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First-principles calculation of the structural, electronic, dynamical and thermodynamic properties of γ-$LiAlO_2$

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ABSTRACT

The structural, electronic, dynamical and thermodynamic properties of γ-$LiAlO_2$ are investigated using density-functional perturbation theory (DFPT). The calculated structural parameters are found to differ by less than 0.5% from the available experimental data. The electronic band structure and DOS indicate that γ-$LiAlO_2$ is an insulator with a direct gap of 4.85 eV. Using the linear response theory, vibrational properties are calculated. The phonon dispersion curves, the Born effective charges, the optical-mode frequencies at Γ point and LO-TO splitting are reported for the first time. The Raman and infrared-active phonon modes are further assigned and discussed briefly. Our results indicate that the Born effective charges are −1.74 for O atom and +2.49 for Al atom, which are lower than the formal charges of Al and O atom, and the two giant LO-TO splitting occur in A_2 and E modes. Additionally, the thermodynamic functions such as ΔF, ΔE, C_V and S are predicted using the phonon density of states. The results are in good agreement with experimental values and other available theoretical results. It is expected that these results will provide useful guidance to help with structural characterization of $LiAlO_2$.

Introduction

In recent decades, γ-$LiAlO_2$ has received much attention because of its unique properties and wide applications. Firstly, the tritium breeders are the key materials of a deuterium-tritium fusion reactor in ITER (International Thermonuclear Experimental Reactor). The γ-$LiAlO_2$ is being considered as a primary solid breeder candidate material in the blanket for the future fusion reactor due to its excellent performance under high neutron and electron radiation through the reactions: $^6Li + n(slow) \rightarrow {}^4He + {}^3T + 4.8(MeV)$, $^7Li + n(fast) \rightarrow {}^4He + {}^3T + n - 2.5(MeV)$ [1–4]. Secondly, γ-$LiAlO_2$ is used as solid matrix material for the fabrication of electrolyte tiles in molten carbonate fuel cells (MCFC) [5]. The MCFC is one of the most attractive methods for future electric power generation,

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and has many advantages, including very high electrochemical conversion efficiency and pollution-free operation [6]. The γ-$LiAlO_2$ powder is also considered as electrolyte substrate which is a porous plate, and is formed into a matrix which will be impregnated with molten carbonate of alkali metals. The thermodynamic stability of γ-$LiAlO_2$ is one of the important physical phenomenon affecting the cell durability. Thirdly, among all of the possible substrates, γ-$LiAlO_2$ is expected to be a promising material for GaN epitaxial growth since the lattice mismatch to GaN is estimated to be less than 1.4% [7]. The compressible strained M-plane GaN film is grown on γ-$LiAlO_2$ (100) [8,9]. Finally, γ-$LiAlO_2$ is one of a potential candidate for the ultrasonic device applications [10]. Therefore, the deeper research of γ-$LiAlO_2$ is necessary for the good use of it.

There are some investigations on γ-$LiAlO_2$. From an experimental point of view, the lattice parameters were determined by Marezio with a general Electric XRD-3 spectrometer [11]. The infrared and Raman spectra of polycrystalline $LiAlO_2$ were reported by G.D. Chryssikos et al. [12]. Heiko Kleykamp [13] measured the enthalpy and the heat capacity by isothermal drop calorimetry. L.M.Carrera et al. [14] Studied tritium recovery from nanostructured $LiAlO_2$ and discussed how superlattice nanostructure may modify tritium release. The elastic constants were determined by Fabian Jachmann et al. using an acoustic pulse-echo technique [10]. Mitch M.C. Chou et al. [15] investigated Czochralski growth including the micro-structure defect study and thermal expansion coefficients. Taohua Huang et al. [16] Studied growth, etching morphology and spectra of γ-$LiAlO_2$ single crystal. Phase transitions of $LiAlO_2$ at high pressure and high temperature are studied by Li Lei et al. [17]. Theoretically, Sylvio Indris and Paul Heitjans [18] investigated the local electronic structure with Li nuclear magnetic resonance (NMR) measurements. S.Q. Wu [19] studied the structural, elastic, and electronic properties by employing *ab initio* approaches based on density functional theory (DFT). Recently, H. Tsuchihira et al. [20] used molecular dynamics to elucidate the radiation damage process in $LiAlO_2$.

Nevertheless, there are only a little theoretical information on γ-$LiAlO_2$ and the knowledge of the dynamical and thermodynamic properties of γ-$LiAlO_2$ single crystal is still incomplete. Raman and infrared (IR) spectra are well known methods to study atomic dynamics. Therefore, the assignment of the Raman active modes is essential for crystallographic analysis and the detection of defects. For example, the X-ray diffraction (XRD) pattern for γ-$LiAlO_2$ is very similar to the ε-$LiAlO_2$ phase [11], they will differ by dynamical properties including Raman active modes. In addition, as the heat generated by the nuclear fusion reaction is also absorbed by the blanket and is transferred to the coolant [1], the thermal properties of breeder materials are primary importance for the design of a blanket system. In this study, we will employ first principles DFT and DFPT to investigate the structural, electronic, lattice dynamical and thermodynamic properties of γ-$LiAlO_2$. The optical phonon frequencies including Raman and infrared (IR) active modes at Γ point will be discussed in detail. The thermodynamic functions such as ΔF, ΔE, C_V and S are predicted from 0 K to 1800 K.

This paper is organized in the following way: In Section Computational details, we briefly describe the computational method. In Section Results and discussions, the results and discussions are presented including the structural, electronic, dynamical and thermodynamic properties. Finally, conclusions are summarized in Section Conclusions.

Computational details

Our calculations on γ-$LiAlO_2$ are performed using the *Vienna ab initio simulation package* (VASP) [21,22], which is based on first-principles density functional theory (DFT), and the projector augmented wave method [23]. In this study, all calculations are done using the PAW pseudo-potential and the generalized gradient approximation (GGA) [24] within Perdew and Wang scheme (PW91) exchange-correlation functions. Spin-orbit coupling is neglected in our calculations due to its relatively small effect on binding energies. The total energy was converged within 10^{-7} eV to minimize the errors in the calculation of the forces. As kinetic energy cutoff and k-point meshes are significant for the accuracy of the first principle calculations, we make a test before calculation to guarantee an excellent convergence. A kinetic energy cutoff of 400 eV is used for the set of plane waves, and the k-point meshes in the full Brillouin-zone (BZ) are sampled by 6 × 6 × 6 k-mesh, obtained using the Monkhorst-Pack (MP) method [25].

In the phonon dispersion curves and thermodynamic calculations, we employed the *Phonopy* software package [26], which is based on density-functional perturbation theory (DFPT). Through the linear-response method [27,28], in which derived for the second derivatives of the total energy on atomic displacements, the interatomic forces were calculated. Then the interatomic force constants were obtained from the calculated forces and the displacements. Using these force constants, the phonon frequencies were calculated. The Born effective charges are obtained in order to study the longitudinal optical and transverse optical (LO-TO) splitting at $\mathbf{k} = 0$ (Γ point) and the vibrational spectrum including infrared (IR) and Raman active. The thermodynamic functions are further evaluated at a given range of temperature from the phonon dispersions and the phonon densities of states.

Results and discussions

Structure optimization and electronic properties

Our calculations start with the structural optimization by minimizing the total energy to obtain the equilibrium lattice constants. As shown in Fig. 1, the crystal structure of γ-$LiAlO_2$ has a tetragonal symmetry with the space group $P4_12_12$ [11]. Obviously, Fig. 1 shows that there are 4 formula units (f.u.) in each unit cell with 16 atoms. The occupied Wyckoff positions are 4*a* of Li, 8*b* of O and 4*a* of Al. The unit cell lattice parameters and atomic coordinates are fully relaxed to find the equilibrium structure. The calculated lattice parameters comparing with experimental data [11] and other theoretical results [18,19] are displayed on Table 1. From Table 1, the largest deviation from experiment data is less than 0.5%. The