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Ab Initio Study of Structural, Thermal Stability and Electronic Properties of LiRuPO4 Compound: A Storage Energy Application

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Abstract

In this paper, we investigated the structural, electronic, and thermal stability of the LiRuPO4 compound. We applied the ab-into-density functional to conduct all our calculations. We used gradient generalized approximation with Hubbard correction implemented in the CASTEP (Cambridge Serial Total Energy Package) code. Results indicate that LRP crystallizes in the orthorhombic structure after phonons and thermal stability analysis. LRP is a semiconductor with an indirect gap after analysis of band structure curves within electronic properties and an energy gap of 2,18 eV. LiRuPO4 will be an effective alternative to LiFePO4 in storage energy applications such as electric batteries in vehicle fabrication technology.

Keywords: $LiRuPO_4$, density functional calculations, semiconductor, storage energy applications.

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1. Introduction

As the demand for electrical energy increases and the available sources are finite, efficient utilization of energy has become an important issue. In this regard, energy storage devices are required to ensure uninterrupted power supply and to regulate power generation. The lithium-ion battery is one of the smartest choices for energy storage devices due to its long charge/discharge cycling, low self-discharge, high energy density, and design flexibility. Improving the performance of lithium-ion batteries is a topic of interest, and numerous investigations have been performed to enhance the capacity and cycle stability of lithium-ion batteries. The cathodes of lithium-ion batteries are typically inorganic materials, and the most attractive cathode material is $LiFePO_4$ (LFP) due to its low cost and large operating voltage window. Although its operating voltage may be limited compared to NCM or LCO, these types of cathodes may fail explosively due to thermal runaway. LFP has better electronic conductivity than NCA and LCO. The poor electronic conductivity of pure LFP can be improved by cation and anion surface doping, and under optimum conditions, LFP shows about 10-11 orders of increased electronic conductivity. [1-3]

The driving force to study the LFP properties has been the significance of the ab-initio (DFT based) method available for studying the material properties down to the atomic scale level that links the material behavior at different length scales and the experimentation as well. Typically, available investigations were just based on experimental analysis. Various studies so far have been performed for LFP, like calculation of structural and electronic properties, effect of defects on the electrochemistry of LFP, lithium diffusion paths, electronic and ionic conductivities, etc.

In this work we studied a compound similar to LFP, which is $LiRuPO_4$ when we applied ab-initio study to calculation its structural, electronic and thermal stability properties of this compound. Lithium ruthenium phosphate, $LiRuPO_4$, is a promising material for batteries in hybrid electric vehicles and for future nano-electronics, due to its stable ruthenium-redox potential and large lithium de-intercalation reaction occurring at a voltage around 3.5 V with respect to Li+/Li. In an energy storage device, lithium is released (de-intercalated) from an electrode during the discharge process, where it reacts with an electrolyte phase and an electronic conductor to complete the intercalation reaction. [4, 5]

2. Computational Methods

The properties of LRP, including its structural, electronic, and thermal stability, were studied using ultra-soft pseudopotential plane waves in the CASTEP package [6]. The exchange-correlation potential was represented by the generalized gradient approximation of Perdew et al. with a Hubbard correction of 3 eV (GGA-PBE+U) [7, 8]. The plane wave cut-off energy was set at 480 eV, and a 6 ×

6 × 6 special k-points mesh as per Monkhorst and Pack was used. Electrons and ions were relaxed when the variation of successive energies and forces exceeded 10^{-5} eV and 0.02 eV/Å, respectively. Energy convergence was considered achieved within an error of 10^{-5}.

3. Results And Discussion

3.1. Thermal Stability Properties

3.1.1. Phonons

Figure 1 shows stability thermal and energies are calculated as functions of the wave vector of phonons in the long-wavelength limit, and together these fold points become the complete phonon dispersion curves if extended over a whole reciprocal space of the appropriate size. In the frequency versus q-space plot (phonon curve), regions of linear dispersion correspond to frequencies of transverse phonons, while curvilinear dispersion corresponds to LA phonons. Branches with negative curvature also refer to (nonzero) low-frequency TA phonons. After the test of the stable crystal of $LiRuPO_4$, The positive range of the density phonon of states and phonon dispersion indicate that the orthorhombic structure in Pnma space group is the stable structure of LRP.

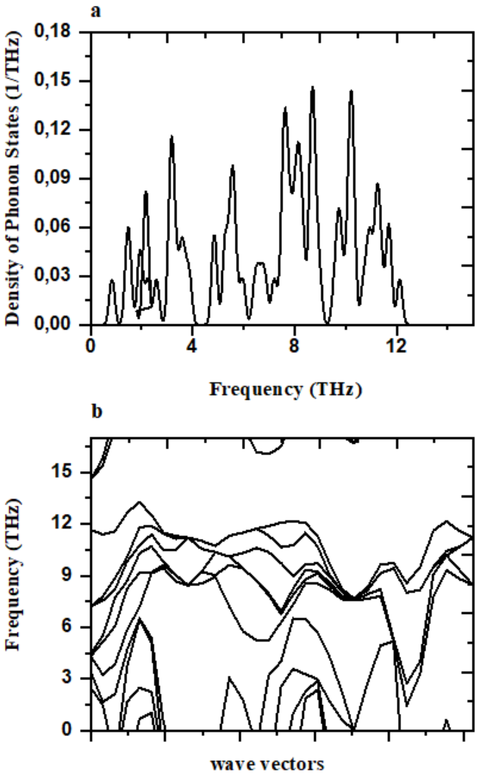

Figure 1. Phonons of $LiRuPO_4$ using GGA+U in Pnma orthorhombic structure.

3.1.2. Thermal Conductivity

In three-dimensional (3D) materials, the discussion of lattice thermal conductivity focuses on the transfer of phonon energy (see Figure 1). This energy transfer occurs through various mechanisms, including acoustic-optical interactions, regular and anharmonic processes, and Umklapp scattering, which are influenced by temperature and crystal structure. At low temperatures, research indicates that the thermal resistivity of these 3D crystals is proportional to the cube of the temperature, as explained by the Debye theory, which limits the density of states for phonons. Many studies prioritize thermal conductivity, a more practical parameter for applications that can be measured using experimental equipment. Generally, reducing thermal conductivity is essential for decreasing the thermal resistance of a given material. This knowledge is often applied in technologies for electronic devices, among other uses. However, lithium-ion systems have more stringent requirements for these materials, particularly regarding the interaction between battery and thermal systems, due to the significant heat generated while cycling high-specific energy storage.

From the phonons curves, the thermal conductivity (κL) of $LiRuPO_4$ is typically compared with that of other conducting nitride-phosphates that have pyrophosphate-related structures. It is generally understood that in $LiMPO_4$ materials, the thermal conductivity decreases as the conductivity of heat or Li^+ carriers diminishes. At elevated temperatures, the κL of $LiRuPO_4$ is comparable to the values found in many mixed characteristic materials; however, it is lower than that of Li^+-high-conducting sulfates and oxides. To date, the temperature dependence of the κL of $LiRuPO_4$ has not been investigated. Therefore, it is essential to extend the previously studied characteristics of κL in $LiRuPO_4$ to higher temperatures, considering both thermally and structurally related properties.

3.2. Structural properties

Lithium Ruthenium phosphate ($LiFePO_4$) was the first olivine type cathode material for rechargeable lithium batteries. However, this compound belongs to the Pnma orthorhombic space group ,This structure (Figure2) consists of 6-coordinated PO4 tetrahedra sharing corners with RuO6 octahedra in edge-shared chains of corner linked LiO6 octahedra that run along the a coordinate. The endo-octahedra of the Ru chains complete the orthorhombic coordination of the Li atoms. There is a direct correlation between the Li^+ diffusion and the low dimensional octahedral interstices present in the Pnma orthorhombic space group of the olivine structure. First-principles calculations converge to the orthorhombic cell parameters ; a = 10.38 Å, b = 5.99 Å, and c = 4.78 Å, see (table1) and to the mitigated atomic coordinates to the Pnma crystal structure, with Li1 atoms in (4f) positions 0,0,z with z = 0.20 and 0.327, Ru (4c) in 0.555, 0.25, 0.247, P in (4e) 0.918, 0.25, 0.728, and O in (4d) at

0.276,0.25,0.255 and 0.637, 0.25, 0.113. Bond valence sum analysis of $LiRuPO_4$, using 25 val, 1.04 vil, and 3.84 μB per Ruthenium ion, providing bond lengths between semiconductor and ligands between 2 and 3 Å.

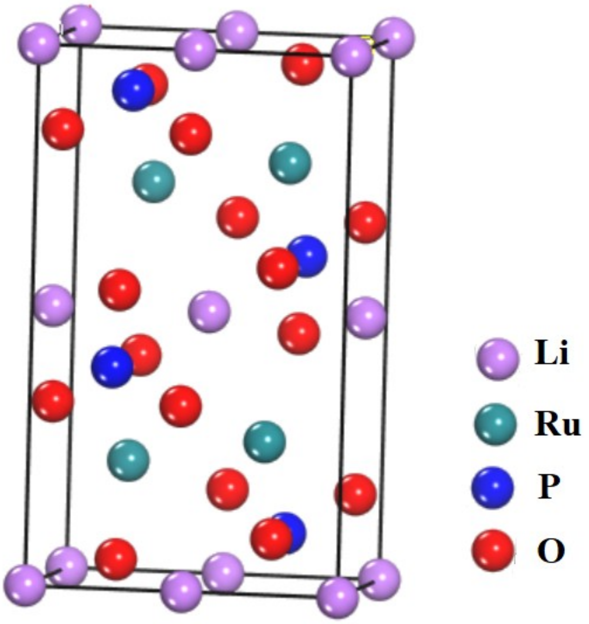

Figure 2. Primitive cell of $LiRuPO_4$ orthorhombic structure Pnma space group (No.62)

Table1. lattice parameter calculated of $LiRuPO_4$ in orthorhombic Pnma space group with using GGA+U (Hubbard correction U = 3.0 eV)

Compound	*Functional*	*Ground state energy (eV)*	*Lattice constants (Å)*	*Bulk modulus B_0(GPa)*
$LiRuPO_4$	GGA +U	-18889,71	a=10,38 b=5,99 c=4,78 V=297,20A°^{3}	236,62

3.3. Electronic properties

3.3.1 Band structures

The band structure of $LiRuPO_4$ has seen little theoretical focus, and that too via an effective one-electron single-electron-electron based theory. Here, using much more robust and rigorous computational quantum physics methods of GGA+U, we present in Figure3 the theoretical results of the band structure curves of LiRuPO4, The fermi level was fixed at 0 and we got indirect energy gap between two points in Brillouin zone, Z and X, the value of this gap is 2,18eV, so that LRP is semiconductor compound.

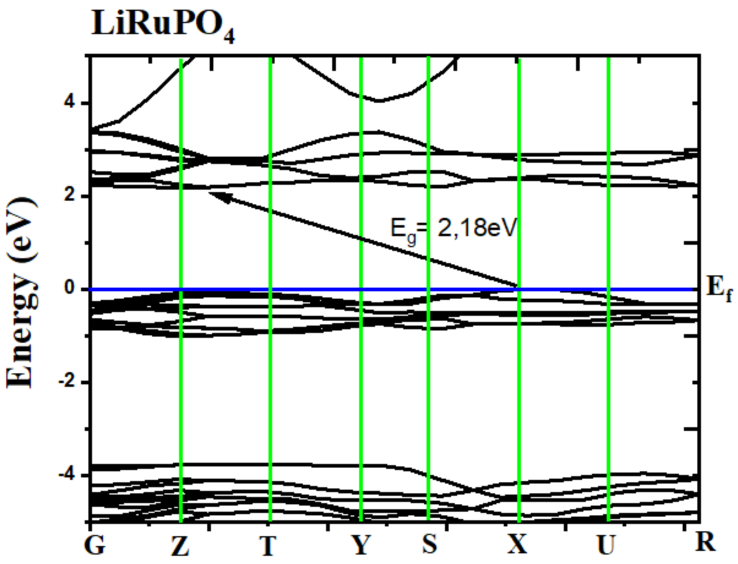

Figure 3. Band structure curve of $LiRuPO_4$ using GGA+U

4. Conclusion

In this study, ab initio calculations based on Density Functional Theory (DFT) were used to examine the thermal stability, structural, and electronic properties of $LiRuPO_4$. The study employed the pseudo-potential plane waves method, using a primitive cell instead of the standard approach. This method determined that the concentration window for the atomic distance of the orthorhombic phase olivine-$LiRuPO_4$ (LRP) was about 0.05–0.1 Å of Li atoms per unit cell of LRP, a finding that is higher than the reported insertion composition of Li for phase transformation of LRP, and has significant implications for the understanding of LRP's behavior. Additionally, the material LRP exhibited semiconductive behavior.

Our ongoing efforts to extend the duration of the two-stage reduction process are nearing completion. The charge-discharge kinetics, primarily influenced by the intercalation reaction of lithium, are a key focus. In future research, we are exploring atomistic modeling of high capacities in both the cathode olivine $LiRuPO_4$ and the anode ternary orthosilicate $Li_{4-\delta}Ru_{1-x}Ti_xPO_4$. This development aims to achieve rapid charging by combining efficient 3D lithium migration with excellent electronic and ionic conductivities. We are also proposing an analytical method for developing high-capacity silicon-based anodes with significantly less experimental screening work. The key parameters relevant to the reversible capacitive energy during the insertion process are under thorough study. After that, we have not forgotten the thermodynamics of the phosphate $Li_{4-\delta}Ru_{1-x}Ti_xPO_4$ olivine in comparison to lithium lithiated phosphate phases and oxide spinel, providing comprehensive insight into the chemical behavior of the metastable phase.

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