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Theoretical investigation of the structural and elastic properties of Lanthanum monopnictide: A first Principle study

Abstract

In the present work, density functional theory within the generalized gradient approximation (GGA) is used to predict various ground state properties for Lanthanum monopnictide as especially for LaN. At ambient conditions LaN crystallize in rock-salt (B1) structure. The results for ground state properties (lattice parameter a_0, cohesive energy E_c, bulk modulus B_0 and its pressure derivative B_0') and elastic constants at ambient conditions are in good agreement with experimental and other such theoretical findings. Result of phonon dispersion spectra shows some anomalous result for LaN in B1 phase at ambient conditions. We found complete phonon softening with negative frequencies at all main symmetry direction in Brillouin zone (BZ).This clearly indicates structural instability of LaN as a single crystal at ambient conditions. Moreover, the anomalous behaviour is also seen in elastic properties of LaN. Though, computed result of three independent elastic constants C_{11}, C_{12} and C_{44} satisfy the Born criteria of stability but, the value of elastic anisotropy factor is much larger which confirms relatively high instability of LaN system compare to other compound in B1 phase.

Keywords: *first principles calculations, elastic properties*

I. Introduction

Due to wide array of chemical compositions, group III B transition metal nitrides exhibit excellent combinations of optical, magnetic, catalytic and electronic properties [I,II]. Because of this fact, they find several technological and scientific importances. Stampfl et al. [III] have reported ground state properties of several transition metal mononitrates with the help of full potential linearized augmented plane wave method with generalized gradient approximation local density approximation. Ghezail et al. [IV] have investigated structural and electronic properties of LaN. Recently, Schneider et al. [V] confirm that at ambient conditions and high temperature LaN crystallize in B1 (NaCl-type) structure with space group ($Fm\bar{3}m$, no. 225) by using In situ X-ray powder diffraction experiment. Moreover, it has attracted remarkable attentions to the experimental as well as theoretical people in last few years [VI-VIII]. Unfortunately, only one attempt is done to investigate the lattice dynamics of LaN by Gökhan et al [IX]. They found phonon softening with negative frequencies for LaN in B1 phase.

II. Computational scheme

In the present study, all the calculations were performed based on the plane wave pseudopotential density functional theory within the generalized gradient approximation (GGA) [X] as implemented in Quantum Espresso code [XI]. The atomic species for LaN in B1 phase is (0.5,0.5,0.5) and (0,0,0) for La and N atom respectively [V].The electron-ion interactions were described by Norm-conserving scalar-relativistic type pseudopotential with generalized gradient approximation (GGA). Perdew, Burke and Ernzerhof (PBE) [XII] exchange and correlation function is used in the present study. We have expanded the wave function in the plane waves up to kinetic-energy cut-off 240 Ry for proper convergence. Besides, k-point integration over the Brillouin zone was performed for 14x14x14 Monkorst-Pack [XIII] mesh for B1 phase. Accuracy of self-consistent calculations for total energy is set to 0.01mRy. Once the total energy as a function of lattice parameter is known, the results of total energy were fitted to third order Murnaghan [XIV] EOS to obtain ground state properties. Moreover, the cohesive energy, which

binds its constituting atoms together in solid phase, has also been calculated. Phonon dispersion spectra was obtained with, eight dynamical matrices on a 4x4x4 grid in q-space for B1 phase of LaN. These computed matrices were then Fourier interpolated to gain the phonon dispersion curves.

To check mechanical stability of the structure one should know the brief knowledge of elastic constants. Present structure possesses the cubic structure at ambient conditions. And as we know that all cubic crystal has only three independent elastic constants namely, C_{11}, C_{12} and C_{44}.The second order elastic constant are calculated through the ElaStic tool [XV]. Moreover, this calculated value of elastic constants is used to report the elastic modulus by adopting the Voigt-Reuss-Hill approximation [XVI].

III. Results and discussion:

Present ab initio results for the ground state properties are tabulated in the table 1. Computed equilibrium properties such as, equilibrium lattice parameter, bulk modulus and its pressure derivative are in excellent agreement with the available experimental and other theoretical findings. Only 0.35% discrepancy was obtained particularly for lattice parameter with the experimental value reported by Schneider et al [V]. This overestimated value of lattice parameter can be attributed to the GGA approximation. In the fig. 1 we have shown the cohesive energy of LaN in B1 phase with other theoretical finding. In fig 2 we have plotted the phonon dispersion spectra for LaN in B1 phase. Phonon dispersion spectra contain large soft modes with the negative frequencies in all main symmetry directions in BZ. A result of this spectrum is somehow strength; though the experimental result [V] conveys that LaN is stable in B1 phase, phonon should not be contain negative frequencies. Gökoğlu and et al. [IX] have also noticed this anomalous behavior in major symmetry direction for LaN. Further, anomalous behavior of phonon dispersion curve is also seen in the elastic properties. Elastic properties define the behavior of the solid under the different stress and strain conditions. Moreover, they provide information about mechanical stability, stiffness, brittleness, ductility and anisotropic character of bonding [XVII].We, all know that mechanical stable system is always satisfying the Born criteria for stability [XVIII].

Table 1. Equilibrium propertiesfor B1-LaN.

Property	Present	Experiment	Others theoretical data
a_0 (Å)	5.308	5.295 [III], 5.291 [V], 5.301 [XXIII]	5.307[I], 5.315[II], 5.320[III],5.280[IV], 5.150[VI], 5.287 [IX]
B_0 (GPa)	123.7	135.5 [V],	117.0 [I], 123.2 [II],148.0 [III], 124.4 [IV], 152.0 [VI],119.7 [IX],
B'	3.21	5.00 [V]	3.66 [I], 3.38 [II],4.48 [IV], 4.39 [IX]

Computed results for the second order elastic constant and elastic modulus are also shown in table 2 with other theoretical findings. Results for the elastic constants also satisfy the stability Born criteria for the stability. Further elastic anisotropy factor is calculated using equation given by N. Wei et al. [XIX]. Presently calculated value for A is found to 1.20. Compare to the most of rare-earth monopnicitides this ration is almost double for LaN, which also clearly indicate less stability in B1 phase compare to other rare-earth monopnicitides. Elastic moduli are also calculated from the expressions given by R. Hill [XVI,XX,XXI]. Ductility or brittleness of the system can be predicted form the Pugh's [XVII] criteria.

Figures with captions

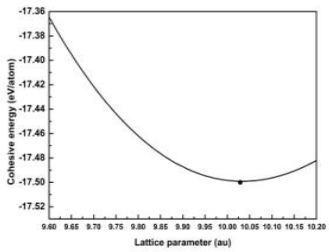

Figure 1 Cohesive energy curve for B1-phase of LaN. Present results, solid line. Theoretical result: Pentagon Ref [I]

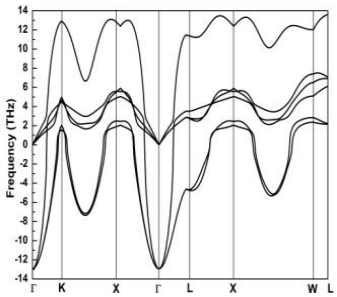

Figure 2 Phonon dispersion curve for B1-LaN.

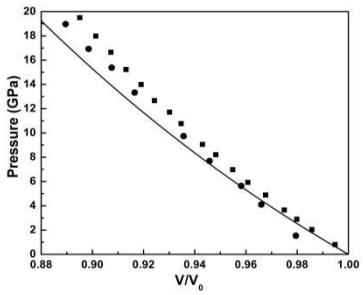

Figure 3 Thermal Equation of State for B1- LaN. Present result, line. Experimental result: square is from Ref. [V]. Theoretical result: circle is from Ref. [II].

Table 2. Elastic properties for B1-LaN.

Property	Present	Others theoretical data
C_{11}*(GPa)*	204.9	213.0 [I], 208.0 [II], 201.0[VIII], 219.2 [IX]
C_{12}*(GPa)*	85.1	84.0[I], 81.0 [II], 65.0[VIII], 70.0 [IX]
C_{44}*(GPa)*	72.0	71.0 [I], 69.0 [II], 49.0[VIII], 77.5 [IX]
G (GPa)	66.90	
Y (GPa)	170.33	

According to this ductile material have the ration of G/B less than 0.57 while in other case material is brittle. In the present case the ration of G/B is 0.53 indicating that LaN is ductile in nature. The Poisson's ratio (ν) is 0.27, which informs about the compressibility of the material.

Summary and conclusion:

Calculated equilibrium and elastic properties are in well agreement with experimental and other's findings. Result for phonon shows that large structural instability due to softening phonon frequency in almost all major direction of LaN singal crystal in B1 phase. This anomalous behaviour is also reflected in elastic properties. This anomalous behaviour may be attributed to the anharmonic effects of electron-phononinteraction in this system, which requires further attention.

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