2_1$ structure has been observed as ordered arrangement of the cations in $ZnGeN_2$ or any other II-IV-nitride we know of, a disordered phase has been found for $ZnGeN_2$ as well and in $ZnSnN_2$ only the disordered phase has been observed. At present it is not at all clear how one would stabilize the $Pmc2_1$ structure or if it could occur as a “growth accident” in small regions within disordered $ZnGeN_2$. Nonetheless, it is of some interest to predict how its properties would differ. In particular, the vibrational modes could provide a sensitive way to identify the structure via for example Raman spectroscopy or infrared absorption spectroscopy. Thus in this paper we study how the vibrational normal modes and the associated Raman and infrared spectra differ between the two structures.

2. Computational methods

The calculations were performed within density functional perturbation theory, [5, 6] using a plane wave basis set and norm-conserving pseudopotentials of the Fritz-Haber type.[7] The calculations were performed using the ABINIT code.[8] In addition, we also tested Hartwigsen, Goedecker, Hutter (HGH) pseudopotential.[9] The plane wave energy cut-off was chosen similar to that in previous work, [10] higher than 80 Hartree. The structures were relaxed until the residual forces were smaller than 10^{-5} Hartree/Bohr. The exchange correlation potential was modeled in the local density approximation (LDA).[11] Brillouin zone integrations in the electronic structure portion of the calculations were carried out with a $8 \times 4 \times 4$ Monkhorst-Pack mesh for the $Pmc2_1$ and $4 \times 4 \times 4$ for the $Pnb2_1$ structure respectively. These are chosen to be

Table 1: Phonons frequency of ZnGeN₂ for 8 atom cell Pmc2₁ and 16 atom cell Pnb2₁ in unit of cm⁻¹.

Freq.	Pmc2 ₁	Pnb2 ₁	mode	basis
n(a ₁)	7	11	a ₁ (IR/Raman)	z, x^2, y^2, z^2
ω_{TO}	137, 222, 312, 501, 585, 681, 775	135, 170, 192, 224, 300, 482, 485, 587, 623, 758, 765		
ω_{LO}	137, 224, 313, 541, 662, 684, 840	135, 170, 192, 226, 301, 482, 527, 623, 668, 765, 827		
n(a ₂)	4	12	a ₂ (Raman)	xy
ω	124, 141, 456, 644	132, 163, 184, 201, 267, 341, 471, 554, 579, 655, 753, 818		
n(b ₁)	3	11	b ₁ (IR/Raman)	x, xz
ω_{TO}	174, 465, 658	168, 194, 239, 308, 325, 511, 550.22, 597, 652, 769, 813		
ω_{LO}	174, 501, 777	169, 194, 240, 310, 325, 537, 557, 651, 708, 796, 824		
n(b ₂)	7	11	b ₂ (IR/Raman)	y, yz
ω_{TO}	173, 278, 347, 544, 613, 685, 798	130, 167, 209, 267, 339, 480, 506, 601, 671, 776. 791		
ω_{LO}	173, 285, 348, 557, 676, 732, 828	130, 167, 211, 267, 339, 490, 561, 630, 671, 790, 863		

equivalent in terms of reciropal space sampling because Pmc2₁ has half the a lattice constant size of Pnb2₁ and thus twice as large a Brillouin zone size in this direction. Calculations with smaller $2 \times 2 \times 2$ mesh for Pnb2₁ agreed on the phonons to better than 1 %. For phonon band structure and density of states calculations, which rely on interpolation from a separate mesh for the phonons, we used a $4 \times 2 \times 2$ Monkhorst-Pack mesh for Pmc2₁ and $2 \times 2 \times 2$ for Pnb2₁ structure. The energy cut-off was slghtly reduced to 70 Hartree for the phonon calculations to speed up the calculation without loss of accuracy.

3. Results

Group theory is used to analyze the number of vibrational modes of each type. The point group for both structures is C_{2v} and contains four irreducible representations. Among these a_1 , b_1 , b_2 are infrared active for polarizations along z , x , y . The latter are chosen along the c , a , b directions of the crystal respectively.

The character table can be found for example in Ref.[12]. The a_2 mode is even under rotation about the z -axis but odd under both mirror planes. All modes are Raman active and the polarizations for which there are non-zero Raman tensor components are also indicated in Table 1.

Figure 2: IR spectrum in $Pmc2_1$ crystal structure.

Table 1 also lists the number of modes of each type in both crystal structures. Thus clearly, already from the different number of modes one should, in principle, be able to distinguish the two crystal structures. The mode frequencies for the $Pmc2_1$ and $Pnb2_1$ are given in Table 1. Although the ones for $Pnb2_1$ have been reported before in Refs.[13, 10], we here repeated the calculations for both structures, to make sure all computational parameters such as choice of exchange correlations and various convergence parameters are identical for both. Good agreement is obtained with Paudel *et al.* [10] for $Pnb2_1$. When using the HGH pseudopotential, the relaxed lattice constants agreed with the FHI pseudopotential to better than 1 %. The phonons showed at most a 2 % change.

In Figs. 2,3 we show the infrared spectra for $Pmc2_1$ and $Pnb2_1$ respectively. For each mode, we show the real and imaginary part of the dielectric function, the loss function $-\text{Im}\{\varepsilon(\omega)^{-1}\}$ and the reflectivity. The imaginary part of the dielectric function has peaks at the TO modes, the real part has zeros at the LO modes and the loss function as peaks at the LO modes. The reflectivity shows the well-known Reststrahlen bands. We can see that in spite of the different number of modes, the a_1 spectra look very similar between the two spectra. This is because the vibrational modes which differ have actually very low oscillator strength. The b_1 symmetry spectra also show only two strong vibrational modes but their relative intensity appears to be reversed between $Pnb2_1$ and $Pmc2_1$ and the two strongest modes seem to be somewhat wider separated in $Pmc2_1$. Finally, the b_2 modes appear the most different. In all cases, we should keep in mind that we here used a uniform lifetime broadening for all modes. However, this may broadening may in reality differ from mode to mode due to different

Figure 3: IR spectrum for Pnb₂₁ structure in arb. unit.

anharmonic interactions between phonons and this may reduce the peak height of some modes. When taking into account possible broadening effects, it appears that the IR spectra of the two crystal structures show strong similarities for all mode symmetries. Nonetheless if sufficiently high quality crystals of Pmc₂₁ could be obtained to actually carry out polarization dependent IR spectroscopy on oriented samples, then the spectra should be sufficiently distinct to see the difference.

Raman spectroscopy is more commonly used to characterize vibrational modes on polycrystalline materials and in micro Raman mode can be applied to small regions of a sample. Thus, perhaps more relevant to the problem of distinguishing the two crystal structures is Raman spectroscopy. In Fig. 4 we show the Raman spectra corresponding to each Raman tensor component for the TO modes. The a_1 modes correspond to parallel polarizations of incident and scattered light, the a_2 to xy polarization, the b_1 to xz and b_2 to yz polarization. We show the Raman spectra for transverse modes in zz , xx and yy polarization because this is the easiest to measure for needle type crystals along the c -axis if one has incident and scattered light normal to the needle's long axis and depending on whether the polarization is parallel to or perpendicular to the needle. Needle type crystallites are common in wurtzite based material and for example occurred for ZnGeN₂ in the Pnb₂₁ structure.[12]

We also show in Fig. 5 the xx yy spectra for longitudinal modes a_{1LO} modes since this would be easiest to measure on c -oriented basal plane films or platelet crystals under normal incidence. The light wave vector would then be along $c = z$ and hence a_1 modes would feel non-analytic long-range force effects. In other words, we would measure the LO modes. The spectra overall are significantly different from those of the Pnb₂₁, indicating that Raman

Figure 4: Intensity of Raman active modes in two different crystal structures.

Figure 5: Intensity of Raman active $a_{1LO/TO}$ (xx , yy) modes in two different crystal structures.

Table 2: Born-effective charges ($Z_{\alpha,ii}^*$) in atomic units (electron charge).

Atom α	Pmc2 ₁			Pnb2 ₁		
	Z_{xx}^*	Z_{yy}^*	Z_{zz}^*	Z_{xx}^*	Z_{yy}^*	Z_{zz}^*
Zn	1.666	2.063	1.991	1.818	1.776	1.986
Ge	3.446	2.869	3.334	3.172	3.325	3.339
N ₁	-2.308	-2.503	-2.938	-2.498	-2.281	-2.938
N ₂	-2.805	-2.429	-2.387	-2.492	-2.820	-2.387

Table 3: Dielectric constant for each crystal structures..

crystal	ϵ_{xx}^∞	ϵ_{yy}^∞	ϵ_{zz}^∞	ϵ_{xx}^0	ϵ_{yy}^0	ϵ_{zz}^0
Pmc2 ₁	5.37	5.59	5.71	9.98	9.21	10.35
Pnb2 ₁	5.15	5.24	5.55	9.25	9.33	10.36

Figure 6: Phonon total density of states comparison for two different crystal structures

spectroscopy would enable one to distinguish the two crystal structures. Interestingly the strongest mode for the a_{1xx} polarization of Pmc2₁ has very little LO/TO splitting, which is consistent with the fact that this mode at 681/684 cm^{-1} has low IR oscillator strength. On the other hand, the modes at 585/662 and 775/840 cm^{-1} show stronger IR intensity and LO/TO splitting and have a stronger Raman intensity for the a_{1yy} Raman tensor component.

On the other hand, we caution that in disordered material or if Pmc2₁ only exists in a very small region where the crystal momentum conservation selection rule is relaxed, one would see a density of states like spectrum for both structures. We therefore also calculated the phonon density of states for Pmc2₁ integrated over the Brillouin zone. Fig. 6 shows a comparison of total phonon density of states for Pmc2₁ and Pnb2₁ structures. From this Fig. 6, one can see that the phonon density of states almost perfectly agree in the pseudo-acoustic range of 0-350 cm^{-1} . However, in the higher energy region, between 400 and 850 cm^{-1} there is an appreciable difference. In particular, the spectrum for Pmc2₁ appears slightly narrower and more peaked in the middle, whereas the Pnb2₁ spectrum is more separated in several peaks. This may be related to the wider spread bond length distribution in Pnb2₁. While peaks cannot be classified simply as Zn-N or Ge-N related, the Zn contribution to the phonon DOS is somewhat stronger in the lower part of the optic frequency range (450-600 cm^{-1}) and the Ge contribution in the upper part (600 – 850 cm^{-1}). The whole optic

range however is dominated by N, the lighter atom. The more complex Pnb2₁ structure implies that there are more possible interactions between a wider spread of possible Zn-N, Ge-N bonds.

The Born charges are listed in Table 2 for both structures. Note that for each component, the contributions for the 4 atoms add up to zero as required. Table 3 shows the dielectric tensor for each structures. The dielectric constant are generally slightly smaller in the Pnb2₁ structure than in the Pmc2₁ as tabulated in the Table 3 which is consistent with the change in phonon frequencies given in Table 1.

4. Conclusions

We showed that the vibrational spectra of the Pmc2₁ and Pnb2₁ show similarities as well as differences. The differences for polarization resolved allowed first order Raman and b_1 , b_2 infrared spectra should be sufficient to distinguish the two crystals structures. On the other hand the a_1 infrared spectrum for both structures should be very similar. Also, the phonon density of states, which one would find in nanocrystalline regions of Pmc2₁ in which the crystal momentum conservation is lost are very similar in the low energy region but still sufficiently different in the optical mode region to distinguish the materials.

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