Lattice dynamical, dielectric, and thermodynamic properties of β-Ga$_2$O$_3$ from first principles

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Lattice dynamical, dielectric, and thermodynamic properties of β-Ga$_2$O$_3$ are investigated by first principles. The calculated phonon frequencies for the Raman-active and the infrared-active modes are assigned. The phonon dispersion curves along high symmetry lines in the Brillouin zone and the phonon density of states are also calculated. The electronic and static dielectric tensors are calculated. The calculated static dielectric constants are much larger than the electronic constants, showing the rather strong ionic contributions to static dielectric constants. These calculated results are in a good agreement with available experimental values. The thermodynamic functions are calculated by using the phonon density of states. © *2007 American Institute of Physics.*
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Monoclinic β-Ga$_2$O$_3$ is an important wide-band-gap semiconductor (E_g=4.9 eV), which has wide applications, for instance, as optical windows,[1] semiconducting lasers,[2] high-temperature stable gas sensors,[3] dielectric thin film,[4] and magnetic memory material.[5] β-Ga$_2$O$_3$ has also become a promising candidate for ultraviolet transparent conductive oxide.[6] Recent theoretical investigations on Ga$_2$O$_3$ using the first-principles calculations report the fundamental electronic and optical properties.[7–9] Lattice dynamical properties are fundamentally important for a better understanding of the optical Raman and infrared (IR) characters, the electronic and static dielectric properties, which could be related to its practical applications. The experimental and theoretical Raman frequencies for Ga$_2$O$_3$ are reported.[10] However, these results are constrained to the Γ point of Brillouin zone (BZ). Therefore, the investigations of lattice dynamical properties in the whole Brillouin zone, the dielectric properties, and the thermodynamic properties are highly desirable.

In this letter, we study the lattice dynamical and thermodynamic properties of β-Ga$_2$O$_3$ by using density-functional perturbation theory.[11] The phonon frequencies at the Brillouin zone center, the phonon dispersion curves, the dielectric permittivity tensors, and the thermodynamic properties are calculated. The thermodynamic properties including the phonon contribution to the Helmholtz free energy ΔF, the phonon contribution to the internal energy ΔE, the entropy S, and the constant-volume specific heat C_v are calculated within the harmonic approximation.[12]

The calculations are performed using the ABINIT package,[13,14] which is based on pseudopotentials and plane waves. The generalized gradient approximation as parametrized by Perdew-Burke-Ernzerhof[15] is used to describe the exchange correlation interactions. The wave functions are expanded in plane waves up to a kinetic energy cutoff of 50 hartrees. The BZ is sampled by a $4 \times 4 \times 4$ Monkhorst-Pack mesh of k points. Convergence tests show that the BZ

sampling and the kinetic energy cutoff are sufficient to guarantee an excellent convergence within 1 cm^{-1} for the calculated phonon frequencies. The phonon frequencies are obtained as second-order derivatives of the total energy with respect to an external electric field or to atomic displacements. The linear response method allows the calculation of the dynamical matrix at arbitrary q-vectors.

The calculated lattice constants (a=12.31, b=3.08, and c=5.89 Å and β=103.9°) are very close to the experimental values (a=12.23, b=3.04, and c=5.80 Å and β=103.7°).[16] In the following calculations, the optimized structure is used. There are ten atoms in the primitive unit cell of β-Ga$_2$O$_3$ hence 30 normal modes of vibrations. Therefore, group-theoretical analysis predicts the following irreducible representation for acoustical and optical zone center modes: $\Gamma_{\text{aco}}=A_u+2B_u$ and $\Gamma_{\text{opt}}=10A_g+4A_u+5B_g+8B_u$. For the optical modes, A_g and B_g modes are Raman active, while A_u and B_u modes are IR active. The calculated phonon frequencies at the Γ point of β-Ga$_2$O$_3$ are listed in Table I. For the Raman-active phonons, the present calculations are in good agreement with the results from local density approximation calculations[10] and experimental results.[10,17] The errors of the present calculated values with experimental values are within 0.1%–5.0%. The frequencies of IR-active phonons for longitudinal optic (LO) and transverse optic (TO) modes are presented in Table I.

Phonon dispersion curves along symmetry lines in the Brillouin zone and the corresponding phonon density of states for β-Ga$_2$O$_3$ are plotted in Fig. 1. The phonon frequencies are in the range of 0–793 cm^{-1}, in which there is a small phonon band gap between 557 and 567 cm^{-1}. One can find the discontinuity in the vicinity of the Γ point which is a typical feature in uniaxial crystal structures.

Due to the monoclinic structure of β-Ga$_2$O$_3$, the electronic (ε_∞) and static (ε_0) dielectric permittivity tensors have three independent components. The calculated dielectric tensors for ε_∞ and ε_0, listed in Table II, show to be slightly anisotropic. The theoretical values are larger than the experimental ones[1,4,18] by about 10%. The static dielectric tensor
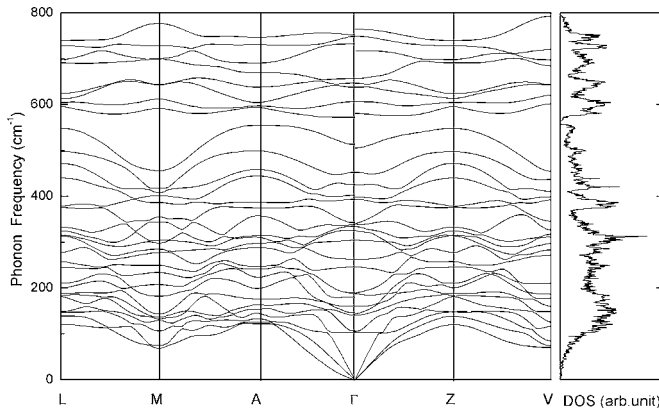
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TABLE I. Phonon frequencies (unit: cm^{-1}) at the Γ point of β-Ga$_2$O$_3$.

Mode Raman	Calculated results		
	Present	VASP[a]	Experimental results[a]
A_g (1)	104.7	104	110.2
A_g (2)	163.5	165	169.2
A_g (3)	202.3	205	200.4
A_g (4)	315.8	317	318.6
A_g (5)	339.7	346	346.4
A_g (6)	420.2	418	415.7
A_g (7)	459.4	467	
A_g (8)	607.1	600	
A_g (9)	656.1	637	652.5
A_g (10)	757.7	732	763.9
B_g (1)	112.1	113	113.6
B_g (2)	141.3	149	144.7
B_g (3)	348.3	356	
B_g (4)	472.8	474	473.5
B_g (5)	627.1	626	628.7
Infrared			
A_u (TO1/LO1)	141.6/146.5		
A_u (TO2/LO2)	296.2/325.5		
A_u (TO3/LO3)	383.5/510.6		
A_u (TO4/LO4)	647.9/738.5		
B_u (TO1/LO1)	187.5/190.5		
B_u (TO2/LO2)	251.6/264.5		
B_u (TO3/LO3)	265.3/283.6		
B_u (TO4/LO4)	343.6/354.1		
B_u (TO5/LO5)	410.5/484.7		
B_u (TO6/LO6)	574.3/625.3		
B_u (TO7/LO7)	672.6/728.2		
B_u (TO8/LO8)	741.6/764.6		

[a]Reference 10.

TABLE II. Electronic (ε_∞) and static (ε_0) dielectric tensors for β-Ga$_2$O$_3$.

	Calc.		
	Present	Ref. 8	Expt.
ε_∞	(3.81, 4.08, 3.85)	(2.78, 2.84, 2.86)	
$\overline{\varepsilon_\infty}$	3.91	2.82	3.57[a] 3.53[b]
ε_0	(10.84, 11.49, 13.89)		
$\overline{\varepsilon_0}$	12.07		10.2, 9.93[c]

[a]Reference 18.
[b]Reference 1.
[c]Reference 4.

can be decomposed in the electronic and ionic contributions. The electronic dielectric tensors are related to the optical properties of material. The calculated refractive index (1.98) is determined by square root of electronic dielectric constants, which is larger than the experimental values (1.89, 1.84, and 1.88) (Ref. 1 and 18) by about 5%–7%. Our present calculated values[8] are much higher than the previous calculated values which were calculated by using a different method and showed to be much smaller than experimental values. In that calculation, a sum over states of interband transitions was used to calculate the frequency-dependent real and imaginary parts of electronic dielectric function.

The thermodynamic functions of β-Ga$_2$O$_3$ can be determined by the entire phonon spectrum. In the present work, the phonon contribution to the Helmholtz free energy ΔF, the phonon contribution to the internal energy ΔE, the entropy S, and the constant-volume specific heat C_v, at temperature T, are calculated using the formulas in Ref. 19 within the harmonic approximation, as shown in Fig. 2. ΔF and ΔE at zero temperature represent the zero-point motion, which can be calculated from the expression as $\Delta F_0 = \Delta E_0 = 3nN\int_0^{\omega_{max}}(\hbar\omega/2)g(\omega)d\omega$, where n is the number of atoms per unit cell, N is the number of unit cells, ω is the phonon frequencies, ω_{max} is the largest phonon frequency, and $g(\omega)$ is the normalized phonon density of states with $\int_0^{\omega_{max}}g(\omega)d\omega=1$.

The calculated $\Delta F_0 = \Delta E_0 = 33.7$ kJ/mol. The calculated entropies of β-Ga$_2$O$_3$ exhibit reasonable agreement with the experimental values[20] above room temperature. The calculated values are slightly smaller by about 2% than the experimental values. The constant-volume specific heats C_v are calculated and are shown in Fig. 2(d). In the low-temperature limit, the specific heat exhibits the expected T^3 power-law behavior and approaches at high temperatures the classical asymptotic limit of $C_v = 3nNk_B = 99.8$ J/mol K. The experimental C_v cannot be found, but the experimental constant-pressure heats C_p are 92.392, 102.868, 110.541, 115.827, and 119.573 J/mol K at temperatures of 300, 400, 500, 600, and 700 K, respectively, which are systemically larger than the calculated C_v, due to the thermal expansion caused by anharmonicity effects.[21]

In summary, the phonon frequencies at Γ point and the dialectic tensors of β-Ga$_2$O$_3$ are calculated. The results are in good agreement with the experimental and previous calculated results. The phonon frequencies along symmetry lines in the Brillouin zone and the corresponding phonon density of states are also calculated. Finally, using the calculated phonon density of states, the thermodynamic functions are determined within the harmonic approximation.

FIG. 1. Calculated phonon dispersion curves along symmetry lines in the Brillouin zone and the phonon density of states for β-Ga$_2$O$_3$.
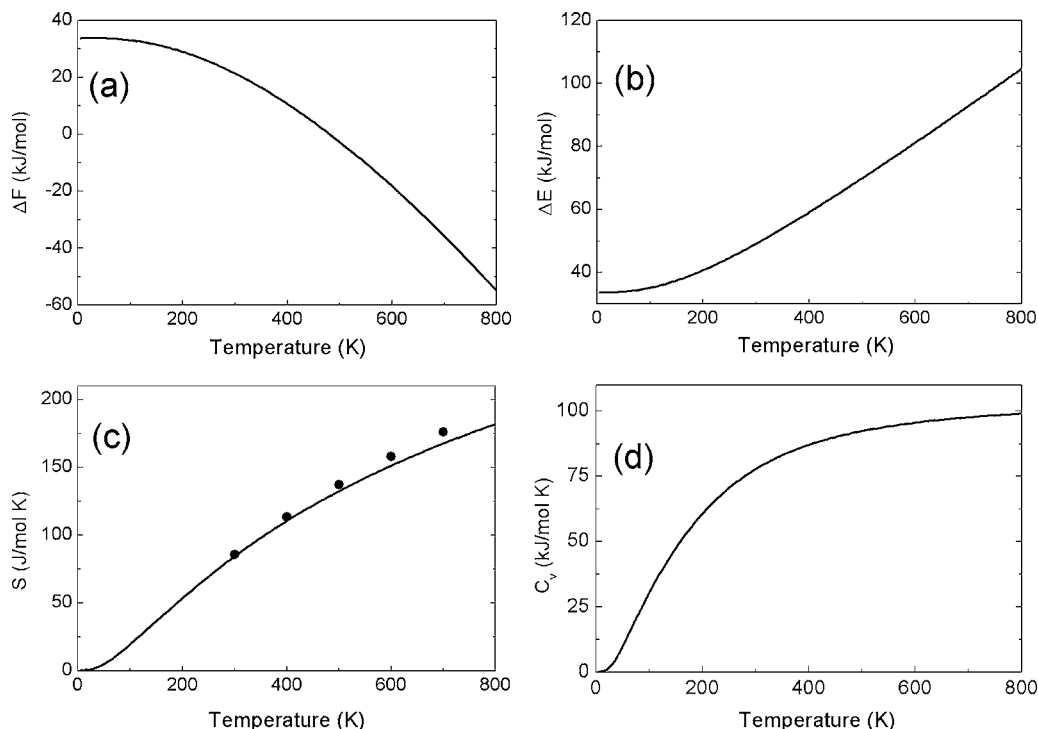
FIG. 2. The calculated phonon contribution to the Helmholtz free energy ΔF (a), the phonon contribution to the internal energy ΔE (b), the entropy S (c), and the constant-volume specific heat C_v (d) for β-Ga_2O_3. The experimental values of entropy (solid circles) are also shown in (c).

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