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# First-principles Investigation on Structural and Electronic Properties of Cubic $Na_2O$

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## Abstract

The structural and electronic properties of cubic $Na_2O$ were investigated by first-principles calculations. The calculated structural parameters ($a$, $\boldsymbol{B_0}$, and $\boldsymbol{B_0'}$) show a good agreement with the available values. Furthermore, the electronic band structure and density of states were obtained. We found that the cubic $Na_2O$ is a direct band gap material. In addition, the electron localized function (ELF) was analyzed to give more explanation of the bonding nature of cubic $Na_2O$. The ELF analysis indicates that the Na-O band is a typical ionic bond. The analysis details were presented and discussed.

**Keywords:** $Na_2O$, electronic structure, first-principles

## 1. Introduction

It is well known that $Na_2O$ is the alkali metal oxide and crystallizes in the cubic structure (antifluorite type, space group $Fm\bar{3}m$). $Na_2O$ has been reported to be a promising candidate for various technological applications such as solid-state batteries, fuel cells, and solid-state gas detectors [1-3]. It is difficult to prepare and preserve $Na_2O$ at ambient condition. Thus, a little experimental study has been reported for $Na_2O$. Zintl *et al.* [4] determined the room temperature lattice parameter of $Na_2O$ by using a powder diffraction experiment. Recently, Wu *et al.* [5] studied the high-pressure behavior of $Na_2O$ up to 30 GPa by synchrotron angle-dispersive powder X-ray diffraction in a diamond anvil cell at room temperature. On the theoretical side, the lattice constants, and elastic properties of $Li_2O$, $Na_2O$, and $K_2O$ were computed via the ab initio Hartree-Fock LCAO method by Dovesi *et al.* [6]. This method also was used to study the stability of the alkali metal oxides under pressure by Čančarević *et al.* [7]. Moakafi *et al.* [8] reported results of first-principles calculations for the electronic and optical properties under pressure effect of $Li_2O$, $Na_2O$, $Ki_2O$, and $Rb_2O$ compounds in the cubic antifluorite structure. Thompson *et al.* [9] presented a theoretical study of electronic and phonon spectra of $Na_2O$ using density functional theory with a plane-wave in both local-density approximation and generalized gradient approximation. In this work, the first-principles calculations with the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) were carried out to investigate the structural and electronic properties of cubic $Na_2O$. The structural parameters, electronic band structure, density of states (DOS), and electron localized function (ELF) of cubic $Na_2O$ were presented and discussed.

## 2. Computational details

First-principles calculations were performed using Vienna Ab-inito Simulation Package (VASP) [10]. The generalized gradient approximation (GGA) proposed by Perdew-Burke-Ernzerhof (PBE) was used to describe an exchange-correlation functional [11-12].

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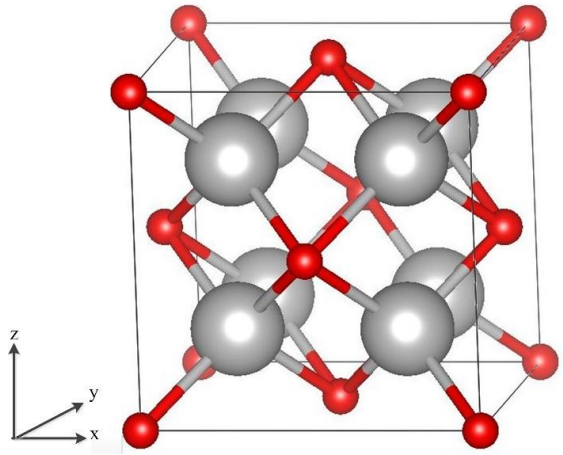


**Fig. 1.** Crystal structure of cubic $Na_2O$. The Na and O atoms are represented with gray and red balls, respectively.

The projector-augmented-wave (PAW) method was treated to perform the electron wave functions [13]. For the plane-wave expansion of the wave functions, a cut off energy of 600 eV was used. The Brillouin zone integrations were performed using Monkhorst-pack grids with 8×8×8 *k*-points mesh to obtain well convergence of total energy [14]. The total change in energy less than $10^{-4}$ eV and the force less than $10^{-3}$ eV/Å were used as convergence criteria for structural relaxation. The unit cell of cubic $Na_2O$ used in this calculation consists of 12 atoms per unit cell (Na 8 atoms and O 4 atoms). The cubic structure of $Na_2O$ is shown in Fig.1.

## 3. Results and discussion

### 3.1 Structural properties

The total energies as a function of volume, E ($V$), of a unit cell of cubic $Na_2O$ were calculated and fitted into the Birch-Murnaghan's equation of state [15-17] to obtain the equilibrium volume ($V_0$), the bulk modulus ($B_0$), and its pressure derivatives ($B_0'$). The Birch-Murnaghan's equation of state is written as,

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

where $E_0$ is the equilibrium energy, $V_0$ is the equilibrium volume, $B_0$ is the bulk modulus, and $B_0'$ is its pressure derivative. The relationship between total energy and volume ($E$-$V$) of cubic $Na_2O$ is shown in Fig. 2. The $E$-$V$ data was fitted to the Birch-Murnaghan's equation of state and the fitting parameters ($a = \sqrt[3]{V_0}$, $B_0$, and $B_0'$) are listed in Table 1. Our calculated results agree with previous calculations. Note that our calculated lattice constant is larger than the experimental value, reflecting in a smaller in the bulk modulus. However, the disagreement between our calculated lattice constant and the experimental value is only 1.95%, indicating that the calculations are reliable.

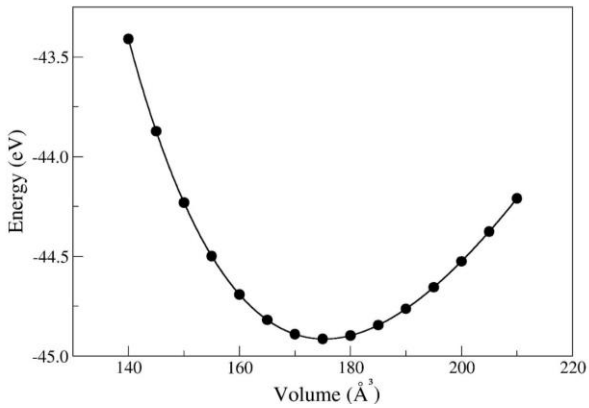


**Fig. 2.** The relationship between total energy and volume of cubic $Na_2O$. The solid line represents Birch-Murnaghan equation of state fits to the calculated data (solid points).

**Table 1.** Calculated lattice constant ($a$), bulk modulus ($B$), pressure derivative of bulk modulus ($B_0'$) along with the previous calculations and available experimental data of cubic $Na_2O$.

| | $a$ (Å) | $B$ (GPa) | $B_0'$ |
|---|---|---|---|
| This work | 5.597 | 45.40 | 4.35 |
| Calculations | 5.398(LDA) [9] | 56.00 (LDA) [9] | |
| | 5.408 (LDA) [8] | 57.79 (LDA) [8] | 4.20 [8] |
| | 5.583 (GGA) [9] | 54.00 (GGA) [9] | 4.71 [8] |
| | 5.592 (GGA) [8] | 47.11 (GGA) [8] | |
| Experiment | 5.490 [4] | 55.60 [5] | - |

### 3.2 Electronic properties

The calculated energy band structure of cubic $Na_2O$ along with the high symmetry point of the Brillouin zone is shown in Fig. 3. The energy band gap of cubic $Na_2O$ was calculated to be 1.88 eV with a direct gap, which is in good agreement with the previous GGA calculation value of 1.83 eV from Moakafi *et al*. [8]. To further explain the electronic band structure, the total and partial density of states (DOS) also were calculated as shown in Fig. 4. We found that the main bonding peaks located close to the Fermi level (or the upper valence band (VB)) at the energy range between -3 and 0 eV. The contribution of O-p, Na-s, and Na-p states are dominant. However, the O-p state is mainly dominant at the Fermi level. For investigating the bonding nature of materials, the electron localization function (ELF) is used to analyzes the characteristics and types of chemical bonds [18]. The ELF = 1 shows the strongest covalent bond, ELF = 0.5 shows the metallic bond, and $0 \leq$ ELF $< 0.5$ shows the ionic bond. The electron localization function (ELF) of cubic $Na_2O$ was calculated and shown in Fig. 5. It is clearly seen that the Na-O bonds are in the blue area which corresponds to the ELF $< 0.5$. Thus, the bond formed between Na and O is an ionic bond.

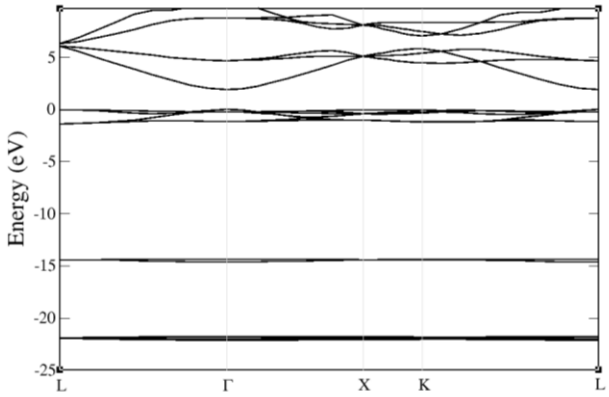


**Fig. 3.** Calculated band structure of cubic $Na_2O$.

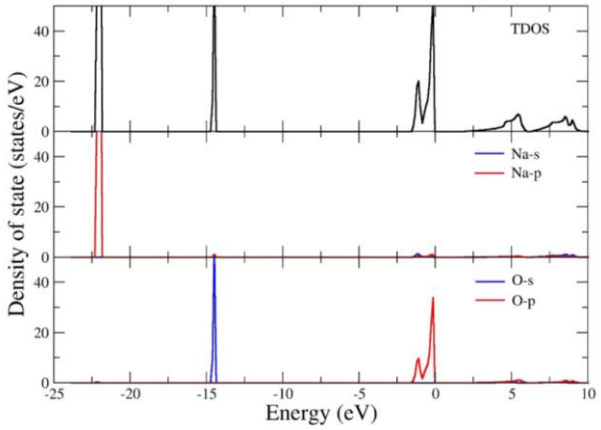


**Fig.4.** Calculated total and partial density of states (DOS) of cubic $Na_2O$.

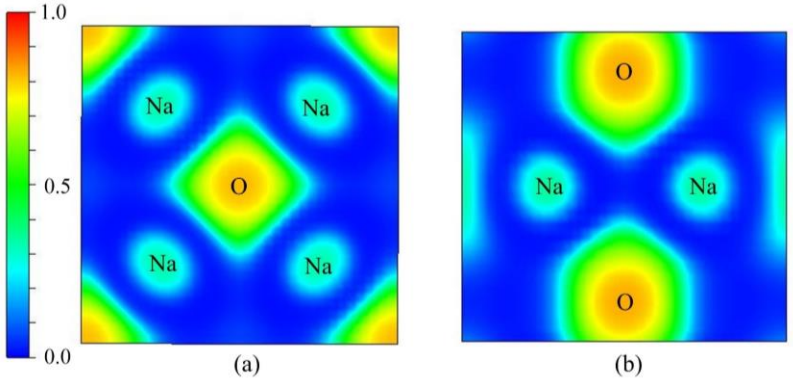


**Fig. 5.** Calculated electronic localization functions (ELF) of cubic $Na_2O$. Electron localization function isosurface maps for (a) Miller indices: (0 0 1) and (b) Miller indices: (1 1 0).

## 4. Conclusion

The first-principles calculations based on density functional theory within PBE-GGA were used to investigate the structural and electronic properties of cubic $Na_2O$. The calculated structural parameters such as lattice constant, bulk modulus, and its pressure derivative are in good agreement with the available data. The electronic band structure and the density of states were determined. The cubic $Na_2O$ was found to be a direct band gap material with the band gap value of 1.88 eV, which is consistent with the previous study. Moreover, the electron localized function (ELF) was also analyzed and the result indicates that the Na-O is ionic bonding. We hope that this work will be used as a reference data for both theoretical and experimental studies based on $Na_2O$ compound.

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## References

[1] Jamal M, Venugopal G, Shareefuddin M, Chary MN. Sodium ion conducting glasses with mixed glass formers NaI–$Na_2O$–$V_2O_5$–$B_2O_3$: application to solid state battery. Materials Letters. 1999;39(1):28-32.
[2] Cho KI, Lee SH, Cho KH, Shin DW, Sun YK. $Li_2O$–$B_2O_3$–$P_2O_5$ solid electrolyte for thin film batteries. J. Power Sources. 2006;163(1):223-8.
[3] Lee KB, Beaver MG, Caram HS, Sircar S. Performance of $Na_2O$ promoted alumina as $CO_2$ chemisorbent in sorption-enhanced reaction process for simultaneous production of fuel-cell grade $H_2$ and compressed $CO_2$ from synthesis gas. J. Power Sources. 2008; 176(1):312-9.
[4] Zintl E, Harder A, Dauth B. Lattice Structure of the oxides, sulfides, selenides and tellurides of lithium, sodium and potassium. Z Elektrochem. 1934;40:588.
[5] Wu X, Zhang Y, Zhang J, Liu R, Yang J, Yang B, Xu H, Y Ma. High pressure X-ray diffraction study of sodium oxide ($Na_2O$): Observations of amorphization and equation of state measurements to 15.9 GPa. J. Alloys Compd. 2020;823:153793.
[6] Dovesi R, Roetti C, Freyria-Fara C, Prencipe M, Saunders VR. On the elastic properties of lithium, sodium and potassium oxide. An ab initio study. Chem. Phys. 1991;156:11-9.
[7] Čančarević Z, Schön JC, Jansen M. Stability of alkali-metal oxides as a function of pressure: Theoretical calculations. Phys. Rev. B: Condens. Matter. 2006;73:224114.
[8] Moakafi M, Khenata R, Bouhemadou A, Khachai H, Amrani B, Rached D, Rérat M. Electronic and optical properties under pressure effect of alkali metal oxides. Eur. Phys. J. B. 2008;64(1):35-42.
[9] Thompson M, Shen X, Allen PB. Density functional calculation of electronic structure and phonon spectra of $Na_2O$. Phys. Rev. B. 2009;79(11):113108.
[10] Kresse G, Furthmuller J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B. 1996;54:11169-86.
[11] Perdew JP, Chevary JA, Vosko SH, Jackson KA, Pederson MR, Singh DJ, Fiolhais C. Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation. Phys. Rev. B: Condens. Matter. 1992; 46(11):6671-87.
[12] Perdew JP, Burke K, Ernzerhof M. Generalized Gradient Approximation Made Simple. Phys Rev Lett. 1996;77(18):3865-8.

[13] Blöchl P E. Projector augmented-wave method, Phys. Rev. B: Condens. Matter. 1994;50: 17953–79.
[14] Monkhorst J, Pack JD. Special points for Brillouin-zone integrations, Phys. Rev. B: Condens. Matter. 1976; 13:5188 –92.
[15] Birch F. Finite Elastic Strain of Cubic Crystals. Phys. Rev. B: Condens. Matter. 1947; 71(11):809-24.
[16] Murnaghan FD. Finite Deformations of an Elastic Solid. Am. J. Math. 1937;49:235-60.
[17] Murnaghan FD. The Compressibility of Media under Extreme Pressures. Proc Natl Acad Sci U S A. 1944;30:244-7.
[18] Burdett JK, Mc Cormick TA. Electron localization in molecules and solids: The meaning of ELF. J. Phys. Chem. A 1998;102:6366-72.