

A DFT STUDY OF Li IN $H_2Ti_3O_7$ “BULK”: INTERCALATION AND THERMODYNAMIC PROPERTIES



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Abstract

A Li intercalated in $H_2Ti_3O_7$ bulk theoretical study was performed. The electronic, thermodynamic and diffusion properties of the doped and pure systems were performed. The Density Functional Theory (DFT) based calculations were performed with the VASP software¹. The Hubbard parameter was included in order to take into account the Ti transition metal effect. Three different intercalation sites were tested, and the stability of each site was studied. Afterwards, the densities of states were calculated, and showed a shift of the doped systems and the presence of a magnetic moment. The Bader² method was applied to study the charge transfer, finding a transfer of the electron to the titanate. Moreover, vibrational calculations were performed in order to obtain the phononic densities of states and the thermodynamic properties with the implementation of Phonopy³. In order to do this, we checked that no extra imaginary frequency vibrational mode was present, which also showed the stability of the studied systems. Thermodynamically, the doped systems presented to be more stable. MLFF-AIMD calculations were performed to confirm the stability of the systems with temperature. The NEB⁴ methodology was applied to find the energetic barriers of the Li intercalated system. A direction of preference for diffusion was found, with an energy barrier of 0.33 eV, which is more favorable than the second barrier, which was 1.75 eV. Therefore, these results show promising aspects of this candidate material as an anode, which can be studied more in future theoretical and experimental studies.

Computational Method

- The DFT calculations were implemented with the VASP software.
- GGA-PBE. Hubbard $U_{ef} = 5$ eV, for Ti.
- 500 eV of cutoff energy.
- KPOINTS 4x4x4 Monkhorst-Pack grid.
- Selected criteria of energy and forces convergence: 1×10^{-4} eV and 1×10^{-2} eV/Å.
- The intercalation voltages were calculations according to:

$$V = \frac{E(Li_xA) - E(A) - xE(Li_s)}{Fx}$$

- Thermodynamic parameters for the calculations:
 $T = 0$ K to $T = 1000$ K
 Vol. variation: -7%, 3.5%, 0%, 3.5%, 7%.

Computational Model

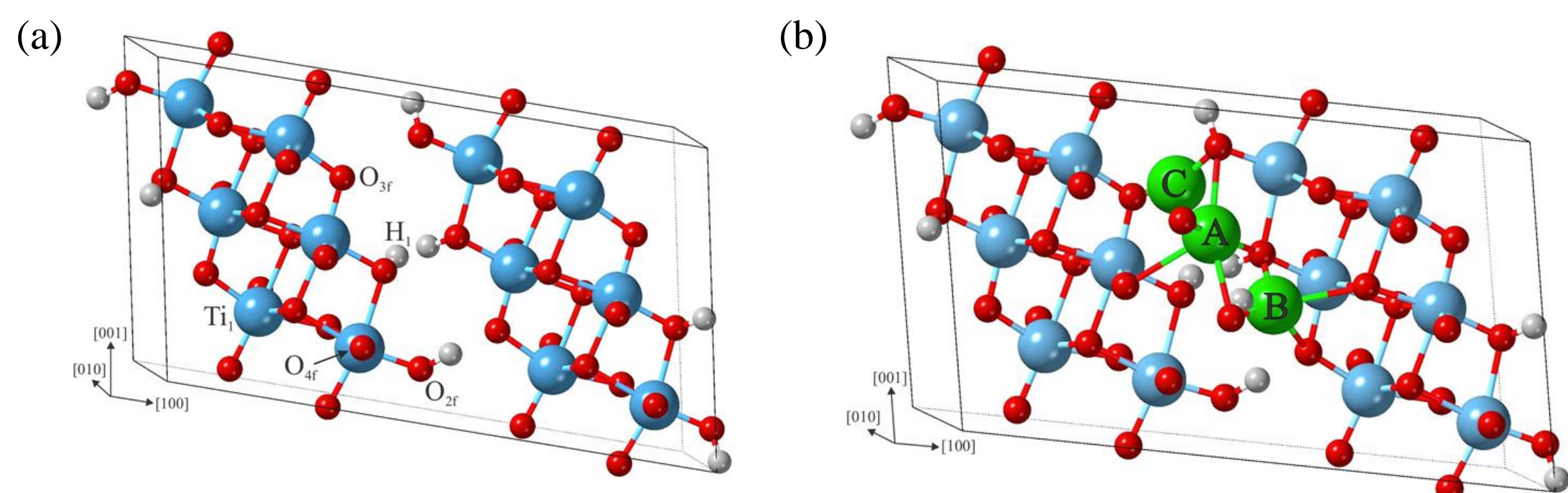


Fig. 1. Schematic view: (a) unit cell of $H_2Ti_3O_7$ and (b) intercalation sites (A, B, C) in “bulk”. The light grey, light blue, red and green spheres represent H, Ti, O and Li atoms, respectively.

Intercalation Sites

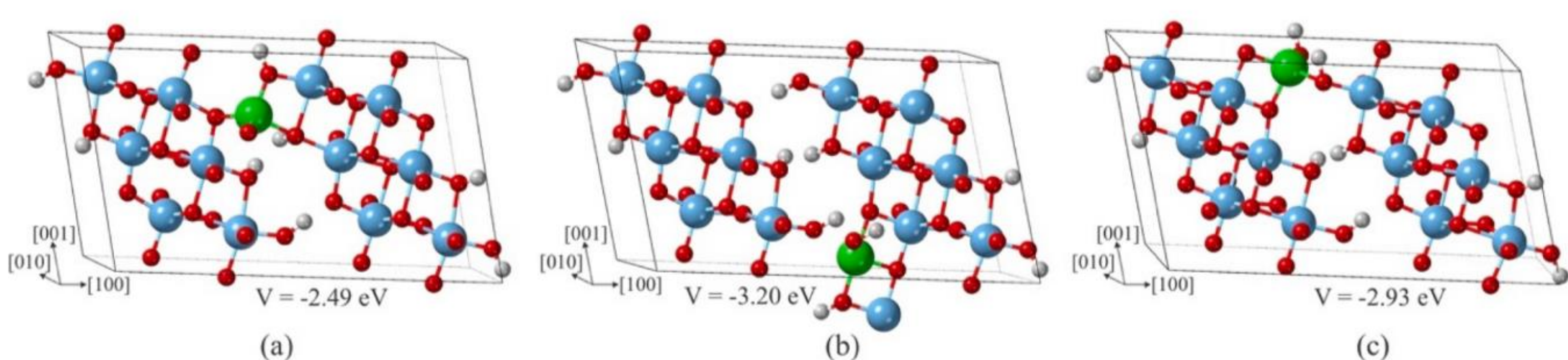


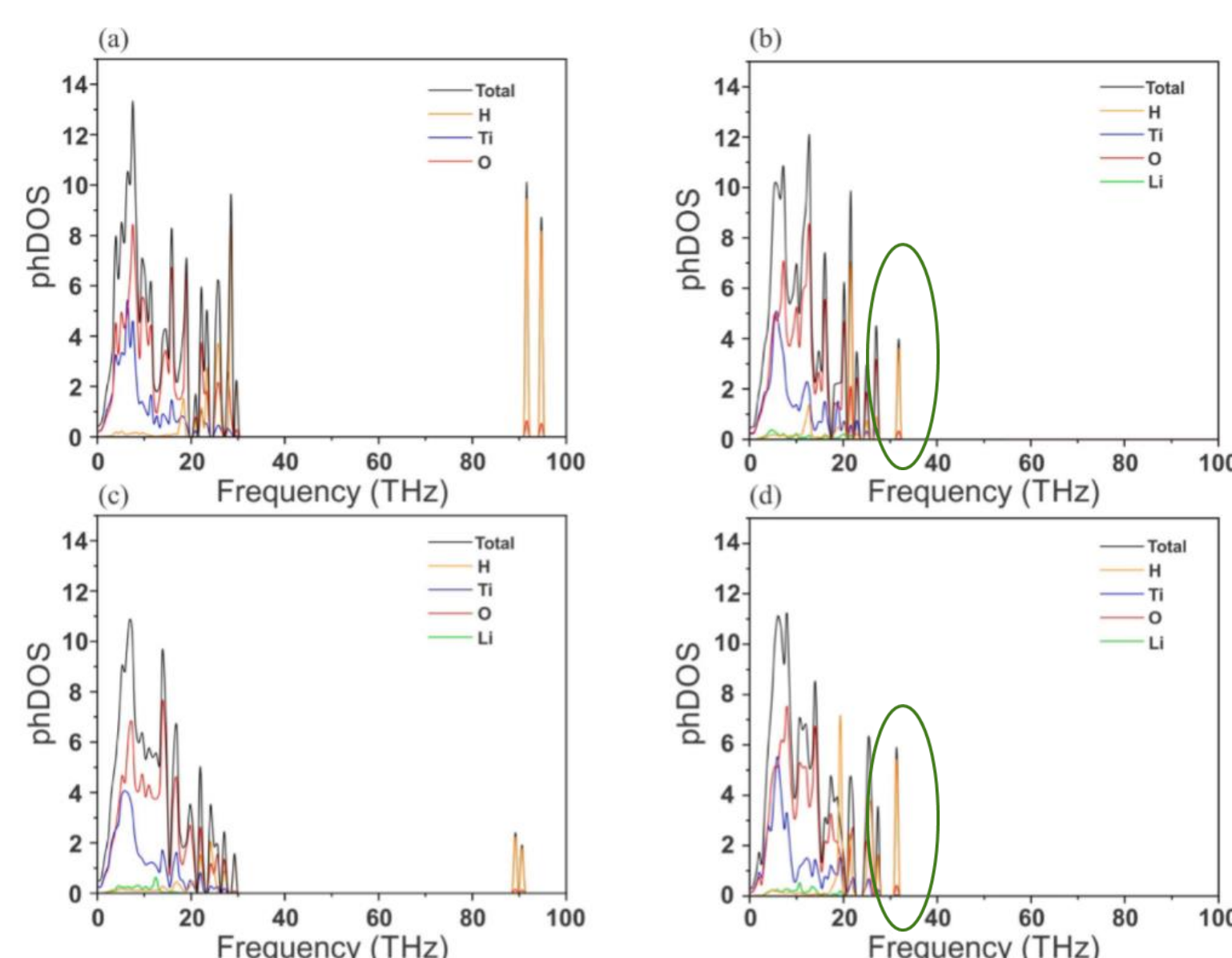
Fig. 2. Schematic view of the stable intercalated systems after the relaxation together with their intercalation voltages: (a) Li intercalated in site A, (b) Li intercalated in site B, (c) Li intercalated in site C.

- Intercalation voltages: C and A sites are less energetically favourable than site B (8 % and 12 %, resp.).
- A charge transfer of 0.6e, 0.7e and 0.7e from the Li atom to the structure in site A, B and C, respectively, was found via the Bader method.

Phononic density of states (pDOS)

- Obtaining and visualizing vibrational modes. Extra optimization step.
- There are no negative vib. – Very stable systems.
- O and H peaks interactions.
- Most important contributions are from O.
- At Sites A and C, the O and H peaks are coupled.
- Localization of Li – Low Frec.

Fig. 3. Phononic densities of states for $H_2Ti_3O_7$: (a) “bulk”; (b) Li at site A, (c) Li at site B and (d) Li at site C. The black line is the total DOS, and the projected DOS for H 1s, Ti 3d, O 2p y Li 2s are the orange, blue, red and green lines, respectively.



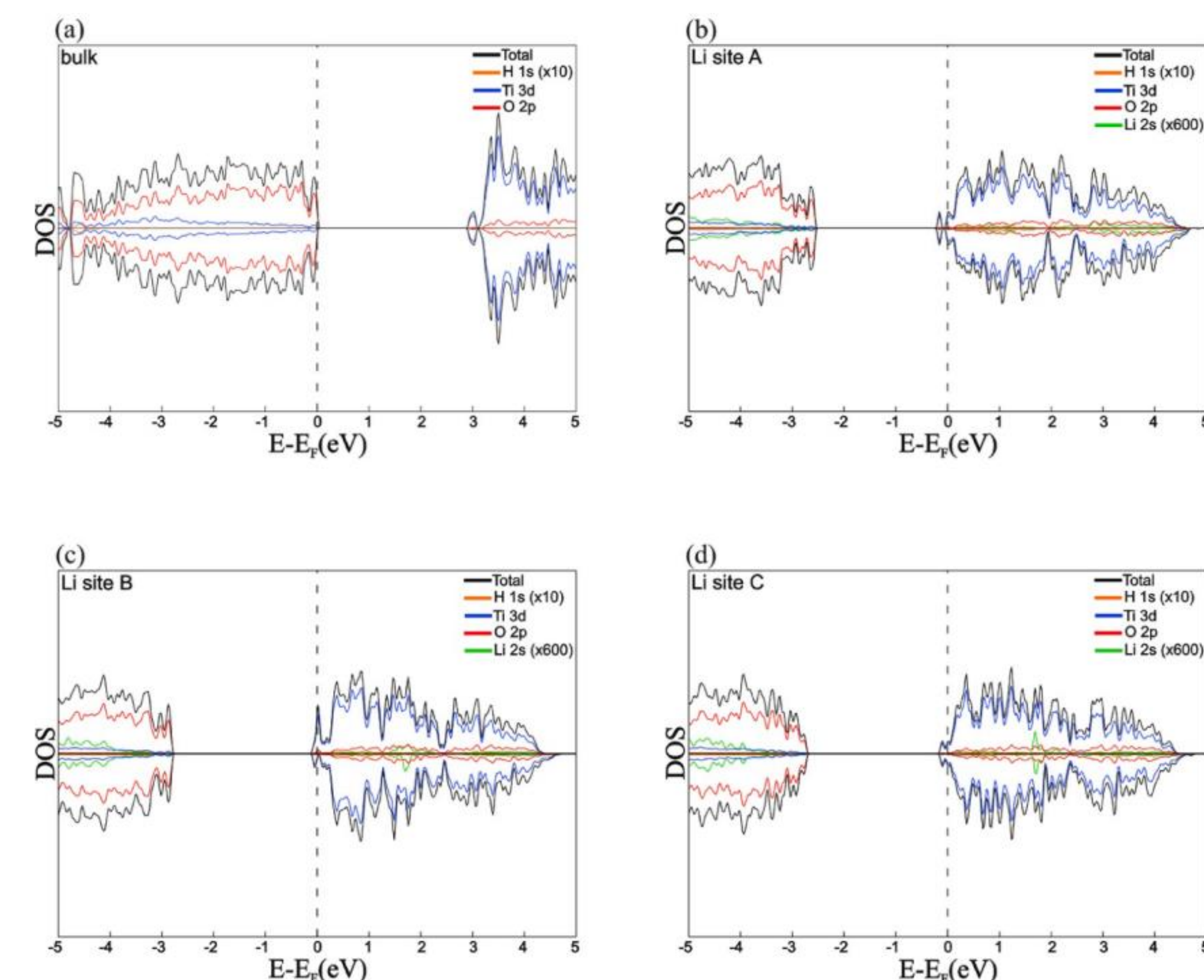
Conclusions

- Three stable intercalation sites were found, with relevant voltages, being Site B the one with the highest voltage.
- The DOS have a very similar behavior with other Li-doped titanates. There is a presence of defect states in the E_F and an induced magnetic moment. There is a displacement of the valence band.
- The phononic study shows the predominance of H and O in high frequencies for the B site.
- The NEB studies indicate a diffusion preference in the [010] direction, with a lower barrier of 0.33 eV in comparison to the 1.75 eV barrier in the less favourable.

Electronic structure

- Asymmetric contribution in the DOS.
- O 2p – VB, Ti 3d – CB.
- Defective states – E_F .
- DOS displacements of the doped systems towards more negative energies.
- Similar to $TiO_2(B)$.

Fig. 4. DOS curves for $H_2Ti_3O_7$: (a) “bulk”, Li in site (b) A, (c) B and (d) C. The black line is the DOS total, meanwhile the projected DOS H 1s, Ti 3d, O 2p and Li 2s are the orange, blue, red and green lines, respectively. The dotted lines in zero correspond to the Fermi level.



Thermodynamic properties

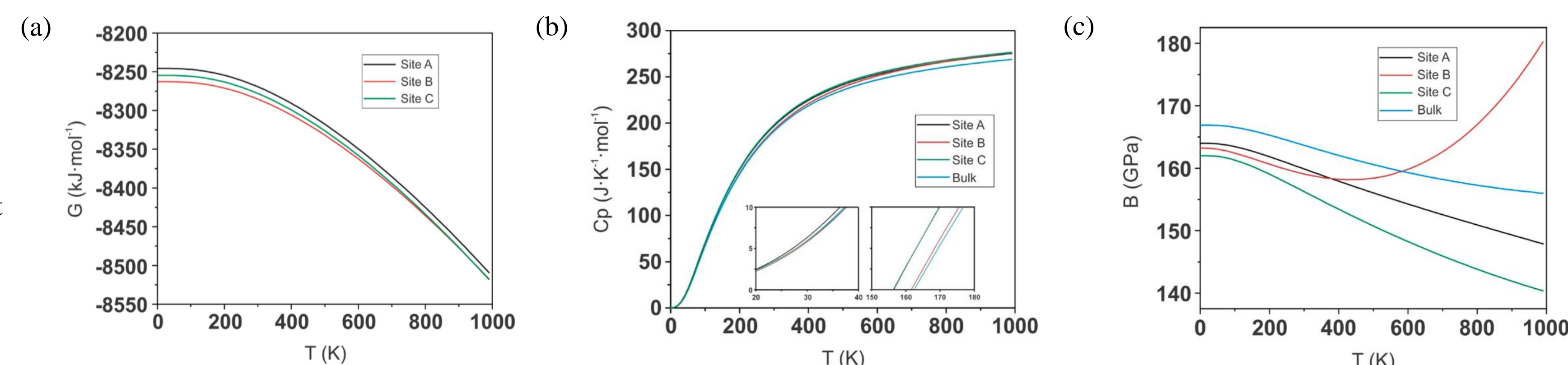


Fig. 5. (a) Gibbs free energy versus temperature for the doped systems. (b) C_p versus temperature for the “bulk” of $H_2Ti_3O_7$ and the doped systems with Li. Inserts: a magnified view of the transition between the curves C and “bulk” (left) and the curves C and A (right) and (c) Bulk modulus (B) versus temperature for the $H_2Ti_3O_7$ “bulk” and the doped systems are shown.

- The B site is the most stable at 960 K. This tendency is according to the voltages. The C site is in second place. In magnitude, similar to $Na_2Ti_3O_7$, of Holzinger et al. (J. Chem. Therm 35 (2003) 1469).
- Without anomalies in C_p . The C site has the highest value since 160 K, overcoming A. Similar to Holzinger et al.
- B at 0 K is 167 GPa, similar to sodium titanate (190 GPa), with decrease with temperature. (Holzinger et al.). The C site is the most compressible.

Diffusion Paths (NEB)

- In Path (I), the Li diffusion throughout the [010] direction was studied.
- For the Path (II), the Li diffusion throughout the [001] direction was studied.
- The total energy barriers were: 0.33 eV and 1.75 eV for [010] and [001], respectively.
- In $Na_2Ti_6O_{13}$ and $Li_2Ti_6O_{13}$ it is of 0.39 eV and 0.25 eV for [010] and [001], respectively. Zulueta et al. J. Solid. Sta. Chem. 279 (2019) 120930 and Kuganathan et al. Materials 12 (2019) 251.
- Presence of H atoms in the tunnels in the [001] direction.
- MLFF-AIMD for $t = 35$ ps and 800 K confirm the stability of the Li selected sites by seeing the evolution of the evolution, and the temperature and kinetic energy evolution.

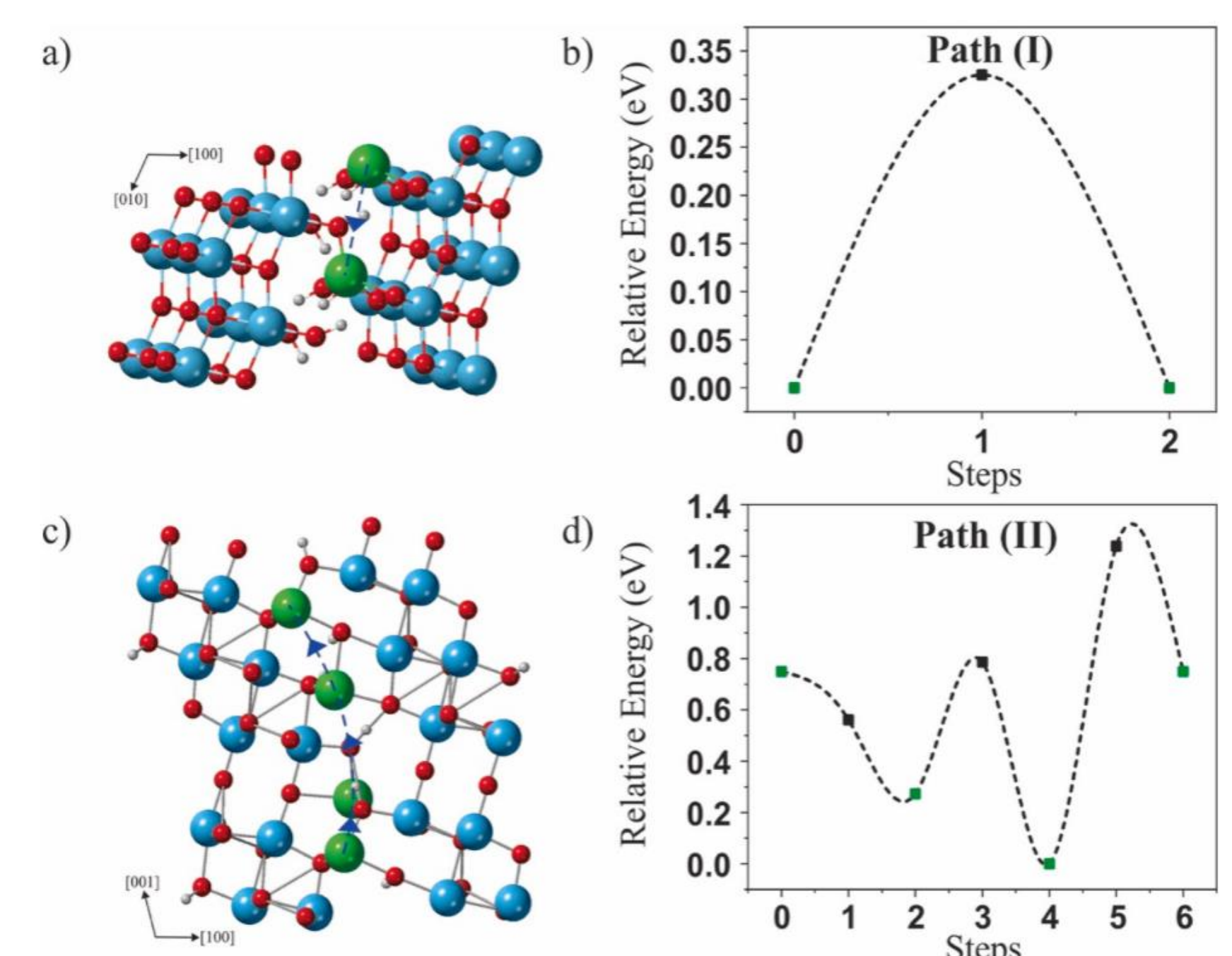


Fig. 6. Diffusion paths of Li in the “bulk” of $H_2Ti_3O_7$: schematic views of (a) Path (I) and (c) Path (II). The relative energy versus diffusion steps graphs for the Paths (I) and Path (II) are shown in (b) and (d), respectively; where the green dots indicate the intercalation sites of Li.

References

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