On Dynamic and Elastic Stability of Lanthanum Carbide

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Abstract. The elastic stability up to 100 GPa and dynamic stability up to ~ 150 GPa of LaC have been investigated in NaCl (B1 phase) type and CsCl (B2 phase) structures, by first-principles calculations using the plane-wave pseudopotential method. The analysis of elastic moduli shows that the shear elastic modulus \( C' = (C_{11}-C_{12})/2 \) of B1 phase is negative up to ~47 GPa, suggesting that the B1 phase is elastic unstable up to this pressure. The theoretically calculated phonon frequencies in various directions of the Brillouin zone are imaginary even up to 150 GPa, indicative of dynamic instability of B1 phase in this compound up to 150 GPa. These analyses in B2 phase of LaC suggest that this phase will also remain unstable elastically and dynamically up to 150 GPa.

1. Introduction

Transition metal carbides are potential candidates for technological applications due to their good mechanical properties such as extreme hardness, corrosive resistance and high melting points. Such properties make these compounds suitable for cutting tools and hard protective coating for magnetic storage devices etc. In past few years many studies have come out on their structural, elastic and thermodynamic properties [1-3].

Among other transition metal carbides, the carbides of group IIIB elements (Sc, Y and La) are also subject of current interest [4, 5]. In ScC and YC, stability of B1 phase at ambient conditions has been found out by Isaev et al. [4] using lattice dynamic simulations and Soni et al. [5] using full potential linearized augmented plane wave (FP-LAPW) calculations, which have been supported by experimental findings [6,7]. However, the stability of LaC has not been studied theoretically as well as experimentally. In fact, to our knowledge, the LaC has not been synthesized yet. From the \textit{ab-initio} LMTO calculations Guillermet et al. [8] have determined the lattice parameters, enthalpy of formation, Debye temperature and cohesive energy for B1 phase of LaC.

In the present work, we have carried out first-principles theoretical analysis to understand the elastic and dynamic stability of B1 and B2 phase in LaC up to hydrostatic pressures of ~ 100 GPa and 150 GPa, respectively, employing plane-wave pseudopotential method

2. Theoretical Method

All the calculations have been performed employing plane wave pseudopotential method within the framework of Density Functional Theory (DFT) [9] implemented in Quantum Espresso package [10]. The elastic moduli of B1 and B2 phase have been determined from static lattice calculations. The \textit{ab-initio} total energy calculations required for this purpose have been performed within generalized gradient approximation (GGA) for the exchange correlation potential [11]. The ultrasoft pseudopotential with valence configurations of 5d\(^{1}\)6s\(^{2}\)6p\(^{0.5}\) for Lanthanum with core radius of 2.2 a.u.
for s and d orbitals and 2.0 a.u. for semicore p orbitals has been used. For carbon valence configuration of 2s22p2 with core radius 1.1 a.u. is used. Also, for C, non-relativistic calculations are performed and for La, non-linear core correction has been added with scalar relativistic calculations. Electronic wave functions are expanded in a plane wave basis set (PWs) with energy cut off, $E_{\text{cutoff}}$, of 60 Ry and charge density is represented in PWs with energy cut off of 400 Ry. A $16 \times 16 \times 16$ Monkhorst–Pack [12] grid of k-points has been used for sampling of electronic Brillouin zone (BZ) with energy convergence criteria chosen to be $10^{-6}$ Ry. Further, we find that increasing the number of k points does not affect the phonon frequency by more than 5 cm$^{-1}$. The dynamic stability of B1 and B2 phase has been analysed from the phonon spectra determined from lattice dynamical calculations using linear response method [13], carried out within the framework of self consistent density functional perturbation theory with $4 \times 4 \times 4$ q mesh in the first BZ for the interpolation of the force constants for phonon dispersion calculations and $12 \times 12 \times 12$ k-mesh used for integration over the Brillouin zone.

To determine the isotherm for B1 and B2 phases of LaC, we have computed the total energy at 0 K as a function of volume. The theoretical isotherm is then determined by finding the negative volume derivative of total energy dependence on unit cell volume. The zero pressure bulk modulus ($B_0$) and its pressure derivative at zero pressure ($B'_0$) were obtained by fitting the P-V data so obtained to the third order Birch-Murnaghan equation of state.

Further LaC single crystal in B1 and B2 phase has only three independent elastic constants, $C_{11}$, $C_{12}$ and $C_{44}$ or equivalently three independent elastic moduli namely bulk modulus (B) and two shear moduli $C'$ = $(C_{11}-C_{12})/2$ and $C_{44}$. To determine the shear moduli $C'$ and $C_{44}$ at a particular volume, the total energy is calculated as a function of different kinds of distortions [14,15] with the dependence of the total energy of the strained lattice on the deformation tensor expressed as [16]:

$$E_s(V, \varepsilon) = E_s(V, 0) + \frac{1}{2} V \sum_{i} \sum_{j} C_{ij} \varepsilon_{ij}$$

The shear elastic moduli are then calculated from the second order derivative of the total energy with respect to strain $\varepsilon_{ij}$ (with $i,j = 1$ to 6).

3. Results and Discussion

The zero pressure equilibrium volume ($V_0$) per formula unit, bulk modulus ($B_0$) and its pressure derivative ($B'_0$) for the B1 phase of LaC obtained by fitting theoretically determined pressure volume data to Birch-Murnaghan EOS are listed in the Table I. Our zero pressure volume, bulk modulus and its pressure derivative agree well with the available other theoretical values [4,8] confirming the accuracy of the calculation. In figure 1 we show the elastic constants of LaC single crystal in B1 phase as a function of pressure. The $C'$ and $C_{44}$ at zero pressure are determined to be -9.59 GPa and 47.81 GPa, respectively (Table I). Moreover, under pressure the $C'$ modulus first decreases with increasing pressure and reaches minimum value of ~ -16 GPa at ~ 21 GPa, thereafter, it increases continuously with further compression and becomes positive beyond 47 GPa. The $C_{44}$ however, decreases monotonically with increasing pressure but remains positive even at 100 GPa. The negative $C'$ modulus up to 47 GPa suggests that B1 phase in LaC is elastically unstable up to this pressure, however, it emerges as elastically stable phase above 47 GPa.

Additionally, we have determined the phonon dispersion relations (Fig. 2) for B1 phase of this carbide at zero pressure from lattice dynamic calculations. As is evident from figure 2, few phonon frequencies in various directions of Brillouin zone are imaginary even at highest pressure of ~ 150 GPa, indicating that the B1 phase in LaC is dynamically unstable up to ~ 150 GPa.

In B2 phase of LaC, the zero pressure equilibrium volume per formula unit, bulk modulus and its pressure derivative derived from the theoretical equation of state are 35.51 Å$^3$, 92.15 GPa and 3.379, respectively. Further, the elastic and dynamic stabilities of LaC have been tested for B2 phase also. As shown in figure 3, at zero pressure though the shear modulus $C'$ is positive (~ 16 GPa), the
Table 1: Various physical quantities at ambient pressure for B1 phase of LaC

|                | Present Work | Other Theoretical Works |
|----------------|--------------|-------------------------|
| $V_0$ (Å$^3$)  | 40.07        | 40.11[4], 39.95[8]      |
| $B_0$ (GPa)    | 83.18        | 80 [4]                  |
| $B_0'$         | 3.502        | --                      |
| $C'$ (GPa)     | -9.591       | --                      |
| $C_{44}$ (GPa) | 47.81        | --                      |

Figure 1. Elastic moduli of LaC as a function of pressure in B1 phase

Figure 2. Phonon spectrum of LaC for B1 phase

Figure 3. Elastic moduli of LaC as a function of pressure in B2 phase

Figure 4. Phonon spectrum of LaC for B2 phase
$C_{44}$ modulus is negative (~ -40 GPa). Further, the $C_{44}$ modulus increases with increasing pressure and become positive above 100 GPa. On the contrary, the $C'$ modulus decreases monotonically with increasing pressure and vanish at ~ 25 GPa. These findings suggest that LaC in B2 phase is elastically unstable up to 100 GPa and expected to remain unstable even at still higher pressures as indicated by the monotonic decreasing trend of $C'$ modulus with increasing pressure. Finally, the phonon spectra of LaC in B2 phase (Fig. 4) shows that many phonon frequencies are imaginary at ambient as well as at 150 GPa, suggesting that the B2 phase will be also dynamically unstable up to 150 GPa.

4. Summary
To summarize, we have examined elastic and dynamic stability of B1 and B2 phase in single crystal of LaC. Analysis of elastic moduli and phonon spectrum as a function of pressure suggests that the B1 phase will be elastically unstable up to ~ 47 GPa, however, it remains dynamically unstable up to ~ 150 GPa. The B2 phase however, will be unstable dynamically as well as elastically up to ~ 150 GPa. This study suggests that the synthesis of LaC in B1 or B2 phase is not possible.

Reference
[1] Aleksandra Vojvodic and Carlo Ruberto 2010 J. Phys. Cond. Matter 22 3755011
[2] Zengtao Lv, Haiquan Hu, Cheng Wu, Shouxin Cui, Guiqing Zhang and Wenhua Feng 2011 Physica B 406 2750
[3] Hui Li, Litong Zhang, Qingfeng Zeng, Haitao Ren, Kang Guan, Qiaomu Liu and Laifei Cheng 2011 Solid. State Comm. 151 61
[4] Isaev E. I., Simak S. I., Abrikosov I. A., Ahuja R., Vekilov Yu. Kh., Katsnelson M. I., Lichtenstein A. I. and Johansson B. 2007 J. Appl. Phys. 101 123519
[5] Soni, Pooja Pagare Gitanjali, Sanyal Sankar P. 2011 J. Phys. and Chem. Solids 72 810
[6] Toth E., Transition Metal Carbides and Nitrides, Academic,NewYork,1971
[7] P.Villars and L.D.Calvet Pearson’s Handbook of Crystallographic Data for Intermetallic Phases, American Society for Metals, Metals Park, OH, 1985
[8] Guillermert A. Fernandez 1993 Phys. Rev. B 48 11673
[9] Baroni S, Giannozzi P and Testa A 1987 Phys. Rev. Lett. 58 1861
[10] Baroni S, Dal Corso A, de Gironcoli S, Giannozzi P, Cavazzoni C, Ballabio G, Scandolo S, Chiarotti G, Focher P,Pasquarello A, Laasonen K, Trave A, Car R, Marzari N and Kokalj A http://www.pwscf.org
[11] Perdew J P and Burke K 1996 Int. J. Quantum Chem. 57 309; Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[12] Monkhorst H J and Pack J D 1976 Phys. Rev. B 13 5188
[13] Giannozzi P, de Gironcoli S, Pavone P and Baroni S 1991 Phys. Rev. B 43 7231
[14] Cohen R. E., Sixtrude L., and Wasserman E. 1997 Phys. Rev. B 56, 8575
[15] Gupta S. C., Joshi K. D., and Banerjee S. 2008 Metall. Mater. Trans. A 39A, 1593
[16] Nye J. F. Physical Properties of Crystals (Oxford University Press, Oxford, 1957)