Mechanical and electronic properties of $LiTi_2(PO_4)_3$ solid-state electrolyte material.

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$LiTi_2(PO_4)_3$ (LTP) is economically viable, and it is receiving significant research attention as a potential solid-state electrolyte for lithium-ion batteries (LIBs). This is due to its NASICON-type structure built from corner-sharing octahedra (LiO_6, TiO_6) and tetrahedra (PO_4) to form a chemically stable structural framework that facilitates Li^+ transport. Unfortunately, the ionic conductivity ($< 10^{-6}$ S/cm) of lithium ions was found to be insufficient for practical use in LIBs. In this study, the electronic, structural and mechanical properties of LTP are studied for model validation, modelling parameter accuracy and to form a foundation for the partial substitution of oxygen with sulphur. The Vienna Ab Initio Simulation Package (VASP) was used to investigate the ground-state structure of LTP. The electronic inactivity of the material was confirmed by band structure and density of states (DoS) calculations through a band gap of ~2.49 eV comparable to the literature value of 2.38 eV. The Bulk, Young's and shear modulus were found to be 101.01 GPa, 151.78 GPa and 60.74 GPa, respectively. The higher shear moduli (> 8 GPa) indicate that the material can resist the formation of the dendrites against Li metal during operation. These lay a solid foundation for future analysis of the impact of sulphur-doping on the mechanical and electronic properties of LTP to yield insights on improvement of its performance and safety.

1. INTRODUCTION

The rapid growing demand of energy storage systems has led to the eruption of studies focusing on the development of the most productive and safe secondary batteries (lithium-ion batteries) [1]. In 1990, Sony engaged in the commercialisation of lithium-ion batteries for the evolution of the energy storage industry [2]. These secondary batteries used conventional organic liquid electrolytes (LEs), which exhibits low thermal stability and high flammability, leading to thermal runaway and fatal explosions during operation [1, 3]. Consequently, solid electrolytes (SEs) are currently potential substitutes for LEs owing to alleviated hazardous gas production, safety concerns, and their high energy density [3]. The SEs exhibit high mechanical strength, which prevents formation of dendrites' and consequently limiting cyclic performance [4]. The predicted shear modulus for an effective solid electrolyte to prevent dendrite formation, as reported by Monroe and Newman, must be twice as high as that of lithium metal. The standard shear modulus of lithium metal is 3.4 GPa, so the shear modulus of the solid electrolyte must be more than 6.8 GPa [5]. Solid electrolytes can be classified into three categories, namely inorganic solid electrolytes (ISE), polymer solid electrolytes (PSE) and composite solid electrolytes (CSE), with ISEs in the forefront due their high the ionic conductivities of $< 10^{-2}$ $S \bullet cm^{-1}$ [4, 1]. The sodium superionic conductor (NASICON)-type solid electrolytes $LiTi_2(PO_4)_3$ (LTP) have been mostly explored and are regarded as the potential future generation of solid electrolytes due to their compatibility with lithium metal electrodes and structural stability [6]. NASICON-type solid electrolytes adhere to a chemical formula $AM_2(PO_4)_3$ (A = Li, Na; M = Ti, Ge, Zr) and possess a 3D framework comprised of a corner-sharing PO_4 tetrahedra and TiO_6 octahedra, creating channels on the c-axis to facilitate the Li-ion mobility [7]. Its 3D framework portrays a high stability with the Ti^{4+} /Ti^{3+} redox couple to accommodate Li^+ extraction and insertion, which contributes to high ion mobility, and long cycle life [8]. Goodenough and Park have reported that rechargeable batteries with the 30 000 charge/discharge cycle with a decent rate which is equivalent to a 10-year operation life have been obtained. This has mitigated the life cycle issue in the high-performance batteries production industry. Although ISEs demonstrate a very reasonable high ionic conductivity (~10-4 S/cm), the performance of LTP remain inferior to that of ISEs and LEs. This lower ionic conductivity hampers its adoption in commercial

battery industry. . LTP exhibits the total conductivity between 10^{-7} and 10^{-10} units and an activation energy of 0.36 eV [9, 6]. An ideal solid electrolyte must exhibit a wide band gap to inhibit the electronic conduction, to reduce hazardous concerns, and promotes lithium-ion conduction. In addition, the brittle nature of oxides makes it susceptible to mechanical degradation, such as cracking, during electrochemical cycling. These fractures increase interfacial resistance and disrupt lithium-ion pathways thus low ionic conductivity, accelerating the fade over time.

In this study, the Vienna Ab initio simulation package (VASP) [10] has been utilized to study structural and electronic properties of LTP are investigated to validate the viable application of LTP as a solid electrolyte.

2. COMPUTATIONAL METHOD

The Vienna Ab initio simulation package (VASP) [10] implemented in MedeA, was used to execute density functional theory (DFT), computational calculations with projected augmented wave (PAW) pseudo-potentials [11]. The generalised gradient - Perdew, Burke, and Ernzerhof for solid systems (GGA-PBEsol) was used to describe the exchange correlation functional with the simplified LSDA+U approach. The Hubbard U parameter used was 4 eV for Titanium to correct the self-interacting error and improve the description of strongly correlated electron in the d-orbital. The accurate precision for the spin-polarized magnetic calculation was used. Furthermore, the planewave cut-off energy of 650 eV was adopted with the electronic convergence criteria of 10^{-6} eV using the normal (blocked Davidson) algorithm. The real space projection operators. gamma-centred Monkhorst-pack scheme within the Brillouin Zone, K-mesh of 5x5x5. The Gaussian smearing with a width of 0.05 eV was also adopted.

3. RESULTS AND DISCUSSION

3.1 *Thermodynamical and structural properties*

The optimised lattice parameters have been meticulously computed in the VASP code using the GGA-PBEsol. Table 1 below outlines the calculated and experimental values of LTP. The crystal structure of the LTP as reported by Lou et al. [12], is rhombohedral with the space group of R-3c. The calculated lattice parameters are a = b = 8.550 Å and c = 20.770 Å which are comparable with the theoretical values. This validates that our results are accurate. Furthermore, the predicted value of energy of formation was found to be less than zero (exothermic reaction), indicating that LTP is thermodynamically stable. This signifies that the LTP will not chemically react with the electrodes during the charge/discharges process.

Table 1: Lattice parameters and energy of formation of $LiTi_2(PO_4)_3$.

Lattice parameter (Å)	Calculated	Experimental **[13]**	|Δ|(%)
a=b	8.550	8.480	0.82
c	20.770	20.684	0.41
α = β (°)	90.0	90.0	0.00
γ (°)	120.0	120.0	0.00
V (Å3)	1321.60	1288.1	2.53
ΔH_f (kJ/mol)	- 4646,32	-	-

The LTP crystal structure has two different lithium positions, named NI and NII, where the TiO_6 octahedra are aligned along the C-axis with NI sites between two octahedra (sandwich shape). The Li^+ ions preferably occupy the NI which lower energy barriers than the NII [13].

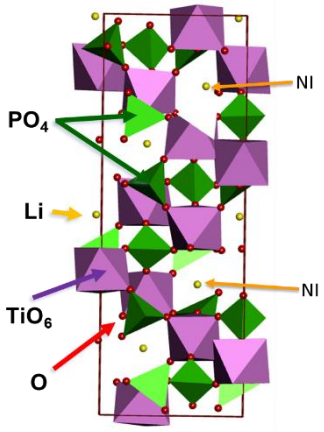

Figure 1: Structural representation of $LiTi_2(PO_4)_3$

3.2. Electronic properties

In this section, observation will be focused on the density of states (DoS) and band structures. This study uses the DoS to validate the electronic properties and the band gap of the LTP. The Partial Density of State (PDOS) shows that titanium has the highest contribution to the overall DOS. Furthermore, Ti exhibits the antiferromagnetic property in figure 2b, signifying that the material's low ionic conductivity is due to the Ti element [14]. DoS shows that the Fermi energy (E_f) lies in the low DoS region, and the broad peak in the valence band shows the vigorous orbital hybridization. As such, this suggest that the LTP exhibits a good stability. The total density of states (TDOS) displayed in Figure 2 (b), shows that the band gap of LTP is ~2.49 eV with a percentage difference of < 5% compared to the experimental value reported by Chen et al [1]. The band structure describes the energy levels the electrons can occupy in LTP, which is efficient for giving a good account of its electronic structure. The energy level is divided and depicted by bands as denoted in Figure 2 (c). The valence band is represented by all the states below the fermi level shown in Figure 2 (c) and the conduction band is given by all the states above the fermi level. The DOS and band structure in figure 2 indicates that LTP is a semiconductor with an indirect band gap of ~2.49 eV, which is essential for preventing short-circuiting during operation.

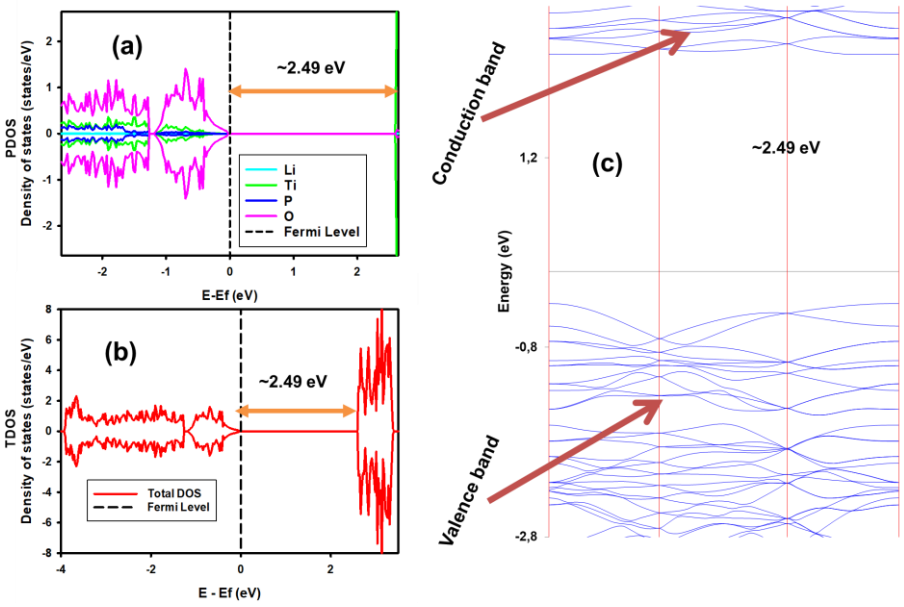

Figure 2: The analysis of a) PDOS,b) TDOS c) band structure $LiTi_2(PO_4)_3$.

3.3 *Mechanical properties*

An understanding of elastic constants gives a full overview of the mechanical stability and the elastic properties of solids. Mechanical stability of the material is usually given by the elastic matrix (commonly called the stiffness matrix) with size of 6X6. This comprises of 21 independent components which consist of several demarcations. The

rhombohedral crystal has seven independent elastic constants C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44}, and C_{66} which follow the Born mechanical stability conditions. This method was discovered by Born, and for a rhombohedral crystal structure to be considered mechanical stable, the following conditions should be met: (1) the matrix C is defined as positive, (2) all eigen values of C are positive, (3) all the leading principal minors of C, (4) an arbitrary set of minors of C are all positive.:

$$C_{11} > |C_{12}| \; ; \; C_{44} > 0 \quad (1)$$

$$C_{13}^2 < \frac{1}{2} C_{33} (C_{11}+C_{12}) \quad (2)$$

$$C_{14}^2 < \frac{1}{2} C_{44} (C_{11}-C_{12}) = C_{44}C_{66} \quad (3)$$

The voigt notation matrix is:

$$\begin{matrix} C11 & C12 & C13 & C14 & 0 & 0 \\ 0 & C11 & C13 & -14 & 0 & 0 \\ 0 & 0 & C33 & 0 & 0 & 0 \\ 0 & 0 & 0 & C44 & 0 & 0 \\ 0 & 0 & 0 & 0 & C44 & C14 \\ 0 & 0 & 0 & 0 & 0 & C66 \end{matrix} \quad (4)$$

The Moduli of the rhombohedral LTP can be obtained from the elastic constants in the following:

$$E = \frac{(C11-C12)(C11C33-C13^2)-C14^2C33}{C11C33-C13^2} \quad (5)$$

$$G = C_{44} \quad (6)$$

$$K = \frac{(C11+C12)C33-2C13^2}{C11+C12+2C33-4C13} \quad (7)$$

$$v = \frac{3B-E}{6B} \quad (8)$$

The shear (G), Young`s (E) and bulk (B) moduli were calculated based on the elastic constants using Voigt-Reuss-Hill approximation method. The Young's modulus determines the stiffness of the material. Shear modulus describes the materials ability to deform under shear stress, whilst the bulk modulus displays the resistance of the material to a volume change under pressure [15]. The shear modulus of an ideal solid electrolyte must be greater than 6.8 GPa for dendrite suppression [5], Young's modulus should be ranging from 10 to 50 GPa to have a well balance interface contact and mechanical strength [16], whilst bulk modulus has to be as high as possible to prevent porosity-induced degradation [5].The calculated Bulk, Young's and shear moduli were found to be 101,01 GPa, 151.78 GPa and 60.74 GPa, respectively. These are in good agreement with the experimental values with < 6%. Moreover, the higher shear moduli (> 8 GPa) indicate that the material can resist the formation of the detrimental dendrites against Li metal during operation.

Table 2: Elastic properties (GPa), Poisson's ratio (v) and Pugh's ratio (K) of $LiTi_2(PO_4)_3$.

Cij	**C_{11}**	**C_{12}**	**C_{13}**	**C_{14}**	**C_{33}**	**C_{44}**	**C_{66}**	***v***	**K**	**C'**	**A**
LTP	221.64	75.64	46.3	-10.2	129.2	67.38	69.29	0.22	1.46	73	0.9230

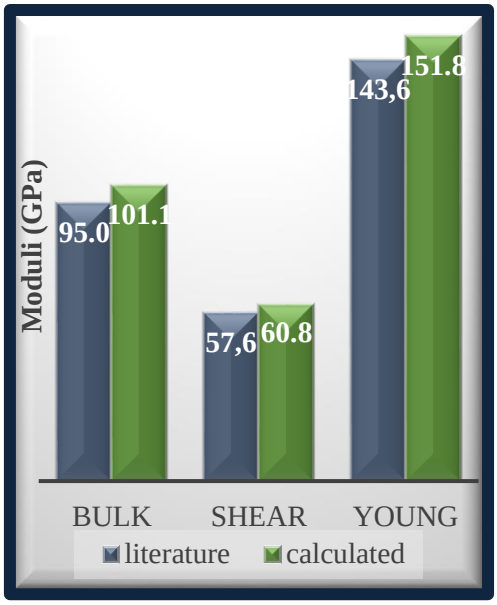

Figure 3: The moduli value of $LiTi_2(PO_4)_3$ [17].

4. CONCLUSION

This study used the computational approach to investigate the electronic, mechanical, structural and thermodynamical properties of $LiTi_2(PO_4)_3$, regarding its potential for a successful implementation in battery storage industry as a solid electrolyte. The electrical properties display a band gap of ~ 2.49 eV, which is imperative for application as SSE in LIBs. This will resist electronic conduction between electrodes through the electrolyte. Then, only focus on the ion transportation. Its antiferromagnetic nature can be improved by cation doping. Even though the Born elastic stability condition is satisfied, the LTP is brittle, which justifies its fragmentation and cracking during the charge/discharge process due to the volume change. This can be mitigated by the partial oxygen substitution by the sulphur. This is motivated by the contribution of sulphur in the lithium sulphur batteries. The shear modulus justifies the ability of the material to prevent the dendrite formation. The structural and the thermodynamical properties reported justify the stability of LTP. The study shows the good attributes of LTP as the SE.

5. ACKNOWLEDGEMENTS

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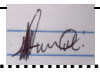
Student Name & Surname: Gift Matleke **Signature:**  **Date:** 31-07-25

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