Lithium Hexastannate: A Potential Material for Energy Storage

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The prediction of a new lithium compound, $\text{Li}_2\text{Sn}_6\text{O}_{13}$, is made from a combined first-principles and classical force-field approach. The electronic, structural, and mechanical properties of monoclinic Li_2SnO_3 , $\text{Li}_2\text{Ti}_6\text{O}_{13}$, and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ are explored. The calculated results for the equilibrium lattice parameters are in agreement with the available experimental data. The thermodynamic stabilities of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ are evaluated. Both compounds are demonstrated to be thermodynamically stable with standard molar formation enthalpies of -5553 and $-6740 \text{ kJ mol}^{-1}$, respectively. Reaction energies for delithiation of 6.41 and $6.90 \text{ eV atom}^{-1}$ are also determined for $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$, respectively. The predicted voltage of Li insertion/extraction process per Li^+/Li is 1.6 V for $\text{Li}_2\text{Sn}_6\text{O}_{13}$, comparable to its isostructural counterpart $\text{Li}_2\text{Ti}_6\text{O}_{13}$. Electronic band structure calculations indicate the insulating character of Li_2SnO_3 with an indirect band gap of 4.4 eV , whereas both $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ appear to be semiconductor compounds with band gaps of 3.1 and 3.0 eV , respectively. The energy barriers for Li^+ migration amount to $\approx 0.5 \text{ eV}$ for both materials. Elastic stiffness coefficients and bulk, shear and Young's moduli were also calculated. The $\text{Li}_2\text{Sn}_6\text{O}_{13}$ derivative is mechanically stable and can be predicted to be a brittle compound that is more resistant to volume change than $\text{Li}_2\text{Ti}_6\text{O}_{13}$. If the $\text{Li}_2\text{Sn}_6\text{O}_{13}$ compound could experimentally be prepared by using ion exchange, it could potentially be an efficient material for anodes in lithium-ion batteries.

1. Introduction

Alkali-metal hexatitanates with a tunnel structure ($\text{A}_2\text{Ti}_6\text{O}_{13}$, $\text{A} = \text{Na}^+$, K^+ , or Li^+) exhibit large specific surface areas and structural anisotropy.^[1–3] Of the possible technological applications, these compounds could be used as anodes in the field of high performance batteries, which is a continuing focus of significant attention.^[4–6] These compounds have the appropriate structural type for this purpose.

These structures contain a one-dimensional (1D) tunnel space within their lattice structure, favoring fast Li^+ -ion conduction.^[5–7] Zhang and coworkers studied the structure and photocatalytic and electrochemical properties of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ nanobelts prepared from $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanobelts as a template (parent) structure via a Li^+/Na^+ ion-exchange method.^[8] Their results revealed that $\text{Li}_2\text{Ti}_6\text{O}_{13}$ exhibits higher photocatalytic efficiency than $\text{Na}_2\text{Ti}_6\text{O}_{13}$, attributed to the expansion of tunnel space in the former structure compared to $\text{Na}_2\text{Ti}_6\text{O}_{13}$ nanobelts. The expansion of the tunnel space was also previously reported in Refs. [9–11]. This expansion is ascribed to the change of coordination of lithium into a LiO_4 planar hybridization instead of the

NaO_8 coordination existing in $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Density functional theory (DFT) confirmed the LiO_4 planar coordination in this material.^[9]

Recently, we developed a transferable force field for classical simulations to model the bulk properties of different lithium-based materials, such as Li_2MO_3 , where $\text{M} = \text{Sn}^{4+}$, Si^{4+} , and Ti^{4+} .^[12] These compounds have similar technological applications to $\text{Li}_2\text{Ti}_6\text{O}_{13}$ as a result of their fast ion conduction. The transferability of this new force field has been successfully verified by testing the structural and mechanical properties of monoclinic $\text{Li}_2\text{Si}_2\text{O}_5$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ compounds. The experimental properties of these materials were well reproduced by the theoretical simulations.^[12]

In this context, we have extensively applied this simulation approach in the search for new compounds featuring better properties for ionic conduction. Our calculated results predict that lithium hexastannate ($\text{Li}_2\text{Sn}_6\text{O}_{13}$) may be appropriate for this purpose. In addition, monoclinic $\text{Li}_2\text{Sn}_6\text{O}_{13}$ could also be experimentally prepared via the $\text{Ti}^{4+}/\text{Sn}^{4+}$ ion-exchange method from the known $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structure.

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In this study, we report predicted results for the stannate derivative with the hope that it could stimulate further experimental research. We report not only the structural, mechanical, thermomechanical stability and electronic properties of monoclinic $\text{Li}_2\text{Sn}_6\text{O}_{13}$ via empirical force-field calculations, but also those obtained using DFT methods as a further verification of the force-field-based results.

2. Results and Discussion

2.1. Methods and Structures

For comparative purposes, we consider the known compounds, Li_2SnO_3 and $\text{Li}_2\text{Ti}_6\text{O}_{13}$, together with the new compound, $\text{Li}_2\text{Sn}_6\text{O}_{13}$. Structural, electronic and mechanical properties are obtained by using two sets of computations.

We first use classical simulations based on the force-field approach for an extensive search of compounds with interesting and related properties. DFT computations are carried out as a necessary confirmation of the properties revealed by the force-field method. This provides us with a further validation and transferability of the force field in determining the physicochemical properties of these types of compounds. For the classical simulations, the same setup and transferable force field reported in Ref. [12] are adopted. DFT calculations are carried out with the aid of the CASTEP code.[13] We employ various exchange-correlation functionals including the Perdew, Burke and Ernzerhof (PBE), Revised Perdew, Burke and Ernzerhof (RPBE), Perdew-Wang (PW91) and PBE with Wu-Cohen (WC) functionals over the generalized gradient approximation (GGA).[14–17] The pseudo atomic functions for $\text{Li-}2s^1$, $\text{O-}2s^2\ 2p^4$, $\text{Ti-}4s^2\ 3d^2$, and $\text{Sn-}5s^2\ 5p^2$ in their reciprocal representations are used. A plane wave cut-off energy of 550 eV is adopted for the standard norm-conserving pseudopotentials. The choice of convergence threshold criteria is taken with a total energy change of $5 \times 10^{-6} \text{ eV/atom}^{-1}$ and maximum force, stress and atomic displacements of $10^{-2} \text{ eV/\AA}^{-1}$, $2 \times 10^{-2} \text{ GPa}$, and $5 \times 10^{-4} \text{ \AA}$, respectively. A custom k-point grid of $6 \times 6 \times 2$ for $\text{Li}_2\text{M}_6\text{O}_{13}$ ($\text{M} = \text{Ti}^{4+}$ and Sn^{4+}) and $5 \times 5 \times 2$ for Li_2SnO_3 is used to calculate the total and projected density of states in their primitive representation. A Γ -centered Monkhorst-Pack scheme[18] was used during the geometry optimization and elastic constant calculations.

We first explore the lattice parameters of these compounds. Monoclinic Li_2SnO_3 ($C2/c$) consists of layers of $[\text{SnO}_6]$ combined with lithium ions forming planes without hybridization. In the conventional representation, two $[\text{SnO}_6]$ layers are connected with three lithium planes. The reported lattice parameters of $a = 5.2889 \text{ \AA}$, $b = 9.1872 \text{ \AA}$, $c = 10.026 \text{ \AA}$, and $\beta = 100.348^\circ$ are derived at 1000°C . [19,20]

Figure 1 displays the structure of the $\text{Li}_2\text{Sn}_6\text{O}_{13}$, adopted from the lattice structure of $\text{Li}_2\text{Ti}_6\text{O}_{13}$, with Ti^{4+} replaced by Sn^{4+} (see Figure 2). Monoclinic $\text{Li}_2\text{Sn}_6\text{O}_{13}$ could be synthesized by a doubly ion-exchange method as follows:

Figure 1. Conventional (a) and primitive (b) cells of $\text{Li}_2\text{M}_6\text{O}_{13}$ in the $C2/m$ space group.

Figure 2. Schematic representation of $\text{Ti}^{4+}/\text{Sn}^{4+}$ ion exchange to form the $\text{Li}_2\text{Sn}_6\text{O}_{13}$ from $\text{Li}_2\text{Ti}_6\text{O}_{13}$. Grey, dark grey, red and blue balls represent Ti^{4+} , Sn^{4+} , O^{2-} , and Li^{+} ions, respectively.

where $\text{Li}_2\text{Ti}_6\text{O}_{13}$ is an intermediate product of the Na^+/Li^+ ion exchange reaction to obtain $\text{Li}_2\text{Sn}_6\text{O}_{13}$.

The starting lattice parameters of $\text{Li}_2\text{Sn}_6\text{O}_{13}$ are $a = 15.307 \text{ \AA}$, $b = 3.747 \text{ \AA}$, $c = 9.140 \text{ \AA}$, and $\beta = 99.379^\circ$ in the $C2/m$ space group.^[21] $\text{Li}_2\text{M}_6\text{O}_{13}$ ($\text{M} = \text{Ti}^{4+}$ or Sn^{4+}) consists of a $[\text{M}_6\text{O}_{13}]$ framework combined with Li^+ ions in square planar hybridization with oxygen ions.^[19–21] It is noteworthy that the $\text{Ti}^{4+}/\text{Sn}^{4+}$ ion exchange proposed in this study maintains the $\text{Li}_2\text{Ti}_6\text{O}_{13}$ as the skeleton lattice structure to form the new $\text{Li}_2\text{Sn}_6\text{O}_{13}$. In this scenario, Li^+ migration is not possible because all the Li^+ atomic positions are occupied.

The results of the lattice parameters obtained by geometry optimizations based on both DFT and force-field approaches are compiled in **Table 1**. During the geometry optimization with the force field, no negative frequencies are found in the structures studied.^[12]

In the case of the ideal $\text{Li}_2\text{Sn}_6\text{O}_{13}$ structure, the GGA + RPBE functional provides the best fit to the perfect $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structure. The a and c lattice parameters increase, while b and β decrease by a lower percent with respect to the ideal (parent) $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structure. This is ascribed to the Ti^{4+} ion having a smaller ionic radius ($0.608 \text{ \AA}$) compared to that of Sn^{4+} ($0.69 \text{ \AA}$) in octahedral hybridization.^[22] The cell parameters of the $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structure calculated by DFT are consistent with the values determined by X-ray, synchrotron and neutron powder diffraction.^[9,10] The GGA + WC functional yields the best fit to the perfect $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structure. For $\text{Li}_2\text{Sn}_6\text{O}_{13}$, the GGA + RPBE functional also yields the best fit with respect to the cell parameters.^[19,20]

2.2. Mechanical Properties and Mechanical Stability

Mechanical properties, together with analysis of the mechanical stability, are important keys to evaluate the feasibility of an unknown compound. Born and co-authors^[23,24] reported fundamental ideas to understand the conditions of mechanical stability of a crystalline structure. They established the main necessary and sufficient conditions of mechanical stability known as the Born criteria.^[23] Subsequently, many researchers have used alternative conditions.^[25–28]

Mechanical stability is important for materials used, among others, in solid breeder ceramic compounds used in the International Thermoelectric Reactors (ITER), since during the tritium production it is important that the original structure should be preserved to ensure its breeding action and durability.^[29,30] The mechanical response of a crystal structure is described by the elastic (stiffness) constant matrix (C_{ij}) defined as follows:

$$C_{ij} = \frac{1}{V_0} \left(\frac{\partial^2 E}{\partial \varepsilon_i \partial \varepsilon_j} \right) \quad (3)$$

where V_0 represents the crystal equilibrium volume, E its energy and ε denotes a strain load. The Born criteria establishes that the energy, defined as:

$$E = E_0 + \frac{V_0}{2} \sum_{i,j=1}^6 C_{ij} \varepsilon_i \varepsilon_j + O(\varepsilon^3) \quad (4)$$

for an arbitrary homogeneous deformation loaded by an infinitesimal strain, is always positive,^[23,24] where the 0 subscript in Eq. (4) refers to the equilibrium state of the crystal.

Table 1. Cell parameters obtained by DFT using different exchange-correlation functionals, including static simulations employing the force-field parameters. Deviations (in %) with respect to experimental values are listed in brackets.

Li_2SnO_3 ($C2/c$)						
	PBE	RPBE	PW91	WC	Ref. [9]	FF
a ($\text{\AA}$)	5.03 (−4.94)	5.04 (−4.8)	5.02 (−5.0)	5.02 (−5.16)	5.29	5.19 (−1.85)
b ($\text{\AA}$)	8.72 (−4.79)	8.74 (−4.6)	8.71 (−4.9)	8.70 (−5.0)	9.16	9.01 (−1.65)
c ($\text{\AA}$)	9.65 (−3.11)	9.70 (−2.59)	9.63 (−3.28)	9.58 (−3.8)	10.0	9.59 (−3.7)
β ($^\circ$)	100.13 (−0.22)	100.17 (−0.18)	99.97 (−0.37)	100.12 (−0.23)	100.35	100.32 (−0.03)
$\text{Li}_2\text{Sn}_6\text{O}_{13}$ ($C2/m$)						
	PBE	RPBE	PW91	WC	Ref. [11]	FF
a ($\text{\AA}$)	14.76 (4)	14.76 (−3.57)	14.75 (−3.64)	14.75 (−3.67)	15.31	15.99 (+4.49)
b ($\text{\AA}$)	3.97 (+5.88)	3.97 (+6.0)	3.96 (+5.72)	3.96 (+5.8)	3.75	3.83 (+2.1)
c ($\text{\AA}$)	8.79 (−3.87)	8.82 (−3.54)	8.78 (−3.94)	8.76 (−4.2)	9.14	9.43 (+3.2)
β ($^\circ$)	98.75 (−0.63)	99.06 (−0.33)	98.71 (−0.67)	98.42 (−0.97)	99.38	97.21 (−2.18)
$\text{Li}_2\text{Ti}_6\text{O}_{13}$ ($C2/m$)						
	PBE	RPBE	PW91	WC	Ref. [11]	FF
a ($\text{\AA}$)	15.57 (+1.71)	15.60 (+1.88)	15.55 (+1.62)	15.53 (+1.48)	15.31	15.59 (+1.7)
b ($\text{\AA}$)	3.77 (+0.72)	3.79 (+1.1)	3.77 (+0.72)	3.77 (+0.51)	3.75	3.74 (−0.40)
c ($\text{\AA}$)	9.26 (+1.22)	9.29 (+1.60)	9.24 (+1.14)	9.20 (+0.61)	9.14	9.18 (+0.4)
β ($^\circ$)	99.47 (+0.09)	99.68 (+0.30)	99.40 (+0.03)	99.24 (−0.14)	99.38	97.45 (−1.94)

This criterion is equivalent to the fact that the C_{ij} matrix should be positive definite, which means that all its eigenvalues must be positive. Some authors have used other criteria, such as the Fedorov criteria, where only the diagonal elements of C_{ij} must be positive. Such a condition turns out to be necessary but not sufficient.^[27] In such cases, the Fedorov criteria^[27,28] leads to incorrect conclusions concerning the mechanical stability of systems, such as MOF-74 materials with CH_4 molecules.^[25]

The C_{ij} matrix of the new $\text{Li}_2\text{Sn}_6\text{O}_{13}$ compound, obtained from DFT calculations, is:

$$C_{ij} = \begin{pmatrix} 241.28 & 19.72 & 122.83 & 0 & 24.31 & 0 \\ 19.72 & 264.22 & 63.25 & 0 & 0.43 & 0 \\ 122.83 & 63.25 & 300.27 & 0 & 71.65 & 0 \\ 0 & 0 & 0 & 74.35 & 0 & 13.36 \\ 24.31 & 0.43 & 71.65 & 0 & 72.38 & 0 \\ 0 & 0 & 0 & 13.36 & 0 & 28.45 \end{pmatrix} \quad (5)$$

The eigenvalues λ_i of C_{ij} ($i, j = 1, 2, \dots, 6$) are obtained by $\text{DET}(C_{ij} - \lambda_i I_{ij}) = 0$, where DET denotes the determinantal and I_{ij} the unity matrix of the same size as C_{ij} . The calculated λ_i are: $\lambda_1 = 24.85$, $\lambda_2 = 49.31$, $\lambda_3 = 77.95$, $\lambda_4 = 147.63$, $\lambda_5 = 246.85$ and $\lambda_6 = 434.36$ GPa. All the values are positive and thus confirm the mechanical stability of $\text{Li}_2\text{Sn}_6\text{O}_{13}$. Similar results can be obtained by using the C_{ij} components resulting from the force-field approach. Other equivalent necessary and sufficient conditions can be used and derived from the properties of the positive matrix, with the aid of other linear algebra subroutines.^[27] The obtained elastic constant components for $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and Li_2SnO_3 are given in **Table 2**. For monoclinic structures, there are 13 independent constants along the plane $y=0$, together with 12 relations to satisfy the Born criteria.^[23,24] The C_{ij} values collected in Table 2 reveal that the stability conditions are satisfied. To our knowledge, no experimental data exist for a comparison of the values of C_{ij} for $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and Li_2SnO_3 .

The force-field method provides us with expectation values of the mechanical properties in the case of $\text{Li}_2\text{Ti}_6\text{O}_{13}$. The negative value of C_{15} for Li_2SnO_3 is analogous to that of the Li_2TiO_3 structure reported previously.^[31] In our previous work, the values of C_{ij} for Li_2SnO_3 were also calculated via both DFT and the force-field methods.^[12] The small discrepancies in the C_{ij} values obtained using DFT are attributed to the use of different exchange-correlation functionals.

Other standard parameters can also be determined. The bulk (B), shear (G) and Young's moduli (E) are then calculated after geometry optimization. The relevant magnitudes are compiled in **Table 3**. To our knowledge, previous studies based on DFT computations or experimental results did not report on the exploration of mechanical properties of these structures.

However, for Li_2SnO_3 , the difference in the values calculated by DFT and force-field methods can be attributed to the contraction in the c axis. Both Li_2SnO_3 and Li_2TiO_3 exhibit a similar c -axis contraction in the $C2/c$ space group.^[31] In general, the calculated values are consistent for this type of structure.

In the case of the unknown $\text{Li}_2\text{Sn}_6\text{O}_{13}$ structure, its values for mechanical properties obtained by both DFT and force-field

Table 2. Elastic constant tensor components (in GPa) of Li_2SnO_3 , $\text{Li}_2\text{Ti}_6\text{O}_{13}$, and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ compounds, obtained upon full geometry optimization using the force field and/or DFT calculations.

	Li_2SnO_3		$\text{Li}_2\text{Ti}_6\text{O}_{13}$	$\text{Li}_2\text{Sn}_6\text{O}_{13}$	
	DFT	FF	FF	DFT	FF
C_{11}	267.90	196.22	138.11	241.28	116.49
C_{12}	98.68	73.76	48.75	19.72	36.58
C_{13}	39.40	36.48	83.70	122.83	81.61
C_{15}	-62.84	-11.80	14.40	24.31	7.23
C_{22}	330.0	190.02	240.43	264.22	202.58
C_{23}	23.12	36.30	89.37	63.25	76.57
C_{25}	19.50	16.42	4.02	0.426	1.08
C_{33}	213.71	108.09	208.83	300.27	180.51
C_{35}	15.67	2.09	17.56	71.65	15.88
C_{44}	36.09	29.16	33.93	74.35	25.25
C_{46}	16.23	15.82	1.59	13.36	1.50
C_{55}	59.33	29.66	51.25	72.38	44.89
C_{66}	122.45	60.02	5.14	28.45	4.66

approaches can best be considered as the lower and upper limits of these quantities, with the hope that their experimental confirmation could be a subject for future studies.

The ductility and brittleness criteria are calculated by the Pugh formula B/G ,^[3,32] including the degree of elastic anisotropy defined as:

$$F_B = \frac{B_{\text{Voigt}} - B_{\text{Reuss}}}{B_{\text{Voigt}} + B_{\text{Reuss}}}; \quad F_G = \frac{G_{\text{Voigt}} - G_{\text{Reuss}}}{G_{\text{Voigt}} + G_{\text{Reuss}}} \quad (6)$$

All the values of B/G are greater than 1.75, which reveals that all the structures considered behave as brittleness materials.^[32] It can be noted that all the structures exhibit a very low bulk and shear anisotropy. Both compounds $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ have a similar degree in anisotropy with respect to the volume and shape change. Li_2SnO_3 is more anisotropic with respect to the shape change than for the volume change. Li_2SnO_3 has thus the largest value of F_B/F_G , followed by $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$. Thus, Li_2SnO_3 is the most balanced material in elastic isotropy.

$\text{Li}_2\text{Sn}_6\text{O}_{13}$ is more elastically isotropic and more resistant regarding volume changes than $\text{Li}_2\text{Ti}_6\text{O}_{13}$.

The elastic isotropy/anisotropy is not only significant for solid breeder materials, but it is also very important to determine the nature of microcrack sources and propagations in polycrystalline materials.

These results reveal the general mechanical behavior of the essential lithium-based materials that can be used as breeder and in Li^+ -ion batteries.

2.3. Thermodynamic Stability

Having confirmed the mechanical stability of $\text{Li}_2\text{Sn}_6\text{O}_{13}$, it is highly desirable to further examine its thermodynamic stability by evaluating its standard molar formation enthalpy.

Table 3. Bulk (B), Shear (G), and Young's (E) moduli and anisotropy factors of Li_2SnO_3 , $\text{Li}_2\text{Sn}_6\text{O}_{13}$, and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ (bold values are obtained by DFT).

	<i>B</i> (GPa)			<i>G</i> (GPa)			<i>E</i> (GPa)		
Force field	Reuss	Voigt	Hill	Reuss	Voigt	Hill	x	y	z
Li ₂ SnO ₃	77.41	87.49	82.45	36.63	46.95	41.79	151.11	143.50	98.10
Li ₂ Sn ₆ O ₁₃	88.63	98.79	93.71	15.12	35.28	25.20	79.57	169.31	106.96
Li ₂ Ti ₆ O ₁₃	102.78	114.56	108.67	17.55	42.44	30.0	102.58	200.19	140.41
	<i>B</i> (GPa)			<i>G</i> (GPa)			<i>E</i> (GPa)		
DFT	Reuss	Voigt	Hill	Reuss	Voigt	Hill	x	y	z
Li ₂ SnO ₃	117.54	126.01	121.78	54.04	86.94	70.49	145.66	251.76	193.08
Li ₂ Sn ₆ O ₁₃	120.03	135.26	127.64	52.13	75.03	63.58	190.36	246.71	176.18
Li ₂ Ti ₆ O ₁₃	—			—			—		
Values of <i>B</i> / <i>G</i> , <i>F_B</i> , <i>F_G</i> , and <i>F_B</i> / <i>F_G</i>									
	<i>B</i> / <i>G</i>			Anisotropy factors					
Compound	Reuss	Voigt	Hill	<i>F_B</i>		<i>F_G</i>		<i>F_B</i> / <i>F_G</i>	
Li ₂ SnO ₃	2.11/ 2.18	1.86/ 1.45	1.97/ 1.73	0.061/ 0.035		0.123/ 0.233		0.50/ 0.149	
Li ₂ Sn ₆ O ₁₃	5.86(2)/ 2.30	2.80/ 1.80	3.72/ 2.01	0.054/ 0.060		0.400/ 0.180		0.136/ 0.331	
Li ₂ Ti ₆ O ₁₃	5.85(6)	2.70	3.62	0.054		0.415		0.131	

The procedure to obtain the standard molar enthalpy is well established.^[33,34] Considering the thermodynamic cycle to form the $\text{Li}_2\text{M}_6\text{O}_{13}$ ($\text{M} = \text{Ti}^{4+}$ or Sn^{4+}) compounds:

the standard molar formation enthalpy ($\Delta_f H_m$) can be estimated by:

$$\Delta_f H_m = \Delta_f H_m(\text{Li}_2\text{M}_6\text{O}_{13}) - \Delta_f H_m(\text{Li}_2\text{O}) - 6\Delta_f H_m(\text{MO}_2) \quad (8)$$

which can be written in terms of total energy (E) as follows:

$$\Delta_f H_m = E(\text{Li}_2\text{M}_6\text{O}_{13}) - E(\text{Li}_2\text{O}) - 6E(\text{MO}_2) \quad (9)$$

where the values of the total energy of the considered oxide compounds were taken from the results of the geometry optimization based on DFT calculations with the same setup used previously. Finally, the standard molar formation enthalpy of $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ can be obtained by:

$$\Delta_f H_m(\text{Li}_2\text{M}_6\text{O}_{13}) = \Delta_f H_m + \Delta_f H_m(\text{Li}_2\text{O}) + 6\Delta_f H_m(\text{MO}_2) \quad (10)$$

The total energies under the GGA + RPBE approximation are -820.06 , -1915.40 , -1914.87 , -12387.25 , and -12382.04 eV for Li_2O , rutile TiO_2 , SnO_2 , $\text{Li}_2\text{Ti}_6\text{O}_{13}$, and $\text{Li}_2\text{Sn}_6\text{O}_{13}$, respectively.

With the available information of the standard molar formation enthalpy of Li_2O , rutile TiO_2 , and SnO_2 taken from Refs.^[35–37], the values of the standard molar enthalpy and the standard molar formation enthalpy of $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ are obtained and presented in **Table 4**. To our knowledge, no data for the standard molar formation enthalpy of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ was previously reported.

The thermodynamic stability of the parent structure to form the $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structure via Na^+/Li^+ ion exchange was previously

studied.^[35] Considering the thermodynamic data of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ ($\Delta_f H_m = -6277.9 \pm 6.5$ kJ mol⁻¹^[35]) and $\text{K}_2\text{Ti}_6\text{O}_{13}$ ($\Delta_f H_m = -6035$ kJ mol⁻¹^[38]), the values of $\Delta_f H_m$ of $\text{Li}_2\text{M}_6\text{O}_{13}$ ($\text{M} = \text{Ti}^{4+}$ or Sn^{4+}) agree with these structural types. Hence, it can be concluded that both $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ have high thermodynamic stability.

To further explore the thermodynamic properties of the $\text{Li}_2\text{M}_6\text{O}_{13}$ compounds, the energetic cost required for the inclusion-extraction of its individual constituent elements are calculated using the hypothetical reactions:

Note that the stoichiometry in Eqs. (11) to (13) of $\text{Li}_2\text{M}_6\text{O}_{13}$ is augmented by 2 because the Z formula unit is 2 for the $\text{A}_2\text{M}_6\text{O}_{13}$ unit cells.^[10,39] The procedure exposed here was also used satisfactorily in Ref. 40 to elucidate the energetics of Li_2TiO_3 .

Table 4. Standard molar $\Delta_f H_m$ and formation $\Delta_f H_m$ enthalpy of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ (in kJ mol⁻¹).

	$\text{Li}_2\text{Ti}_6\text{O}_{13}$	$\text{Li}_2\text{Sn}_6\text{O}_{13}$
$\Delta_f H_m$	-7217.55	-7022.18
$\Delta_f H_m$	$-6740.14^\dagger$	$-5552.55^\text{a)}$

^{a)} Referred to the primitive cell, for the conventional representation the values are the doublet.

To obtain the total energy by DFT calculations, a $1 \times 2 \times 1$ supercell is used for the non-stoichiometric reactants. The reaction energy is then obtained as:

$$\Delta E = E(\text{Li}_4\text{M}_{12}\text{O}_{26}) - [E(\text{Li}) + E(\text{Li}_3\text{M}_{12}\text{O}_{26})] \quad (14)$$

$$\Delta E = E(\text{Li}_4\text{M}_{12}\text{O}_{26}) - [E(\text{M}) + E(\text{Li}_4\text{M}_{11}\text{O}_{26})] \quad (15)$$

$$\Delta E = E(\text{Li}_4\text{M}_{12}\text{O}_{26}) - [E(\text{O}) + E(\text{Li}_4\text{M}_{12}\text{O}_{25})] \quad (16)$$

for reactions (11) to (13), respectively. ΔE denotes the reaction energy and $E(X)$ the total energy of the compound X. Table 5 compiles the results of ΔE in different energy units for comparison.

As shown in Table 5, the energy needed to remove a Li^+ ion or cleave a $\text{Li}-\text{X}$ bond in $\text{Li}_2\text{Sn}_6\text{O}_{13}$ is comparable with the value obtained for $\text{Li}_2\text{Ti}_6\text{O}_{13}$. This means that, if the new compound can be synthesized, it should be as stable as its hexatitanate counterpart. The tritium release in the ITER depends on the $\Delta E(\text{Li})$ value during the reaction of ^6Li with neutrons.^[29,30] In the ITER, the liberation/production of lithium/tritium ions will take place at the same range of temperature in $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ compounds due to the small difference in ΔE of $\approx 11 \text{ kcal mol}^{-1}$ between both compounds. The values are lower compared with Li_2TiO_3 , which is the best candidate for use in the ITER.^[40]

Furthermore, the $\Delta E(\text{Li})$ values are the lowest in both $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$, revealing that Li^+ is the most mobile ion and responsible for the transport properties in these structures. From the point of view of the values of $\Delta E(\text{M})$ and $\Delta E(\text{O})$, the $\text{Li}_2\text{Sn}_6\text{O}_{13}$ compound is quite comparable to $\text{Li}_2\text{Ti}_6\text{O}_{13}$.

The values of $\Delta E(\text{Sn})$ and $\Delta E(\text{Ti})$ have a relatively small difference of 17 kcal mol^{-1} and are the second lowest values of reaction energy, followed by a small difference of 14 kcal mol^{-1} of $\Delta E(\text{O})$ between both compounds, revealing the possibility of $\text{Ti}^{4+}/\text{Sn}^{4+}$ ion exchange. Compiling these results and the values of the standard molar formation enthalpy, both $\text{Li}_2\text{M}_6\text{O}_{13}$ compounds appear to be thermodynamically stable.

Table 5. Reaction energy (ΔE) of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$.

Reaction	$\text{Li}_2\text{Sn}_6\text{O}_{13}$		
	Li	Sn	O
	$\text{LiSn}_6\text{O}_{13}$	$\text{Li}_2\text{Sn}_5\text{O}_{13}$	$\text{Li}_2\text{Sn}_6\text{O}_{12}$
$E(X) [\text{eV atom}^{-1}]$	−298.33	−297.14	−293.12
$\Delta E [\text{kcal mol}^{-1}]$	229.81	774.83	1045.74
$\Delta E [\text{eV atom}^{-1}]$	6.41		
Reaction	$\text{Li}_2\text{Ti}_6\text{O}_{13}$		
	Li	Ti	O
	$\text{LiTi}_6\text{O}_{13}$	$\text{Li}_2\text{Ti}_5\text{O}_{13}$	$\text{Li}_2\text{Ti}_6\text{O}_{12}$
$E(X) [\text{eV atom}^{-1}]$	−298.64	−297.44	−293.58
$\Delta E [\text{kcal mol}^{-1}]$	240.43	791.69	1059.72
$\Delta E [\text{eV atom}^{-1}]$	6.87		

2.4. Electronic Structure

The electronic band structures of $\text{Li}_2\text{Sn}_6\text{O}_{13}$, $\text{Li}_2\text{Ti}_6\text{O}_{13}$, and Li_2SnO_3 are obtained using the calibration by DFT calculations with the GGA + RPBE functional. The total and projected density of states and band structures are obtained with the interpolation integration method with a broadening factor of 0.05 eV.

Figure 3 displays the band structures of $\text{Li}_2\text{Ti}_6\text{O}_{13}$, $\text{Li}_2\text{Sn}_6\text{O}_{13}$, and Li_2SnO_3 at their equilibrium ground state. Li_2SnO_3 exhibits an insulating character considering the large band gap energies. $\text{Li}_2\text{Sn}_6\text{O}_{13}$ has a larger band gap energy in the valence band boundary. The calculated band structure of Li_2SnO_3 also shows an indirect gap from the A point at the valence band maximum to the Γ point (G) at the conduction band minimum, with a calculated value of 4.5 eV. In view of the usual underestimation of DFT + GGA calculated band gap, the calculated value agrees with the estimated value ($\approx 3 \text{ eV}$) from the optical diffuse reflectance spectrum reported for Li_2SnO_3 .^[39] $\text{Li}_2\text{Sn}_6\text{O}_{13}$ also has an indirect gap from the Z-point at the valence band maximum

Figure 3. Band structures of (a) Li_2SnO_3 , (b) $\text{Li}_2\text{Sn}_6\text{O}_{13}$, and (c) $\text{Li}_2\text{Ti}_6\text{O}_{13}$ calculated using the GGA + RPBE exchange-correlation functional.

to the Γ -point at the conduction band minimum, resulting in $E_g = 3.0$ eV.

On the basis of the computed energy gap, the $\text{Li}_2\text{Sn}_6\text{O}_{13}$ compound emerges as a semiconducting material, but the calculated band structure displays an indirect gap from the Z-point at the valence band maximum to the Γ -point at the conduction band minimum. Analogously, $\text{Li}_2\text{Ti}_6\text{O}_{13}$ has also a semiconducting character with a direct gap from the Z-point at the valence band maximum to the conduction band minimum. The obtained E_g of the predicted compound $\text{Li}_2\text{Sn}_6\text{O}_{13}$ is close to the experimental value for the $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ structures, 3.5 eV, while $\text{K}_2\text{Ti}_6\text{O}_{13}$ has $E_g = 3.3$ eV.^[9,38,41]

To further understand the electronic nature of these compounds, **Table 6** displays the calculated E_g of each compound with respect to the exchange-correlation functionals employed. The errors of the mean value of E_g with respect to the experimental data^[38,41] are ≈ 16 , 11, and 13% for $\text{Li}_2\text{Sn}_6\text{O}_{13}$, $\text{Li}_2\text{Ti}_6\text{O}_{13}$, and Li_2SnO_3 , respectively. In view of the usual underestimation of DFT calculations, the errors are less than 30%, making these values acceptable as lower-bounds.^[13] The mean value of E_g for the new compound $\text{Li}_2\text{Sn}_6\text{O}_{13}$ is reduced to 0.18 eV compared to that of $\text{Li}_2\text{Ti}_6\text{O}_{13}$, and this result also emphasizes the efficient use of $\text{Li}_2\text{Sn}_6\text{O}_{13}$ as an electrode in Li^+ -ion batteries.

One of the key requirements for a material to be efficiently used as an anode in lithium-ion batteries is that the material must be a good electronic conductor (preferably a metal).^[42] $\text{Li}_2\text{Ti}_6\text{O}_{13}$ has a dc conductivity of $\sigma_{\text{dc}}(T) = 5.6 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature.^[9] As $\text{Li}_2\text{Ti}_6\text{O}_{13}$ is the parent structure leading to formation of the $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and in considering the results of the band gap energy of both compound, we can estimate the $\sigma_{\text{dc}}(T)$ of $\text{Li}_2\text{Sn}_6\text{O}_{13}$.

As the $\sigma_{\text{dc}}(T)$ follows an Arrhenius type dependence $\sigma_{\text{dc}}(T) \sim \exp(-E_g/2k_B T)$,^[43] the reduction of 0.18 eV of the energy gap with respect to the Sn^{4+} ion exchange in $\text{Li}_2\text{Ti}_6\text{O}_{13}$ leads to an increment of the dc conductivity of $2.05 \times 10^{-4} \text{ S cm}^{-1}$ for the unknown hexastannate compound. The estimated electrical conductivity of the new $\text{Li}_2\text{Sn}_6\text{O}_{13}$ compound at room temperature is about two orders of magnitude higher compared with its hexatitanate counterpart. This value should be considered with caution because in real samples, other effects will affect the transport properties. Impedance spectroscopy measurements can reveal the electrical conductivity of the new compound when the compound is

prepared. However, this value provides us with a comparison between both compounds.

Other properties, such as the concentration of charge carriers (electrons and holes), are also proportional to $\exp(-E_g/2k_B T)$. As we have the proportion between the energy gaps of both compounds, we can estimate the influence of this small reduction on these properties by using the same procedure as above.

In order to determine the diffusion barrier in $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$, we now use the force field-based nudged elastic band method,^[44–46] as implemented in GULP.^[45] The calculated energy barriers amount to 0.52 and 0.47 eV for the $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structures, respectively. The diffusion barrier in both compound agrees with, is even lower than, the values reported for other Li^+ based compounds, such as $\text{Li}_2\text{Ti}_3\text{O}_7$ (0.67–0.74 eV^[47]), and other Na^+ counterparts (0.9 eV^[48]).

The fact that the energy barrier is lower in $\text{Li}_2\text{Ti}_6\text{O}_{13}$ structure can be ascribed to the lower Li^+ jump distance into the LiO_4 channel compared with $\text{Li}_2\text{Sn}_6\text{O}_{13}$.^[12] The small difference in energy barrier (0.05 eV) again emphasizes the great potential of $\text{Li}_2\text{Sn}_6\text{O}_{13}$ to be used as an alternative compound for lithium-ion batteries.

Equation (11) describes the lithiation/delithiation processes that occur in the negative/positive electrode in lithium-ion batteries. The term $\text{Li}_3\text{M}_{12}\text{O}_{26}$ ($\text{LiM}_6\text{O}_{13}$) corresponds to the delithiated phase of $\text{Li}_2\text{M}_6\text{O}_{13}$ compounds. It is well known that the cell voltage is directly associated with the chemical potential of lithium in the positive electrode. By using DFT calculations, the discharge voltage can be determined through the total energies of the lithiated and delithiated phases of $\text{Li}_2\text{M}_6\text{O}_{13}$ compounds. The discharge voltage is calculated as follows^[49–52]:

$$V = - \frac{E(\text{Li}_2\text{M}_6\text{O}_{13}) - [E(\text{Li}) + E(\text{LiM}_6\text{O}_{13})]}{F} \\ = \frac{1}{4} \frac{q_e \Delta E(\text{Li}) N_A}{F} \quad (17)$$

where $F = 9.65 \times 10^4 \text{ C mol}^{-1}$ is the Faraday's constant, q_e the electron charge, N_A the Avogadro's number and $\Delta E(\text{Li})$ the overcalculated reaction energy of Li listed in Table 5 (in eV atom^{-1}). The calculated voltage values of the Li insertion/extraction process per Li^+/Li are 1.6 and 1.72 V for $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$, respectively. Both voltage values are close to those experimentally reported, ranging between 1.5 and 1.7 V for $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and 1.3 V for $\text{Na}_2\text{Ti}_6\text{O}_{13}$ compounds.^[9,11] These values are also comparable to those determined for the various phases of TiO_2 , which are also investigated as anodes for Li^+ -ion batteries.^[53]

Figure 4 displays the projected (PDOS) and total (DOS) density of states of $\text{Li}_2\text{Sn}_6\text{O}_{13}$, Li_2SnO_3 , and $\text{Li}_2\text{Ti}_6\text{O}_{13}$. The DOS and PDOS plots of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ structures, illustrated in Figure 4 a) and c), exhibit several similarities to those of Li_2SnO_3 . The Li-s states contribution to the valence band is roughly similar, whereas that to the conduction band is quite accentuated. The Sn-(s,p) states, combined with the O-p states, dominate the valence and conduction bands, revealing a SnO_6 octahedral hybridization. On the other hand, the DOSs at both conduction and valence bands are much lower with respect to

Table 6. Energy gap (in eV) obtained using different DFT exchange-correlation functionals.

Exchange functional	$\text{Li}_2\text{Sn}_6\text{O}_{13}$	$\text{Li}_2\text{Ti}_6\text{O}_{13}$	Li_2SnO_3
PBE	2.93	3.12	4.37
RPBE	3.03	3.15	4.47
PW91	2.99	3.15	4.43
WC	2.85	3.09	4.24
Mean	2.95	3.13	4.36
std	0.02	0.003	0.03
Error	0.01	0.002	0.02

Figure 4. Total (DOS) and projected (PDOS) density of states of a) $\text{Li}_2\text{Sn}_6\text{O}_{13}$, b) Li_2SnO_3 , and c) $\text{Li}_2\text{Ti}_6\text{O}_{13}$ in $C2/m$ space group calculated using the GGA + RPBE functional.

those of Li_2SnO_3 , in that the band gap energy has the lowest value. The characteristics of the DOS and PDOS of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ are quite comparable to those of $\text{Li}_2\text{Sn}_6\text{O}_{13}$, confirming that they are partner structures (such as $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$).

Bearing the different properties predicted for the new $\text{Li}_2\text{Sn}_6\text{O}_{13}$ in mind, we can now propose that this compound features potential technological applications. In particular, it can be used as an alternative, or at least an auxiliary, material for energy storage. Its actual experimental synthesis and determination of its physicochemical properties are highly desirable. Compiling the abovementioned properties of $\text{Li}_2\text{Sn}_6\text{O}_{13}$, it is highly required to complete the study of transport properties of this compound, specifically for Li^+ -migration into its lattice structure. The aim of future work could involve theoretical predictions of Li^+ -migration by using classical simulations.

3. Conclusions

The structural, electronic and mechanical properties of Li_2SnO_3 , $\text{Li}_2\text{Ti}_6\text{O}_{13}$, and an unknown material $\text{Li}_2\text{Sn}_6\text{O}_{13}$ were evaluated

using classical simulations and DFT calculations. Mechanical properties were also determined by force-field methods and subsequently validated by DFT computations. After a full geometry optimization for each structure mentioned above, the elastic stiffness coefficients, bulk, shear and Young's moduli were calculated. To the best of our knowledge, the values for $\text{Li}_2\text{Ti}_6\text{O}_{13}$ are reported for the first time in this work by using the force-field method. $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$ are more elastically isotropic and more resistant with respect to volume change.

The lattice parameters obtained by DFT computations agree well with experiment, highlighting the values obtained via the use of GGA + RPBE functionals and the force field approach. This achievement provides us with a strong support for the capability of the force field to model this type of materials, it can be used for extensive search for new and interesting compounds.

The electronic band structure analysis points out the insulator character of Li_2SnO_3 with indirect band energy of 4.4 eV. In addition, both $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ appear to be semiconducting compounds with band gap energies of 3.1 and 3.0 eV, respectively. The thermodynamic stability of $\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Li}_2\text{Sn}_6\text{O}_{13}$ are also reported. Both compounds are thermodynamically stable with a reaction energy for the lithiation of 6.4 and 6.9 eV atom⁻¹, standard molar formation enthalpy of -5553 and -6740 kJ mol⁻¹ for $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$, respectively. The predicted energy barriers for Li^+ migration amount to 0.52 and 0.47 eV for $\text{Li}_2\text{Sn}_6\text{O}_{13}$ and $\text{Li}_2\text{Ti}_6\text{O}_{13}$, respectively. The calculated cell voltage values of Li insertion/extraction process per Li^+/Li are 1.6 V for $\text{Li}_2\text{Sn}_6\text{O}_{13}$. $\text{Li}_2\text{Sn}_6\text{O}_{13}$ is characterized by mechano-thermodynamic stability and electronic properties comparable to those of its partner structures ($\text{Li}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$).

In summary, the hexastannate compound, if it can be synthesized, is recommended as an alternative material for energy storage in Li^+ -batteries.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

energy storage, Li migration barrier, lithium hexastannate, lithium hexatitanate, lithium stannate, standard formation enthalpy

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