

CALCULATION OF ELECTRONIC PROPERTIES OF M (M=Zr, Nb)-DOPED Li₄Ti₅O₁₂ BATTERY MATERIALS

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The results of calculations using density functional theory (DFT) of the crystal structure and electronic properties of supercells of two modifications of materials for batteries: Li_{4-x}M_xTi₅O₁₂ and Li₄Ti_{5-x}M_xO₁₂ (M=Zr, Nb) are presented. It has been shown that doping with Zr and Nb has a noticeable effect on the band gap of Li₄Ti₅O₁₂. As a result of Zr and Nb-doping, the Fermi level of the band structure of the Li_{4-x}M_xTi₅O₁₂ and Li₄Ti_{5-x}M_xO₁₂ supercells is tuned to the conduction band. Compared with undoped Li₄Ti₅O₁₂ structures narrow the band gap of Zr and Nb-doped Li₄Ti₅O₁₂, which can improve the electrical conductivity of the material.

Keywords: battery materials, Li₄Ti₅O₁₂, monoclinic and cubic structure, band structure, electronic properties, Zr, Nb-doped, DFT.

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INTRODUCTION

Rechargeable lithium-ion batteries are gaining significant interest as a promising alternative energy storage system. They offer high energy density and long cycle life, making them suitable for a wide range of applications such as portable electric devices and electric vehicles [1-5]. The power capability of lithium-ion batteries depends on the migration rate of lithium ions and electrons through the electrolyte between the two electrodes. To produce high-power Li-ion batteries, materials with high conductivity for electrons and perfect nanostructures that shorten the diffusion length of lithium ions need to be developed. Graphite-based carbon and lithium titanate are commonly used as anode materials, with graphene being the most widely used. Graphene not only accelerates lithium-ion transport but also provides more active sites for lithium ions, effectively reducing energy loss caused by battery polarization and improving battery life when compared to traditional graphite anode materials [6]. Lithium titanate Li₄Ti₅O₁₂ (LTO) has attracted attention from researchers due to its potential use in compact thin-film batteries with high stability. It has been observed that lithium is located in both octahedral and tetrahedral positions in the spinel-structured material [7].

The main objective of this article is to study the effect of Zr and Nb doping on the structural stability and electronic properties of with a monoclinic and cubic structure Li₄Ti₅O₁₂ (m-LTO and c-LTO) using ab initio calculations based on the DFT. Below we will consider the properties of partial substitution of lithium in modifications m-LTO with Zr→Li or Nb→Li atoms and c-LTO with Zr→Li or Nb→Li atoms.

COMPUTATIONAL DETAILS

First-principles calculations of the properties of supercells based on (Zr or Nb) monoclinic and cubic

modification were carried out on the basis of density functional theory (DFT) [8,9]. The presence of M (Zr, Nb) doping components LTO in the lattice leads to spin-orbit coupling in the electronic structure of LTO-M. The band gap (E_g) of based on monoclinic and cubic modification was calculated taking into account the local spin density approximation and spin generalized gradient approximation method, respectively. The kinetic cut-off energy was 150 Ry. The primitive cell of Li₄Ti₅O₁₂ was relaxed and optimized with force and stress tolerances of 0.01eV/Å and 0.01eV/Å³, respectively. A 2x2x2 k point was used for geometry optimization and total energy calculations.

RESULT AND DISCUSSION

Spinel Li₄Ti₅O₁₂ is a significant member of the solid solution family, Li_{3+x}Ti_{6-x}O₁₂ where 0 ≤ x ≤ 1 [10]. Its existence was first reported by Jonker in 1956 [11]. Materials with a spinel structure are denoted by the chemical formula of AB₂O₄. In this structure, oxygen ions (32e) form a cubic-close-packed (ccp) array, and the interstices are partially occupied by the A and B cations with tetrahedrally (8a, 8b, 48c) and octahedrally (16c, 16d) coordinated. Li_{3+x}Ti_{6-x}O₁₂ attracted early interest due to its superconductivity at low temperatures. Specifically, Li₄Ti₅O₁₂, which represents one extreme of Li_{3+x}Ti_{6-x}O₁₂ (for x = 1), exhibits semiconductor behavior down to liquid helium temperatures [11]. Notably, Murphy et al. reported the capability of Li₄Ti₅O₁₂ for lithium intercalation [12]. In this study, the electronic band structure and density of state for the Li₄Ti₅O₁₂ compound according to two different symmetry groups were investigated. Here, the physical properties were calculated using the Atomistic Simulation Software QuantumATK in accordance with the Li₄Ti₅O₁₂ C2/C base centered monoclinic group symmetry. To simplify, I will label this type structure as m-Li₄Ti₅O₁₂. The lattice parameter

$a=8.35\text{\AA}$, $b=8.32\text{\AA}$, $c=13.17\text{\AA}$. $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ was selected as $Fd\bar{3}m$ face-centered cubic space group symmetry and lattice parameters $a = 8.4\text{\AA}$.

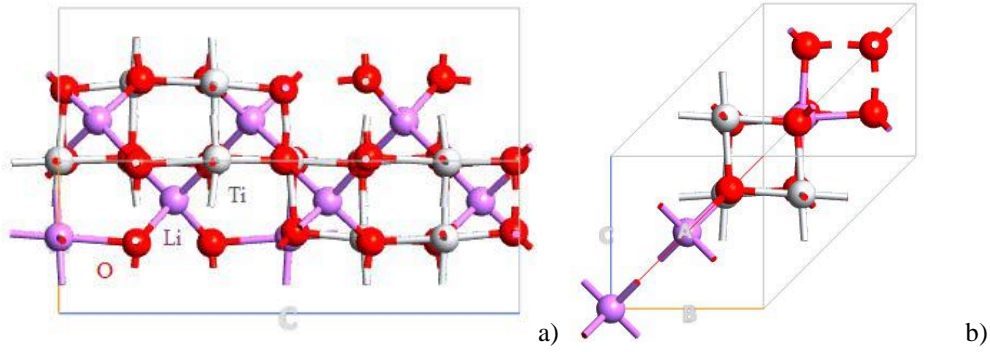


Fig. 1: Atomic structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ a) monoclinic b) cubic modification

The atomic structure of two modification of LTO is displayed in Figure 1. The influence of Zr and Nb doping on the electronic structure of lithium titanate materials was investigated by analyzing the density of states (DOS and PDOS) (Figure 3) using DFT. As presented in Figure 2c, the obtained band structure of $m\text{-Li}_4\text{Ti}_5\text{O}_{12}$ reveals a band gap of approximately 2.59eV at the symmetric point G. Previous study has reported band gap value for $m\text{-Li}_4\text{Ti}_5\text{O}_{12}$ 2.52eV [13]. Using the DFT SGGG method, our calculated band structure of $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ presents a band gap of 2.337eV (Fig.2a). The calculated $E_g = 3.56\text{eV}$ (Fig.2b)

presented that $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ is an insulator with band gap determined by the occupied O-2p states and empty Ti-3d states. The band gap of $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ as a function Hubbard_U (SGGA+U) at $U=4\text{eV}$ are closed to the experimental result [14].

In the electronic structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the valence band is primarily composed of O 2p states, while the conduction band is dominated by Ti 3d states. The overlapping of Ti 3d and O 2p states in their respective electron density of states indicates a strong O-Ti interaction facilitated by the by TiO_6 octahedron [15].

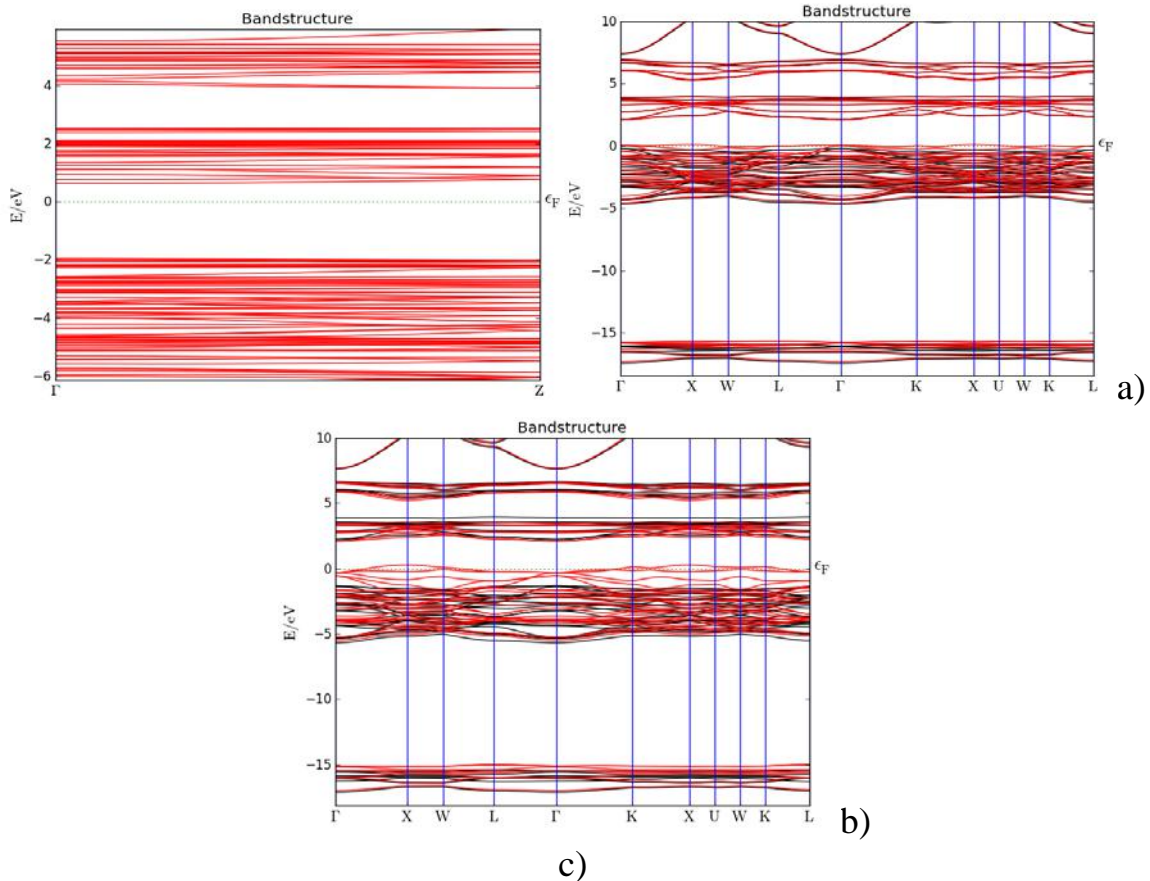


Fig. 2: Band structure of a) $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ and b) $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ with Hubbard_U ($U = 4\text{eV}$, O-2p, Ti-3d) c) $m\text{-Li}_4\text{Ti}_5\text{O}_{12}$.

Table:

Calculated band gap of two supercell structures of Zr and Nb-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$

Zr and Nb-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$	Band structure	
	monoclinic modification	cubic modification
$\text{Li}_4\text{Ti}_5\text{O}_{12}$	$E_g=2.59\text{eV}$	$E_{g\uparrow}=2.337\text{eV}$, $E_{g\downarrow}=2.19\text{eV}$
$\text{Li}_4\text{Ti}_5\text{O}_{12}$ with Hubbard_U (U=4eV, O-2p, Ti-3d)		$E_{g\uparrow}=3.56\text{eV}$, $E_{g\downarrow}=2.4\text{eV}$
Nb(Li) doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$	$E_{g\downarrow}=0.15\text{eV}$, $E_{g\uparrow}=0.215\text{eV}$	$E_g=2.087\text{eV}$
Zr(Li) doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$	$E_g=0.113\text{eV}$	$E_{g\downarrow}=1.952\text{eV}$, $E_{g\uparrow}=2.68\text{eV}$
Nb(Li) doped conventional $\text{Li}_4\text{Ti}_5\text{O}_{12}$ supercell	$E_g=0.207\text{eV}$	
Zr(Li) doped conventional $\text{Li}_4\text{Ti}_5\text{O}_{12}$ supercell	$E_g=0.188\text{eV}$	

Nevertheless, upon Nb and Zr doped, the Fermi level of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and conventional $\text{Li}_4\text{Ti}_5\text{O}_{12}$ supercell shifted to the conduction band. The tail of the conduction band was placed below the Fermi level

and became partially filled, as presented in Figure 2. Additionally, the band gap between the valence band and the conduction band was also narrowed and was described all of result in table.

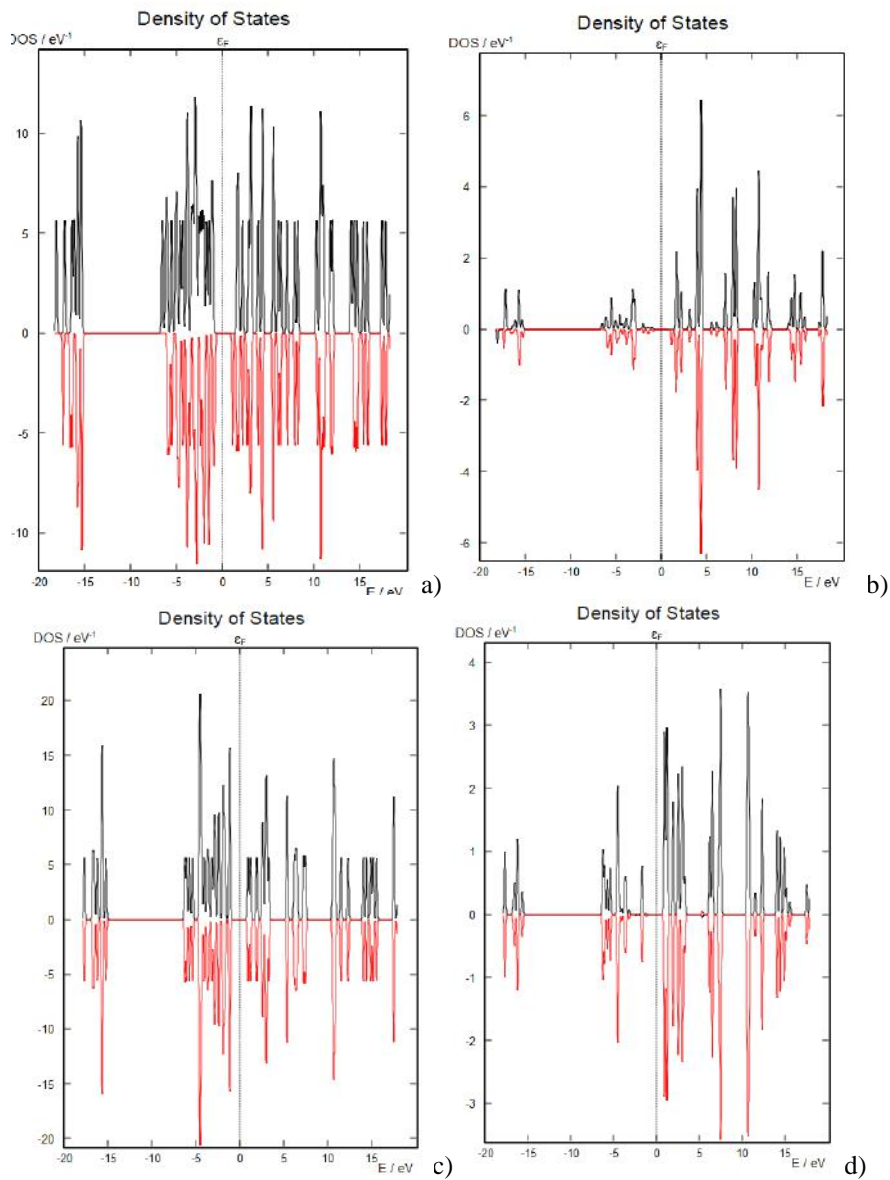


Fig. 3: DOS and PDOS of a), b) Zr-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for cubic modification and c), d) Nb doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for cubic modification.

CONCLUSION

DFT calculations (DFT LSDA, SGGA and DFT GGA+U) were carried out for two supercells of battery anode materials based on the monoclinic $m\text{-Li}_4\text{Ti}_5\text{O}_{12}$ and cubic $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ structure. Zr and Nb-doping allows you to tune the density of localized electrons in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystal, which leads to a shift in the Fermi level and narrowing of the band gap. The contribution of the 4d orbitals of Zr and Nb atoms to the exchange energy in the cubic structure of $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ is confirmed by the change in PDOS and DOS in Zr and Nb-doped $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$ structures. Zr and Nb-doping of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystals noticeably

narrows the band gap of $c\text{-Li}_4\text{Ti}_5\text{O}_{12}$: $E_{g\uparrow} = 2.337$ eV, $E_{g\downarrow} = 2.19$ eV (pure $c\text{-LTO}$) and $E_{g\uparrow} = 3.56$ eV, $E_{g\downarrow} = 2.4$ eV ($c\text{-LTO}$ with Hubbard_U ($U = 4$ eV, O-2p, Ti-3d)) up to $E_g = 2.087$ eV (for $c\text{-LTO-Nb}$), up to $E_{g\downarrow} = 1.952$ eV, $E_{g\uparrow} = 2.68$ eV (for $c\text{-LTO-Zr}$). Thus, doping monoclinic and cubic $\text{Li}_4\text{Ti}_5\text{O}_{12}$ structures increases electronic and lithium-ion conductivity, which is important for anode materials. The results of DFT calculations it follows that Zr and Nb-doping of cubic and monoclinic structure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ crystals enhances electron transfer. This is important for solid battery electrodes and can be used to control the properties and structure of solid-state lithium-ion battery materials.

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