First-principles calculations of zone center phonons and related thermal properties of MgSiN$_2$

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Abstract. MgSiN$_2$ semiconductor is alternative material beyond the family of III-N, which is used widely in optoelectronic devices. This work presents the calculations of the dielectric tensor, Born effective charge tensor, phonon frequencies at Γ point, phonon dispersion, Helmholtz free energy (ΔF), internal energy (ΔE), entropy (ΔS) and specific heat capacity at constant volume (C_v) of MgSiN$_2$ by using the density-functional perturbation theory (DFPT) as implemented in ABINIT. We found that the phonons and thermal properties of MgSiN$_2$ have similar properties to those of ZnSiN$_2$ and C_v of MgSiN$_2$ are in agreement with the available experimental results.

1. Introduction

The discovery of semiconductors has been accepted to dramatically improve the performance of various advanced technologies. For example, III-N such as GaN, InN, and AlN, which have high thermal conductivity and direct band gap, are excellent for optoelectronic applications [1]. The electronic as well as thermal properties of III-N have been extensively studied both theoretically and experimentally [2-4]. Recently, a group of Mg-IV-N$_2$, has been considered as an alternative of III-N [5-7]. The calculations of lattice constants, structural parameters, bulk moduli, energies of formation, and band structures of Mg-IV-N$_2$ compounds have been reported by A.P. Jaroenjittichai and W. R. L. Lambrecht [7]. However, there are still some gaps in the knowledge about phonon properties of these materials. From literature, S. Pramchu et al. have studied about phonons, Raman and IR spectra of MgGeN$_2$ and MgSiN$_2$ by using plane wave method as implemented in Quantum-Espresso [8]. As we know that study of phonon plays a significant role in not only Raman and IR spectra but also in many important physical properties such as sound propagation, specific heat, thermal expansion, thermal conductivity etc. [9]. Thus, in this work, we have studied phonons and some thermal properties of MgSiN$_2$ by using ABINIT code in order to gather more information for the family of Mg-IV-N$_2$ semiconductors.

2. Computational Details

Our calculations were obtained using ABINIT code with the fhi98PP norm-conserving pseudopotential [10]. The exchange-correlation energy was estimated by the local density approximation (LDA). To calculate phonons, the density functional perturbation theory (DFPT) with

the linear-response approach was used [9], and the effect of long-range Coulomb forces were corrected by including the non-analyticity term of the dynamical matrix at the Γ point. We employed cutoff energy of 80 Hartree and $4\times4\times4$ **k**-point mesh to provide well-converged results. The tolerances were set at 10^{-22} Hartree^2 for wavefunction squared residual and 10^{-8} Hartee per Bohr for force components respectively. The $4\times4\times4$ **q**-point grid was chosen for Fourier transformation of force constants in real space.

3. Results and Discussions

The crystal structures of $MgSiN_2$ were optimized and compared with the experiment as presented in table 1. We found that each parameter is different from the experimental results [6] less than 2%. The dielectric and Born effective charge tensors were also obtained during the phonon calculations as shown in table 1. The effective charge tensor of Si in $MgSiN_2$ is less than that of $ZnSiN_2$ [11] suggesting a weaker Coulomb interaction between Si and N.

Table 1. Lattice parameters (Å), Born effective charge tensor($Z_{\alpha\alpha}$) and dielectric tensor ($\varepsilon_{\alpha\alpha}^{\infty}$) of $MgSiN_2$

|	cal.	expt.[a]		Mg	Si	N_1	N_2		
a	6.40	6.47	Z_{xx}	1.90	3.04	-2.48	-2.46	$\varepsilon_{xx}^{\infty}$	4.20
b	5.23	5.31	Z_{yy}	1.89	3.19	-2.05	-3.03	$\varepsilon_{yy}^{\infty}$	4.27
c	4.96	4.98	Z_{zz}	2.05	3.14	-3.03	-2.16	$\varepsilon_{zz}^{\infty}$	4.33

[a] Ref. [6]

The space group and point group of $MgSiN_2$ are $Pbn2_1$ and C_{2v} respectively [7], and there are 48 modes of phonon frequencies according to the number of 16 atoms in a unit cell. If a static electric field is applied on phonon vibrations, it will reveal the splitting between the longitudinal and transverse optical branches at Γ point, which can be seen clearly at the high frequencies. We obtain in total 78 vibrational modes at Γ point and can identify these modes with the irreducible representation of C_{2v} i.e. A_1, A_2, B_1, and B_2. The lowest modes of B_1, B_2, and A_1 are all zero because of the translational invariant of the crystal. The 78 vibrational modes consist of 11 longitudinal optical (LO) modes and 11 translational optical (TO) modes for each B_1, B_2 and A_1 and 12 optical modes for A_2. The LO-TO splitting disappears in case of A_2 because it cannot be represented by a component of a vector x, y or z like B_1, B_2, A_1. The phonon frequencies at Γ point of $MgSiN_2$ are shown in table 2. Moreover, the bond length of Mg-N in $MgSiN_2$ [7] is longer than that of Zn-N in $ZnSiN_2$ [11]. This means that the bond strength of $MgSiN_2$ is weaker than that of $ZnSiN_2$, which is in agreement with the discussion of Born effective charge. Then, the weaker bond strength results in the increment of phonon frequencies due to the decrease in the force constant as shown in table 2. The phonon frequencies at Γ of $ZnSiN_2$ were reported in [11].

Table 2. Phonon frequencies at the Γ of $MgSiN_2$ in cm^{-1}

A_2	B_{1L}	B_{1T}	B_{2L}	B_{2T}	A_{1L}	A_{1T}
218	292	292	224	224	222	222
244	325	325	287	287	302	302
311	396	391	345	345	319	319
357	433	430	396	396	357	353
403	490	490	506	506	433	433
456	526	526	533	533	513	513
509	590	590	573	573	562	558
612	711	706	643	637	680	680
623	751	742	780	780	705	705

751	898	862	862	852	840	840
898	966	925	1031	966	915	909
915						

The phonon dispersions were also examined as shown in figures 1. At Γ point LO-TO spitting can be observed from discontinuity of phonon branches. At low frequency, we indeed observe small LO-TO splitting due to small change in energy. The acoustic and optical branches also overlap each other. They show a more complex phonon band structure than those of the well-known III-N. The complex phonon branches can lead to the phonon-phonon scattering [12], especially the Umklapp process which related to reduction of the mean free path and results in lower thermal conductivity as well as the group velocity of phonons [13]. Furthermore, our phonon dispersions are consistent with previous theoretical works using different software (quantum espresso) and pseudopotentials (GBRV library) [8].

Figure 1. Phonon dispersion of $MgSiN_2$
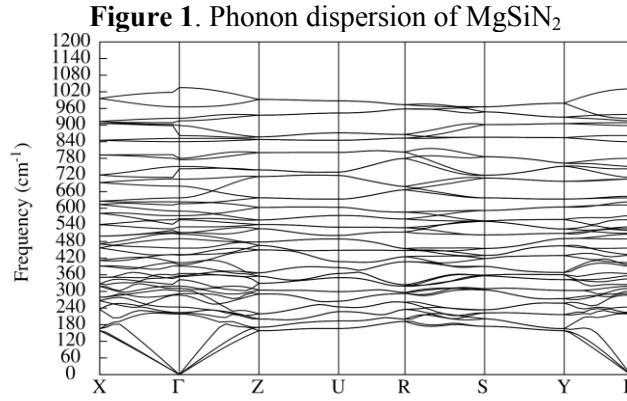
Finally, we extracted thermal properties, which are related to phonons, and are a function of temperature. Helmholtz free energy (ΔF), internal energy (ΔE), entropy (ΔS) and specific heat capacity at constant volume (C_v) were considered from these relations

$$\Delta F = 3nk_BT \int_0^{\omega_m} \ln\left\{2\sinh\frac{\hbar\omega}{2k_BT}\right\} g(\omega)d\omega, \Delta E = \frac{\partial(\beta\Delta F)}{\partial\beta}, C_v = \frac{\partial\Delta E}{\partial T}, \text{ and } \Delta S = (\Delta E - \Delta F)/T$$

where n denotes the number of atoms in a unit cell, $\beta = (k_BT)^{-1}$ and ω_m stands for the maximum phonon frequency. The normalized density of states $g(\omega)$ were defined as in [14].

Figure 2. Helmholtz free energy (ΔF) and internal energy (ΔE) of $MgSiN_2$ as a function of temperature.
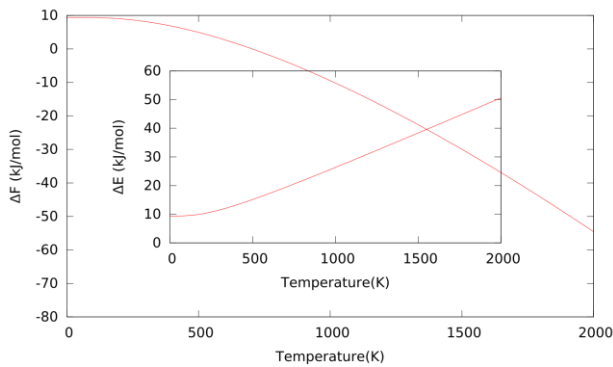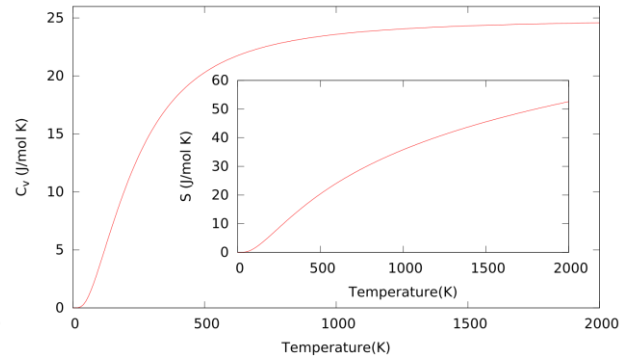
Figure 3. Specific heat capacities at constant volume (C_v) and entropy (ΔS) of $MgSiN_2$ as a function of temperature.

The results of Helmholtz free energy, internal energy, entropy and the specific heat capacity at constant volume are presented in figures 2 and 3. The specific heat capacities of MgSiN$_2$ are lower than those of ZnSiN$_2$ [15] and approach the classical value 24.942 J/ (mol K) at over 2000 K while ZnSiN$_2$ compounds reach this point around 1000 K. As far as we know, the experimental C_v of MgSiN$_2$ are not available at present and there are a few experimental reports about the specific heat capacity at constant pressure (C_p) of MgSiN$_2$ [16-19]. At temperature below 300 K, the resulting C_v are comparable to C_p from [17] and [18] within 0.1 J/(mol K), while at temperature above 300 K, C_p from [17], [18] and [19] are larger. This can be explained by considering the equation of $C_p - C_v = 9 V_m T \alpha^2 / \beta_T$ where α, β_T, and V_m are linear thermal expansion coefficient, isothermal compressibility and molar volume respectively. At temperature below 300 K, the term $9 V_m T \alpha^2 / \beta_T$ can be neglected [18, 20].

4. Conclusion

We completed the calculation of the phonons and some related thermal quantities of MgSiN$_2$ i.e. the dielectric tensor, Born effective charge tensor, phonon frequencies at Γ point, phonon dispersion, Helmholtz free energy, internal energy, entropy and specific heat capacity at constant volume. The results are in good agreement with previous works of ZnSiN$_2$. The phonon dispersion is more complex than those of III-N, which could lead to lower thermal conductivity. The calculated C_v are well consistent with experimental C_p under the assumption $C_p \sim C_v$ at low temperature.

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