

Electronic and optical properties under pressure effect of alkali metal oxides

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Abstract. We report results of first-principles calculations for the electronic and optical properties under pressure effect of Li_2O , Na_2O , K_2O and Rb_2O compounds in the cubic antiferroite structure, using a full relativistic version of the full-potential augmented plane-wave plus local orbitals (FP-APW+lo) method based on density functional theory, within the local density approximation (LDA) and the generalized gradient approximation (GGA). Moreover, the alternative form of GGA proposed by Engel and Vosko (GGA-EV) is also used for band structure calculations. The calculated equilibrium lattices and bulk moduli are in good agreement with the available data. Band structure, density of states, and pressure coefficients of the fundamental energy gap are given. The critical point structure of the frequency dependent complex dielectric function is also calculated and analyzed to identify the optical transitions. The pressure dependence of the static optical dielectric constant is also investigated.

PACS. 71.15.Ap Basis sets – 78.40.Fy Semiconductors – 78.20.Ci Optical constants

1 Introduction

The alkali metal oxides Li_2O , Na_2O , K_2O and Rb_2O crystallize at ambient condition in the cubic antiferroite structure (anti- CaF_2 -type) (#225) [1]. This structure is antiferroite to the fluorite structure (CaF_2). The cation and anion sublattices of these crystals have different symmetry. In the fluorite type-structure, the cations form an FCC lattice and the anions form a simple cubic lattice. In CaF_2 structure, the calcium ions occupy the corner of the face-centered positions and the fluorine ions are situated in calcium tetrahedral. Each calcium ion is surrounded by eight fluorine ions and each fluorine ion is coordinated with four calcium ions. Whereas in the antiferroite-type structure, the cation and anion positions are interchanged, this leads to the formation of large cavities in the crystal structure. In the X_2O ($\text{X} = \text{Li}, \text{Na}, \text{K}$ and Rb) compounds, the oxide atoms are located at (0; 0; 0) and the X atoms are located at (0.25; 0.25; 0.25) and (0.75; 0.75; 0.75) positions. These compounds are characterized by their large band gap and their high ionic conductivity arises as a consequence of Frenkel-defect formation by metal atoms redistributing on their regular sites as well as on the interstitial sites without any significant distortion of the FCC

oxide sublattice. The alkali metal oxides play a crucial role in achieving photocathodes [2,3], promoting catalytic reactions [4] or enhancing the oxidation of semiconductor surface [5]. Hence, they appear to be promising candidates for technological applications in solid state batteries [6,7], in fuel cells or in solid state gas-detectors [8,9].

Experimentally, Hull et al. [10] measured the bulk modulus, lattice parameter and the elastic constants of Li_2O at ambient conditions and under temperature up to 1600 K. The transition temperature $T_c \sim 1200$ K (the melting point is 1705 K) of Li_2O was measured by Oishi et al. [11], who found that the elastic constant C_{11} suddenly decreases at the transition temperature T_c . Mikajlo et al. [12–14] performed the electronic structure of alkali metal oxides by using both the electron momentum spectroscopy measurement and the linear combination of atomic orbitals (LCAO) method. The surface and bulk electronic structure of Li_2O studied by Liu et al. [15] using the photoemission and electron-energy loss spectroscopy measurement. The oxygen species formed in the presence of lithium, potassium and cesium have been studied by Jupille et al. [16], using the ultraviolet and X-ray photoelectron spectroscopy measurements. Structural phase transition of Li_2O from antiferroite to antiferroite (PbCl₂-type structure) is identified by Laziki et al. [17] and Kunc et al. [18] by using the X-diffraction study.

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From theoretical point of view, Dovesi et al. [19] calculated the lattice constants and elastic properties of Li_2O , Na_2O and K_2O at zero pressure via the *ab initio* Hartree-Fock LCAO method. This method (LCAO) is also applied by Cancarevic et al. [20] to study the stability of the alkali metal oxides under pressure. The electronic band structures of these materials at ambient conditions were discussed by Zhuravlev et al. [21] and Eithiraj and co-workers [22] using the self-consistent pseudopotential method (PP) and tight-binding linear muffin-tin orbitals (TB-LMTO), respectively. Dovesi [23] performed the LCAO formalism to study the electronic structure of Li_2O . The Wannier function based LCAO formalism has been reported by Shukla et al. [24] on Li_2O and Na_2O compounds. This study demonstrates the importance of the correlation effects. The superionic behavior of Li_2O was investigated using the molecular dynamics (MD) simulation method [25], from which the lattice constant and the elastic constants under ambient pressure were obtained. Garcia-Rodeja et al. [26] and Wilson et al. [27] investigated the structural and elastic properties of lithium oxide. The authors [26] and [27] used the LDA-pseudopotential plane wave method and the aspherical ion model, respectively. The structural, electronic and defects properties of lithium oxide have been studied by Islam et al. [28], using both the plane wave (PW) and the local combination of atomic orbitals (LCAO) methods. Mauchamp and co-authors [29] simulated the electron energy-loss near edge structure at the lithium K edge in lithium oxide, using the full potential linearized augmented plane wave (FP-LAPW) method.

The knowledge of the electronic and optical properties of materials under pressure effect provides insight view about their performance in practical applications. To the best of our knowledge, there are no earlier theoretical calculations for the optical properties and band gaps pressure dependence for these compounds. It is therefore timely to investigate these properties of Li_2O , Na_2O , K_2O and Rb_2O compounds in order to provide reference data for the experimentalist and to complete exciting theoretical works on this fascinating class of materials, using the full-potential augmented plane-wave plus local orbitals (FP-APW+lo) method which has proven to be one of the most accurate methods [30,31] for the computation of the electronic structure of solids within the density functional theory (DFT).

2 Computational method

The calculations reported here were carried out using the full-potential all-electron with the mixed basis APW+lo method [32,33] implemented in WIEN2K computer package [34]. In this method the space is divided into an interstitial region (IR) and non overlapping muffin tin (MT) spheres centered at the atomic sites. In the IR region, the basis set consists of plane waves. Inside the MT spheres, the basis sets is described by radial solutions of the one particle Schrödinger equation (at fixed

energy) and their energy derivatives multiplied by spherical harmonics. The exchange correlation (XC) effects for the structural properties are treated by the local density approximation (LDA) [35] with and without generalized gradient approximation (GGA) [36]. Moreover, the alternative form of GGA proposed by Engel and Vosko (GGA-EV) [37] is also used for band structure calculations.

In order to achieve energy eigenvalues convergence, the wave functions in the interstitial region were expanded in plane waves with a cut-off $K_{\max} = 12/R_{MT}$, where R_{MT} denotes the smallest atomic sphere radius and K_{\max} gives the magnitude of the largest K vector in the plane wave expansion. The R_{MT} are taken to be 1.6, 1.7, 2.1, 2.25 and 2.3 atomic units (a.u.) for Li, O, Na, K and Rb, respectively. The valence wave functions inside the spheres are expanded up to $l_{\max} = 9$ while the charge density was Fourier expanded up to $G_{\max} = 12$. The self-consistent calculations are considered to be converged when the total energy of the system is stable within 10^{-4} Ry. The integrals over the Brillouin zone are performed up to 18 k -points in the irreducible Brillouin zone (IBZ), using the Monkhorst-Pack special k -points approach [38].

3 Results and discussions

3.1 Structural properties

The fitting of the Murnaghan equation of state [39] to the total energies versus lattice parameters yields to the equilibrium lattice parameter (a_0), bulk modulus B_0 and its pressure derivative B' . In Table 1, we summarize our calculated structural properties (lattice constant, bulk modulus and its pressure derivative) of X_2O compounds at zero pressure. When we analyzed these results we found that there is a good agreement between our results and the previously reported theoretical investigations. In comparison with the experimental data we found that the GGA overestimates the lattice parameters, while the LDA underestimates them, which are consistent with the general trend of these approximations. The calculated bulk modulus decreases from Li_2O to Rb_2O , suggesting that the compressibility increases from Li_2O to Rb_2O . We note that the anion atoms are the same in the four compounds, the cation atoms size are different. The difference size of the cation atoms could be the responsible for the lattice constant increasing from Li_2O to Rb_2O . To verify the accuracy of these results, several tests have been performed using different muffin tin radius as well as different sets of special k -point to ensure the convergence.

3.2 Electronic properties

The self-consistent full relativistic band structures of Li_2O , Na_2O , K_2O and Rb_2O were obtained in the cubic antiferroite phase at equilibrium volume within LDA, GGA and EVGGA schemes. It is well known that the LDA and the GGA usually underestimate the energy