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Structural and Mechanical Properties of Cubic Na_2O: First-Principles Calculations

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ABSTRACT

This work presents the investigation of the structural and mechanical properties of Na_2O in cubic structure (hereafter denoted as cubic Na_2O) by using the first-principles calculations within the local density approximation (LDA) and the generalized gradient approximation (GGA) in the functional form by Perdew-Wang 91 (PW91). The structural parameters such as the equilibrium volume (V_0), the bulk modulus (B_0), and its pressure derivative (B'_0) can be obtained by fitting the calculated energy (E) and volume (V) data with the third-order Birch - Murnaghan's equation of state whereas the elastic constants can be obtained from the stress-strain approach. The calculated equilibrium structural parameters and all three elastic constants (C_{11}, C_{12}, and C_{44}) show a good agreement with the experimental and other theoretical values. All elastic constants and bulk moduli calculated from LDA are slightly larger than those values calculated from GGA, by the reason of the lattice constant calculated from LDA is slightly smaller than that calculated from GGA. By using the calculated elastic constants and Born's criteria, the cubic Na_2O was found to be mechanically stable at ambient pressure. Consistent with the calculated elastic constants (C_{ij}), other elastic moduli such as bulk modulus (B), shear modulus (G), Young's modulus (Y), and Poisson ratio (v) of cubic Na_2O can be obtained by Voigt–Reuss–Hill (VRH) method. Because the B/G and v values can be used to determine the brittleness and ductility of materials, our calculated B/G and v values indicate that cubic Na_2O behaves as a brittle material at ambient pressure.

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Furthermore, the hardness of cubic Na_2O can also be obtained by using *G*/*B* and *G* values. The details of the structural and mechanical properties calculations for cubic Na_2O were presented and discussed.

INTRODUCTION

Sodium oxide (Na_2O) crystallizes in the cubic structure. It has received a great of interest in many applications for instance, solid-state batteries, gas detectors, and fuel cells (1 - 3). There are several research studies about this compound in both experimentally and theoretically, following are some examples. Zintl et al. (4) reported the lattice parameter of Na_2O crystal by powder diffraction experiment. Wu et al. (5) reported the high-pressure behavior of Na_2O by using synchrotron angle-dispersive powder X-ray diffraction. On the theoretical side, Dovesi et al. (6) used the Hartree-Fock method to calculate the lattice constants and elastic properties of Li_2O, Na_2O, and K_2O. Shukla et al. (7) reported the electronic structure calculations of Li_2O and Na_2O by using the Wannier function based on Linear Combination of Molecular Orbital (LCAO) formalism. Moakafi et al. (8) used first-principles calculations to study the electronic and optical properties of Li_2O, Na_2O, K_2O, and Rb_2O. Thomson et. al. (9) investigated the electronic structure and phonon spectra in Na_2O by using density functional theory (DFT) method. Although, there are several experimental and theoretical works on Na_2O have been reported. There are only few works focused on the mechanical properties of Na_2O. Thus, this work presents the study of the structural and mechanical properties of cubic Na_2O by using the first-principles calculations to provide more understanding and information for the researcher in this material.

MATERIALS AND METHODS

Computational Method

The computational method used is based on first principles density functional theory (DFT) (10, 11) with the plane wave pseudo-potential method as implemented in Vienna Ab-initio Simulation Package (VASP) (12). For the exchange- correlation terms, we used both local density approximation (LDA) (13, 14) and generalized gradient approximation (GGA) in Perdew-Wang 91 (PW91) functional form (15). The projector augmented wave (PAW) was used for the pseudo-potential. The calculation was performed on a 4×4×4 Monkhrost-Pack scheme (16) for *k*-point sampling integrations and the plane wave expansion was set up to 600 eV. The total change in energy less than 10^{-3} eV and the force less than 10^{-3} eV/Å were used as convergence criteria for structural relaxation. The cubic structure of Na_2O used in this calculation is shown Fig. 1.

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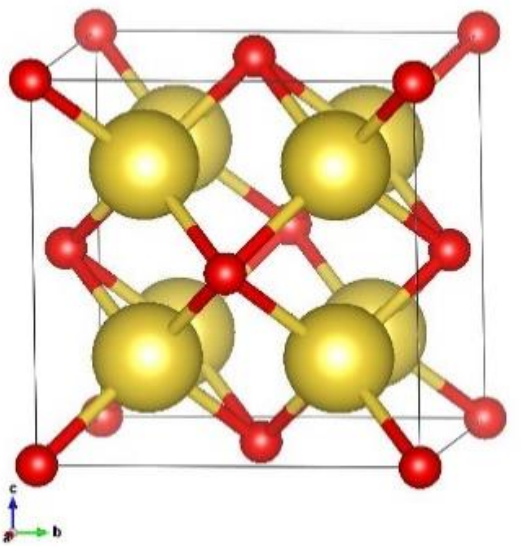

Figure 1 Crystal structure of cubic Na_2O. The yellow spheres correspond to the Na atoms and the red spheres correspond to the O atoms.

The calculated energy (*E*) and volume (*V*) data of a unit cell of cubic Na_2O were fitted to the third-order Birch - Murnaghan's equation of state (17, 18) to obtain the equilibrium volume (V_0), the bulk modulus (B_0), and its pressure derivative (B'_0). The third-order Birch - Murnaghan's equation of state is written as,

$$E(V) = E_0 + \frac{9}{16}V_0B_0\left\{\left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^3 B_0' + \left[\left(\frac{V_0}{V}\right)^{\frac{2}{3}} - 1\right]^2\left[6 - 4\left(\frac{V_0}{V}\right)^{\frac{2}{3}}\right]\right\} \quad ...(1)$$

The elastic constants (C_{ij}) are the crucial parameters for the calculation of mechanical properties of materials. For cubic structure, there are 3 independent elastic constants, namely C_{11}, C_{12}, and C_{44} (19). Their values can be determined from the stress-strain approach. The three independent elastic constants are demonstrated as,

$$\begin{pmatrix}\sigma_{xx}\\ \sigma_{yy}\\ \sigma_{zz}\\ \sigma_{yz}\\ \sigma_{zx}\\ \sigma_{xy}\end{pmatrix} = \begin{pmatrix}C_{11} & C_{12} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0\\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0\\ 0 & 0 & 0 & C_{44} & 0 & 0\\ 0 & 0 & 0 & 0 & C_{44} & 0\\ 0 & 0 & 0 & 0 & 0 & C_{44}\end{pmatrix}\begin{pmatrix}e_{xx}\\ e_{yy}\\ e_{zz}\\ e_{yz}\\ e_{zx}\\ e_{xy}\end{pmatrix} \quad ...(2)$$

where σ_{ij} ($i,j = x,y,z$) are the stress components, e_{ij} ($i,j = x,y,z$) are the strain components, and $C_{\alpha\beta}$ $(\alpha,\beta = 1,2,3,4,5,6)$ are the elastic constants. According to the calculated elastic constants, other elastic moduli including bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*) and Poisson's ratio (*v*) can be obtained by Voigt–Reuss–Hill (VRH) method as described in Ref. (20) and (21). In cubic structure, the equations are demonstrated as

$$B_V = B_R = \frac{1}{3}(C_{11} + 2C_{12}) \quad (3)$$

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (4)$$

$$G_R = \frac{5(C_{11}-C_{12})C_{44}}{4C_{44}+3(C_{11}-C_{12})} \quad (5)$$

$$B = \frac{B_V+B_R}{2} \quad (6)$$

$$G = \frac{G_V+G_R}{2} \quad (7)$$

where *V* and *R* represent the Voigt and Reuss approximation, respectively. Then the Young's modulus (*E*) and Poisson's ratio (*v*) can be calculated from,

$$E = \frac{9BG}{3B+G} \quad (8)$$

$$v = \frac{3B-2G}{2(3B+G)} \quad (9)$$

RESULTS AND DISCUSSIONS

Structural properties

The crystal structure of Na_2O is cubic structure (cubic Na_2O) with Fm-3m (no. 225). The cubic Na_2O contains 12 atoms per unit cell (8 Na

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atoms and 4 O atoms). To obtain the equilibrium structure of cubic Na_2O, we first calculated energy as a function of volume, $E(V)$, as shown in Figure 2 for both LDA and GGA approximation. Then fitted the calculated E-V data with the third-order Birch - Murnaghan's equation of state (17, 18) to obtain the equilibrium volume (V_0), the bulk modulus (B_0), and its pressure derivative (B'_0). The fitting results are listed in Table 1.

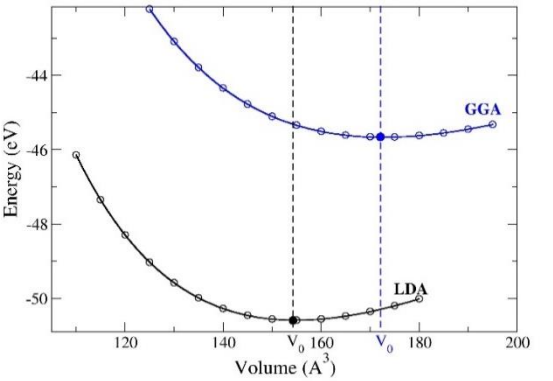

Figure 2 The calculated energy (E) and volume (V) data from LDA (black color) and GGA (blue color) approximations. The solid circles represent the equilibrium volume (V_0).

Table 1 Calculated lattice constants (a), bulk modulus (B), and its pressure derivative (B') of cubic Na_2O

	This work		Other calculations		Exp.
	LDA	GGA	LDA	GGA	
a (Å)	5.363	5.562	5.398[9], 5.408[8]	5.583[9], 5.592[8]	5.49[22]
B (GPa)	59.09	47.04	56[9], 57.79[8]	54[9], 47.11[8]	55.6[5]
B'	4.45	4.41	4.20[8]	4.71[8]	-

Table 2 Calculated elastic constants (C_{ij}) and other elastic moduli of cubic Na_2O.

	This work		Other calculations		Exp.
	LDA	GGA	LDA	GGA	
C_{11} (GPa)	120	98.6	114 [9]	114 [9]	-
C_{12} (GPa)	24.1	12.6	37.8[9]	34.7 [9]	-
C_{44} (GPa)	32.7	25.2	32.8 [9]	27.4[9]	-
B (GPa)	56.1	41.3	56[9], 57.79[8]	54[9], 47.11[8]	55.6[5]
G (GPa)	38.1	31.3	-	-	-
E (GPa)	93.2	75.0	-	-	-
v	0.223	0.197	-	-	-
B/G	1.472	1.319	-	-	-
H_v(GPa)	7.80	7.69	-	-	-

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From Table1, we can see that our calculated results are in good agreement with the previously works. The lattice constant calculated from LDA is 2.32 % smaller than the value from experiment and it is only 1.32 % higher than the experimental value by using GGA. We can see that LDA gives a slightly smaller lattice constant and a slightly larger bulk modulus than GGA.

Mechanical properties

The elastic constants and elastic moduli are the crucial information to study the mechanical properties in materials. All elastic constants and bulk moduli calculated from LDA are slightly larger than those values calculated from GGA, by the reason of the lattice constant calculated from LDA is slightly smaller than that calculated from GGA. The calculated elastic constants for cubic Na_2O are listed in Table2. Our calculated elastic constants are consistent with other calculations. Note that, there are no experimental results for elastic constants in cubic Na_2O.

The elastic constants C_{11} represents the elasticity in length whereas the other elastic constants, C_{12} and C_{44} represent the elasticity in shape. In general, we can see that C_{11} has the largest value, implying that the deformation in length is stronger than the deformation in shape.

Moreover, the stability of crystal can be considered from the mechanical stability. For cubic structure, the mechanical stability must obey Born's criteria (23) by the limitations on elastic constants as following relations, $C_{11} > 0$; $C_{44} > 0$; $C_{11} - C_{12} > 0$; $C_{11}+2C_{12} > 0$. Our calculated results from both LDA and GGA calculations indicate that the obtained elastic constants of cubic Na_2O at ambient pressure satisfy the mechanical stability criteria.

The calculated elastic moduli including the bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*), Poisson's ratio (*v*), and *B/G* ratio are also listed in Table2. The bulk modulus (*B*), shear modulus (*G*) and Young's modulus (*E*) reflect the resistance of materials against volume change, the resistance of materials against shape change and stiffness of materials, respectively. By using VRH approximation, the bulk modulus (B) from both LDA and GGA approximations are consistent with those obtained by the third-order Birch-Murnaghan equation of state fittings. Our calculated bulk moduli are in good agreement with the experimental value. The *v* and *B/G* value are used to determine the brittleness and ductility of materials (24). A material with $v < 0.26$ or $B/G < 1.75$ is brittle, if not it is ductile. From Table2, the calculated *v* and *B/G* values from both LDA and GGA approximations indicate that cubic Na_2O compound can be classified as brittle material at ambient pressure. The *B* and *G* also are used to determine hardness in materials. Hardness is a measure of the resistance of materials against the deformations. The hardness (H_v) of cubic Na_2O is determined using the equation proposed by Tian et. al. (25) for low hardness materials, written as, $H_V = 0.92(\frac{G}{B})^{1.137}G^{0.708}$. From this relation, we can see that the high hardness corresponds to the high *G/B* and *G* values. The

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hardness values calculated from LDA and GGA are 7.80 GPa and 7.69 GPa respectively. The calculated hardness obtained from LDA is a bit larger than that obtained from GGA.

CONCLUSION

In summary, the first-principles calculations method within LDA and GGA approximations were used to investigate the structural and mechanical properties of cubic Na_2O. The calculated lattice constant and elastic constants are in good agreement with the available experimental and theoretical data. All elastic constants and bulk moduli calculated from LDA are slightly larger than those values calculated from GGA, by the reason of the lattice constant calculated from LDA is slightly smaller than that calculated from GGA. By using the calculated elastic constants and Born's criteria, cubic Na_2O was found to be mechanically stable at ambient pressure. Moreover, the elastic moduli such as bulk modulus (*B*), shear modulus (*G*), Young's modulus (*E*), and Poisson ratio (*v*) of cubic Na_2O were obtained by the calculated elastic constants (C_{ij}). The Poisson's ratio and *B/G* ratio indicate a brittle manner of cubic Na_2O. The hardness of cubic Na_2O also were obtained by the *G/B* and *G* values. We hope our work will provide more understanding and information for the researcher in Na_2O material.

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