First-Principles Study of the Structural Stability and Dynamic Properties of Li$_2$MSiO$_4$ (M = Mn, Co, Ni) Polymorphs

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Received: 29 November 2018; Accepted: 7 January 2019; Published: 11 January 2019

Abstract: In recent years, the scientific community has shown an increasing interest in regards to the investigation of novel materials for the intercalation of lithium atoms, suitable for application as cathodes in the new generations of Li-ion batteries. Within this framework, we have computed the relative structural stability, the electronic structure, the elastic and dynamic properties of Li$_2$MSiO$_4$ compounds (M = Mn, Co, Ni) by means of first-principles calculations based on density functional theory. The so-obtained structural parameters of the examined phases are in agreement with previous reports. The energy differences between different polymorphs are found to be small, and most of these structures are dynamically stable. The band structures and density of states are computed to analyse the electronic properties and characterise the chemical bonding. The single crystal elastic constants are calculated for all the examined modifications, proving their mechanical stability. These Li$_2$MSiO$_4$ materials are found to present a ductile behaviour upon deformation. The diffusion coefficients of Li ions, calculated at room temperature for all the examined modifications, reveal a poor conductivity for this class of materials.

Keywords: cathode materials; Li ion battery; structural stability; mechanical stability; DFT study; relative stability; electronic structure; transport properties

1. Introduction

Lithium-ion batteries present an excellent combination of high energy and power density and consequently are currently the most promising technology for energy storage devices as well as for electric vehicles [1,2]. In the course of the last 20 years, this technology has established as the dominant one for rechargeable battery for portable devices. However, their application in other areas is more challenging due to the demanding requirements of high power capability at low cost for large systems and the need of improving the overall safety [3]. The development of novel Li-ion batteries is thus attracting the interest of the scientific community, aimed at the design and production of a high-energy, low-cost and long-life battery technology. The cathode materials are the bottleneck of this Li-ion technology in terms of both the cost of raw materials and the theoretical capacity. Researching novel materials exhibiting a high specific capacity and good retention of the latter upon electrochemical cycling, as well as high operating voltage is therefore crucial in order to advance the overall state of the art of Li-ion-based battery technology. In this context, the main advantage of polyoxoanion intercalation compounds with respect to transition metal oxides is the greater stability upon intercalation/deintercalation of Li$^+$ ions, ensured by the covalence of the bonding between oxygen and the non-metallic atom (e.g., P, Si). This feature ensures an improved capacity retention,
as well as better overall battery safety. Phosphate materials, particularly LiFePO₄, have been the object of detailed studies and have been proven to be excellent cathode materials. While phosphates continue to be relevant, the interest of a large community has recently shifted towards silicates, such as Li₂FeSiO₄, due to the natural abundance of these elements and their consequently low cost. Li₂MnSiO₄ (M = Mn, Fe, Co, Ni) is one of the promising cathode materials for lithium ion batteries, not only because it presents stable polyanion structures, but also due to the larger theoretical capacity with respect to existing cathode materials, due to the possibility of two-electron redox processes [4–8].

Li₂MnSiO₄ has more advantages than Li₂FeSiO₄ with regards to cell safety, ease of preparation and cost effectiveness. The Mn³⁺ ↔ Mn⁴⁺ conversion provides a higher potential than Mn²⁺/Mn³⁺ and Fe²⁺/Fe³⁺ (it is yet to be clarified whether this involves an Fe³⁺/Fe⁴⁺ redox couple or it might just be an electrolyte degradation phenomenon [9–12]). In practical applications, Li₂MnSiO₄ is limited as a cathode by its low electronic conductivity of ∼5 × 10⁻¹⁶ S cm⁻¹ at room temperature (RT) (and ∼3 × 10⁻¹⁴ S cm⁻¹ at 60 °C), which is 5–6 orders of magnitude smaller than that of LiFePO₄ at RT. Co- or Ni-containing salts for preparing Li₂CoSiO₄ and Li₂NiSiO₄ are commercially expensive and environmentally toxic. Li₂NiSiO₄, with the lowest band-gap, does not have the shortcomings of Mn derivatives [9], but the delithiation potentials (≥4.6 V) of Li₂CoSiO₄ and Li₂NiSiO₄ are too high to make the present electrolytes suitable Li⁺ diffusion media. To explore the suitability of silicate materials as sustainable cathode materials for rechargeable Li ion batteries, the voltage plateaus [13–16], cycling and structural stabilities [14,17–20], electrical and ionic conductivities [20–22], site-exchange [23], effect of mixed transition metal [9,24], addition of Na [25,26], high-pressure behavior [18,27] of Li₂MnSiO₄ (M = Fe, Mn, Co and Ni) were investigated by several first principles calculations studies.

Li₂MnSiO₄ compounds belong to a family of tetrahedral oxide structures that consist of slightly distorted close-packed oxygen layers. The cations occupy half of the tetrahedral sites and several distinct ordering patterns are possible. It has been shown that both the crystal structure and the polarisation of a Li₂MnSiO₄ cathode are substantially modified during the first few cycles. The voltage and the kinetics change accordingly. Eventually, a more stable structure is obtained, at the expense of the capacity of the cathode [16]. Half of the Li, M, and Si atoms rearrange upon cycling, resulting in significantly different Li⁺ diffusion pathways. The suitability of Li₂MnSiO₄ for application as cathode materials was discussed in a work dating back 1997, following the early success of the phosphate electrode [28] The electrochemistry of Li₂FeSiO₄, Li₂FeGeO₄ and L₂MnSiO₄ towards Li⁺/Li has been investigated, revealing average operating voltages of ca. 3.1 V, 3.05 V and 4.2 V, respectively. Yang and coworkers succeeded in removing for the first time both lithium atoms from Li₂MnSiO₄ [9]. The electrode is shown to suffer a large polarization as a result of the complete delithiation.

More recently, a great deal of work has been dedicated to addressing the shortcomings of these materials, including capacity fading and low ionic conductivity. The beneficial calcium doping in the Li₂MnSiO₄ matrix has been extensively studied in [29]. A Ca²⁺ ion, shown to preferably occupy the Mn site, is shown to act as a pillar ion, helping to maintain the structural integrity if Li₂MnSiO₄ and to reduce the Li/Mn disorder of the pristine material, leading to an improved ionic conductivity. On top of that, calcium doping is also shown to lower the binding energy of Mn, thus facilitating the extraction of the second Li⁺ ion, resulting in a larger capacity. In [30], the electrochemical performance of a carbon-coated Li₂MnSiO₄ cathode is shown to be enhanced by fluorine doping. The ionic conductivity is greatly improved, due to the double effect of: (i) increasing the equilibrium volume and (ii) reducing the C-O bonding in the carbon layers. Fluorine doping is also shown to increase the structural stability of the cathode and decrease average particle sizes. In [31] the collaborative effect of carbon-coating and P doping is investigated for a Li₂CoSiO₄ cathode. The carbon-coated sample is a stable mixture of Pmn2₁ and Pbn2₁ particles, with improved capacity retention with respect to the pristine material. P-doping is shown to suppress the formation of Pbn2₁ and to increase the experimental capacity of the cathode by promoting the two-lithium intercalation mechanism. A similar effect is reported in reference [32] for Al doping of a carbon-coated Li₂CoSiO₄ cathode.
In a previous work, we have reported the structural stability, dynamical and mechanical properties of the Li$_2$FeSiO$_4$ system [18]. We extend here our study to the physical properties of the Li$_2$MSiO$_4$ ($M = \text{Mn}, \text{Co}, \text{Ni}$), providing in particular a detailed characterisation of the structural stability, electronic structure, and Li-transport properties of the Li$_2$MSiO$_4$ systems.

2. Materials and Methods

Density functional theory calculations were performed using the Vienna \textit{ab initio} simulation package with projected-augmented wave (PAW) potentials [33,34]. The exchange and correlation functionals are treated within the general gradient approximation (GGA), following the approach of Perdew, Burke, and Ernzerhof (PBE) [35]. The Hubbard parameter $U$ is introduced following the rotationally invariant form [36,37]. Effective $U$ values of 4 eV and 4.1 eV were used for the Mn-$d$, Co-$d$ and Ni-$d$ states, respectively.

The optimised geometries were obtained by iterative minimisation of the Hellman-Feynman forces and stress tensor, by means of the conjugate-gradient algorithm with force tolerance of $10^{-3}$ eV Å$^{-1}$. Integration over the Brillouin zone was performed using a Monkhorst-Pack grid and a Gaussian broadening of 0.1 eV. From various sets of calculations it was determined that 512 $k$ points ($8 \times 8 \times 8$ grid) and a 600 eV plane-wave cutoff are sufficient to ensure optimum accuracy in the computed results. From the previously reported total-energy calculation for the Li$_2$FeSiO$_4$-Pmn2$_1$ phase we have found that the antiferromagnetic (AFM) and ferromagnetic (FM) states are lower in energy compared to the paramagnetic (PM) state [18]. The energy difference between AFM and FM states is 2 meV/cell, to the close to the accuracy threshold of our calculations, and both configurations exhibit a similar volume of the elementary cell. Hence, in the present work we have considered only the FM states for all the examined phases (i.e., all the $M$ atoms are treated as up spin configuration with the finite magnetic moment (5 $\mu$B)).

The total energy has been calculated as a function of the cell volume and fitted to the universal equation of state (EOS) [38]. The transition pressures are then obtained from the Gibbs free energy ($G = U + PV - TS$ where $T = 0$; $G =$ total energy + pressure $\times$ volume), calculated following the procedure presented in [39]. A frozen phonon calculation was performed using suitable supercells models, using the phonopy software to calculate the phonon dispersion and the associated density of states [40]. A displacement of 0.0075 Å was applied to the atoms, with a symmetry considerations, to obtain the force constants matrix. Displacements along opposite directions were included to improve the accuracy. The dynamical matrices were calculated from the force constants, and phonon density of states (PhDOS) curves were computed on a Monkhorst-Pack grid [41]. The thermal properties, including heat capacity, free energy and entropy, were obtained from the calculated PhDOS.

The barrier height for the diffusion of a Li$^+$ ion calculated using the Nudged Elastic Band (NEB) on suitable supercell models ensuring that the atoms are separated from their periodic image and thus providing a more accurate result. The dimensions of these systems is reported in Table S1. To determine the minimum energy path (MEP) through the NEB method [42,43], five replicas of the system were created by linear interpolation between the initial and final states.

3. Result and Discussions

3.1. Structure Models Considered

In general, a good agreement is found between experimental data and theoretical DFT-based predictions using structural inputs from the Inorganic Crystal Structure Database (ICSD) [44]. In the course of our long experience in modelling and predicting the structural properties of hydrides and oxides (see [45–47]), we have found that the ICSD/guess approach is a very robust method for identifying local minima and predicting phase transitions, provided that a sufficiently large set of existing configurations is provided. We have analysed input structures from 486 entries with $ABC_2X_4$ composition. Note that the effective set of configuration used is much smaller, as several
compounds/ phases share the same structure type and, in some cases, only small variations in the positional parameters are present for certain atoms. Even though we used different positional parameters, these structures often relaxed to the similar type of structural arrangement upon geometry optimization and hence these possibilities are omitted. By the end of this screening process, we end up with 11 distinct structure types with $ABC_2X_4$ formulae. These structure types are (space group and space group number in the parenthesis; illustrated in Figure 1): Li$_2$FeSiO$_4$ ($P2_1; 4$), Li$_2$BeSiO$_4$ ($Pn; 7$), Li$_2$FeSiO$_4$ ($P2_1/n; 14$), Li$_2$BeSiO$_4$ ($C222_1; 20$), Li$_2$FeSiO$_4$ ($Pmn2_1; 31$), Li$_2$CoSiO$_4$ ($Pna2_1; 33$), Li$_2$FeSiO$_4$ ($Pnma; 62$), Li$_2$CaSiO$_4$ ($I-42m; 121$), EuLi$_2$SiO$_4$ ($P3_i2_1; 152$), Li$_2$BaSiO$_4$ ($P6_3cm; 185$), and Li$_2$MnSiO$_4$-modified-$Pmn2_1$ (here after its called as $Pmn2_1$-mod structure). The cycled $Pmn2_1$ structure is named as $Pmn2_1$-mod structure. The $Pmn2_1$-mod structure can be described as the site-exchange of half of the Li ions and all of the Fe ions in the pristine Li$_2$FeSiO$_4$ structure (in the pristine $P2_1/n$ structure, the Li$^+$ and Fe$^{2+}$ occupy different crystallographic sites, whereas in the cycled structure, the sites normally occupied by Fe$^{2+}$ are now occupied exclusively by Li$^+$, while the remaining Li$^+$ and Fe ions share the conventional Li sites). The structure of cycled Li$_2$FeSiO$_4$ can be understood as a 3D framework connected by [SiO$_4$] and [FeO$_4$] tetrahedra, with Li ions occupying the interstitial tetrahedral sites.

![Figure 1](attachment:figure1.png)

**Figure 1.** Considered structure models for the present theoretical simulations: (a) Li$_2$BeSiO$_4$ ($C222_1$); (b) Li$_2$BeSiO$_4$ ($Pn$); (c) $P2_1/n$-cycled; (d) Li$_2$CoSiO$_4$ ($Pna2_1$) (e) Li$_2$FeSiO$_4$ ($P2_1/n$); (f) Li$_2$FeSiO$_4$ ($P2_1$); (g) Li$_2$FeSiO$_4$ ($Pmn2_1$); (h) modified-$Pmn2_1$; (i) $Pmn2_1$-ncycled and (j) Li$_2$FeSiO$_4$ ($Pnma$); (k) Li$_2$CaSiO$_4$ ($I222$). The legends for the different kinds of atoms are given in the illustration.
At ambient condition most of the Li₂MnSiO₄ compounds stabilised in orthorhombic (Pmn2₁) structure synthesis by various synthesis methods (like hydrothermal methods [48,49], solid-state [5,50], solgel [12,51], spray pyrolysis [52], microwave [53] and combustion methods [54], etc.). It is very stable compound and easy to synthesize via all these techniques.

3.1.1. Li₂MnSiO₄

There are four known Li₂MnSiO₄ polymorphs that form at ambient pressure. Two orthorhombic (i.e., Pmn2₁ and Pnnm) and two monoclinic (P2₁/n and Pn) modifications. Poltiaev et al. synthesised monoclinic (P2₁/n) Li₂MnSiO₄ at 950–1050 °C via a solid-state method [55]. The monoclinic Pn phase transforms into an orthorhombic phase (Pmn2₁) at temperatures above 370 °C [56]. A second, reversible phase transition can be observed by rate-cooling. The orthorhombic (Pmn2₁) modification, synthesised at 800 °C using a solid-state method, transformed to the a P2₁/n phase when cooled to RT at 200 K min⁻¹. The synthesis performed at 700 °C, on the other hand, produced the Pmn2₁ phase thus indicating that the Pnnm phase transformed into orthorhombic disordered structures analogue to wurtzite [57]. The low-temperature orthorhombic modifications are more stable than the monoclinic form, because of their larger volume. The latter can only be produced using high temperature (above 900 °C) synthesis [58]. Experimental investigations clearly reveal that by increasing the s pressure or the temperature of the process, the structural transformations (Pmn2₁ → Pnnm → P2₁/n) will take place [27,58].

Among the structures considered for structural optimization, the Pmn2₁ atomic arrangement is found to exhibit the lowest total energy (see Figure 2). The calculated atomic sites and lattice parameters (see Tables 1 and 2) are in good agreement with experimental findings [5] and with other theoretical calculations [58]. In this structure, chains of LiO₄ tetrahedra run along the a direction, parallel to the chains of alternating MnO₄ and SiO₄ tetrahedra. The second most energetically favourable phase is orthorhombic Pbnn2₁. The energy difference between these two phases at the equilibrium volume is only ca. 30 meV/f.u. (see Figure 2) [59,60]. Interestingly, the energy difference between the Pmn2₁-mod., Pc, P2₁/n, and Pnnm is also very small, and hence, one can easily modify one polymorph into another by application of temperature or pressure; this explains the difficulties in controlling the synthesis of single phase Li₂MnSiO₄ samples, also related to very similar electrochemical properties (voltage, volume variation upon delithiation, and electronic structure) [27,58].

Table 1. The calculated equilibrium structural parameters (a, b and c are in Å), bandgap (E_g in eV), bulk modulus (in GPa) and its derivative for Li₂MnSiO₄ polymorphs.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Lattice Parameter</th>
<th>E_g (eV)</th>
<th>Bo</th>
<th>Bo'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂MnSiO₄-Pmn2₁</td>
<td>a = 6.4102 (6.3360)</td>
<td>5.1034 (5.0730)</td>
<td>2.94</td>
<td>47</td>
</tr>
<tr>
<td>Li₂MnSiO₄-Pnnm</td>
<td>b = 10.9504</td>
<td>5.0512</td>
<td>2.90</td>
<td>46</td>
</tr>
<tr>
<td>Li₂MnSiO₄-Pbn</td>
<td>c = 5.282 (5.0168)</td>
<td>5.0031 (4.9624)</td>
<td>2.97</td>
<td>47</td>
</tr>
<tr>
<td>Li₂MnSiO₄-P2₁/n</td>
<td>β = 90 (90.99)</td>
<td>90</td>
<td>2.00</td>
<td>46</td>
</tr>
<tr>
<td>Li₂MnSiO₄-P222</td>
<td>a = 4.4033</td>
<td>6.4288</td>
<td>2.00</td>
<td>46</td>
</tr>
<tr>
<td>Li₂MnSiO₄-P22</td>
<td>b = 5.3842 (5.3454)</td>
<td>90</td>
<td>2.00</td>
<td>46</td>
</tr>
<tr>
<td>Li₂MnSiO₄-P222</td>
<td>c = 5.282 (5.0168)</td>
<td>5.0031 (4.9624)</td>
<td>2.97</td>
<td>47</td>
</tr>
<tr>
<td>Li₂MnSiO₄-P2/n</td>
<td>a = 4.2623</td>
<td>6.6211</td>
<td>2.2</td>
<td>58</td>
</tr>
<tr>
<td>Li₂MnSiO₄-P222</td>
<td>b = 4.2623</td>
<td>6.6211</td>
<td>2.2</td>
<td>58</td>
</tr>
<tr>
<td>Li₂MnSiO₄-P222</td>
<td>c = 5.282 (5.0168)</td>
<td>5.0031 (4.9624)</td>
<td>2.97</td>
<td>47</td>
</tr>
</tbody>
</table>

*From ref. [55]; ^b From ref. [5]; ^c From ref. [61]; ^d From ref. [9].
Theoretically calculated (derived from the total energies) equilibrium lattice parameters (a, b and c in Å) for Li$_2$MSiO$_4$ polymorphs.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Space Group</th>
<th>Positional Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnSiO$_4$</td>
<td>$Pmn2_1/2$</td>
<td>Li (4b): 0.7490, 0.3289, 0.9420; Mn (2a): 0.175, 0.4384; Si (2a): 0, 0.1766, 0.4502; O1 (4b): 0.71224, 0.6813, 0.4804; O2 (2a): 0, 0.1175, 0.8496; O3 (2a): 0, 0.8205, 0.2820</td>
</tr>
<tr>
<td></td>
<td>$Pbnm$</td>
<td>Li (4a): 0.1607, 0.0034, 0.2580; Li (4a): 0.4233, 0.7444, 0.2582; Mn (4a): 0.1660, 0.4965, 0.2589; Si (4a): 0.4141, 0.2524, 0.2640; O1 (4a): 0.4122, 0.2544, 0.5911; O2 (4a): 0.5566, 0.2520, 0.1557; O2 (4a): 0.3312, 0.0360, 0.1641; O2 (2a): 0.3445, 0.4668, 0.1528</td>
</tr>
<tr>
<td>Li$_2$CoSiO$_4$</td>
<td>$I222$</td>
<td>Li (4d): −0.1/2, 0, 0; Mn (2b): −0.1/2, 0, 0; Si (2a): 0, 0, 0; O (8i): 0.2132, 0.2133, 0.1288</td>
</tr>
<tr>
<td>Li$_2$NiSiO$_4$</td>
<td>$Pn$</td>
<td>Li (2a): 0.9877, 0.1662, −0.6999; O1 (2a): −0.3438, 0.1719, −0.3454; O3 (2a): 0.2617, 0.2613, −0.4081; O3 (2a): −0.1232, 0.6891, −0.4081; O4 (2a): −0.6863, 0.3080, −0.6878</td>
</tr>
<tr>
<td></td>
<td>$P2_1$</td>
<td>Li (2a): 0.6593, 0.9166, 0.6623; Li (2a): 0.1598, 0.8134, 0.1621; Li (2a): 0.5818, 0.4112, 0.0884; Li (2a): 0.0815, 0.383, 0.5883; Ni (2a): 0.2879, 0.9167, 0.5398; Ni (2a): 0.7866, 0.8136, 0.0363; Si (2a): 0.0444, 0.8106, 0.7953; Si (2a): 0.5449, 0.9200, 0.2955; O1 (2a): 0.8656, 0.9064, 0.8318; O2 (2a): 0.2958, 0.9212, 0.8823; O4 (2a): 0.9263, 0.4183, 0.3824; O5 (2a): 0.6875, 0.8084, 0.4409; O6 (2a): 0.1873, 0.9218, 0.9408; O7 (2a): 0.9514, 0.9829, 0.2049; O8 (2a): 0.4305, 0.7475, 0.7407</td>
</tr>
<tr>
<td></td>
<td>$Pmn2_1$</td>
<td>Li (4b): 0.751, 0.3256, 0.9365; Ni (2a): 0.1818, 0.4359; Si (2a): 0, 0.16204, 0.4497; O1 (4b): 0.7119, 0.6922, 0.8502; O2 (2a): 0.1275, 0.8372; O3 (2a): 0.8439, 0.285</td>
</tr>
</tbody>
</table>

Table 2. Theoretically calculated (derived from the total energies) equilibrium lattice parameters (a, b and c in Å) for Li$_2$MSiO$_4$ polymorphs.

In order to determine the critical pressure of these structural transitions we have displayed in Figure 3 the Gibbs free-energy of the involved crystallographic structures, using the low energy structure as a reference for every pressure value. As discussed above, $Pmn2_1$ is the more favourable structure, and it transforms into the $I222$ modification at 8.2 GPa (see Figure 3). The $I222$ structure is...
closely related to the I-42m (space group 121). These modifications are found to have the same energy within standard DFT accuracy.

3.1.2. Li$_2$CoSiO$_4$

Like Li$_2$MnSiO$_4$, Li$_2$CoSiO$_4$ also crystallises in four different polymorphs [62–64] which can be formed by rapid cooling (0.5 °C min$^{-1}$) from above 1000 °C resulted in the formation of Pmnb, while slow cooling (0.1 °C min$^{-1}$) produced the P2$_1$/n phase. Pmn2$_1$ was formed by static heating of any other phase at 640–800 °C followed by quenching, and Pbn2$_1$ was formed by slow cooling of Pmn2$_1$ [56].

Monoclinic Li$_2$CoSiO$_4$ (P2$_1$/n) was prepared at 950 °C and transformed (at 900 °C) into the orthorhombic Pmn2$_1$ and Pna2$_1$ phases under 40/60 kbar, respectively. Both cell volumes are smaller than in the monoclinic case. [62] Orthorhombic Li$_2$CoSiO$_4$ (Pmn2$_1$) was synthesised hydrothermally.
(150 °C/72 h). It transformed to the orthorhombic (Pna2₁) phase when heated at 700 °C over 2 h and to a monoclinic (P2₁/n) phase at 1100 °C over 2 h [65].

Theoretically simulated energy-volume curves for Li₂CoSiO₄ are displayed in Figure 4. According to our simulation at 0 K, Li₂CoSiO₄ crystallises in orthorhombic (Pbn2₁) and has lower energy than the other structures. This structure is based on a distorted hexagonal-close-packing arrangement of O atoms with layers stacked parallel to (001) [64]. The cations occupy half of the available tetrahedral sites and are distributed over the sites on one side of the O layers; three of the four O atoms forming a cation-oxygen tetrahedron (MO₄) are in an O layer, and all pyramids of the MO₄ tetrahedra have the same orientation with respect to the layer. The SiO₄ and LiO₄ tetrahedral pairs share corners to form a chain along a, and these chains are held together through other corners, thus forming puckered layers parallel to (010). In the same way, the CoO₄ and LiO₄ tetrahedral pairs form a chain along a, and these chains also form puckered layers parallel to (010). These two kinds of layers are held together through common corners, thus forming a three-dimensional framework. This structure is isotypic with the low-temperature form of Li₃PO₄ [66] and essentially the same as that of Li₂ZnSiO₄ [64]. It is interesting to note that, in addition to the Pbn2₁ phase, the Pn and the Pmn2₁-mod phases exhibit also very similar energies and equilibrium volumes. The involved energy difference between with respect to Pbn2₁ are 0.8 and 1.8 meV for Pn and Pmn2₁-mod, respectively. This proximity in energy clearly suggests that one can easily change the structure from one phase to another. Application of pressure on this Pbn2₁ modification transforms it into Pmn2₁-mod at 1.4 GPa. Larger pressures would transform this phase into Pmn2₁ and then into the I222 structure. The involved pressure for the phase transition between the Pbn2₁–to–Pmn2₁-mod, Pmn2₁-mod–to–Pmn2₁, and Pmn2₁–to–I222 are 1.4, 5.4 and 20.2 GPa, respectively.

![Figure 4](attachment:image.png)

**Figure 4.** Calculated unit cell volume vs. total energy (per formula unit; f.u.) for Li₂CoSiO₄ in actual and possible structural arrangements (structure types being labeled on the illustration). The magnified version in proximity of the minima of the curves is shown as an insert.

### 3.1.3. Li₂NiSiO₄

Similar to the others two compounds described in this manuscript Li₂NiSiO₄ is also observed most frequently in its orthorhombic structure (Pmn2₁). DFT calculations predict that Li₂NiSiO₄ has very large deintercalation potentials (4.5 V for Ni²⁺/Ni³⁺ and 5.2 V for Ni³⁺/Ni⁴⁺) [20,67], resulting in a challenging electro-chemical behaviour, even though the Li₂NiSiO₄ powder had been successfully
The application of an even larger pressure would produce the lower band gap width. These phases exhibit, however, the worst ionic conductivity in potentially improving the electrical conductivity in these materials. Plots of these quantities are shown in Figure 5. Among the Li silicates, the HP-Li$_2$MnSiO$_4$ exhibits similar total energies (see Figure 5). The next energetically favorable structure is shown in Figure 5. Among the 11 structure types considered here, the monoclinic $P2_1$ and $P2_1/n$ structures exhibit similar total energies (see Figure 5). The next energetically favorable structure is $Pmn2_1$ modification. At the equilibrium volume, the energy difference between these three phases is indeed very small. The involved energy difference between the $P2_1$ and $Pmn2_1$ is only 12 meV (see Figure 5). This proximity in energy suggests that the formation of these phases will strongly depend on external temperature/pressure conditions. For the $Pmn2_1$ modification, the calculated structural parameters are also in very good agreement with the observations [9]. The calculated cell parameters differ by less than 1% from the experimental values. $P2_1$ is found to be the more favourable configuration and to transforms into the $Pmn2_1$–modification at 0.7 GPa. The application of an even larger pressure would produce the I222 modification at 15.9 GPa as shown in Figure 3.

![Figure 5](image_url)

**Figure 5.** Calculated unit cell volume vs. total energy (per formula unit; f.u.) for Li$_2$NiSiO$_4$ in actual and possible structural arrangements (structure types being labelled on the illustration). The magnified version is proximity of the minima of the curves is shown as an insert.

### 3.2. Electronic Structure

In general, the poor electronic conductivity is known as a limiting factors for the application of silicates as electrodes [4–8]. In the present work, we calculate the total density of states (DOS) and its projection onto atomic orbitals (PDOS) for Li$_2$MSiO$_4$, with the aim of better understanding and potentially improving the electrical conductivity in these materials. Plots of these quantities are shown in Figure 6 (only for Li$_2$MnSiO$_4$ in $Pmn2_1$ is displayed and the remaining are shown in Figures S1–S4), and the calculated band gaps of Li$_2$MSiO$_4$ are reported in Table 3. Li$_2$MSiO$_4$ modifications exhibit large band gaps (>1.3 eV), and are consequently poor conductors of electrons. It is well known that the bandgap ($E_g$) values of solids obtained using standard DFT calculations are underestimated due to the discontinuity in the exchange-correlation potential. These values are commonly 30–50% smaller than the experimental references. Hence, the compounds under examination are likely to have a larger bandgap value than the one computed in this study. Among the Li silicates, the HP- Li$_2$MnSiO$_4$ phases present the lower band gap width. These phases exhibit, however, the worst ionic conductivity in the series. The electronic conductivity is increased but the layer to layer interactions are decreases as a result the ionic conductivity decreases. The calculated total and site projected up and down spin
DOS of Li$_2$MnSiO$_4$ in $Pmn2_1$ phase is shown in Figure 7 where the vertical line indicates Fermi level ($E_F$). The DOS histogram of Li$_2$MnSiO$_4$ consists of three parts: (a) the low-energy peak, mainly due to the localised semi-core $s$ electrons of Si, (b) the bonding states of $M$-$d$, Si-$p$, O-$p$, and Li-$s$ orbitals near the Fermi level; and (c) the top of the DOS curve due to antibonding states. It is found that the Si-$s$ electrons are localized and naturally their contribution to the bonding is very small. The electrons from $M$-$d$, Si-$p$ and the O-$2p$ states both contribute to the density of states near to the Fermi level. The DOS of $M$-$d$, Si-$p$ and the O-$p$ are energetically degenerate from the bottom of the valence band to the Fermi level, indicating the possibility of covalent bonding between Si and O, M and O atoms in all these compounds. Due to the charge transfer from the Li site the contribution of the Li-$s$ states are very small (see Figure 7).

![Figure 6](image1.png)

**Figure 6.** Calculated electronic up-spin (a) and down-spin (b) band structure of Li$_2$MnSiO$_4$ in $Pmn2_1$ structure. The Fermi level is set to zero.

![Figure 7](image2.png)

**Figure 7.** Calculated electronic up-spin and down-spin total DOS and site projected DOS of Li$_2$MnSiO$_4$ in $Pmn2_1$. The Fermi level is set to zero.
Table 3. The calculated single crystal elastic constants $C_{ij}$ (in GPa), bulk modulus $B$ (in GPa), shear modulus $G$ (in GPa), Possion’s ratio ($\nu$), Young’s modulus $E$ (in GPa), compressibility ($\text{GPa}^{-1}$), Ductility, Lamé constant, longitudinal ($\nu L$; in m/s), transverse ($\nu T$; in m/s), and average sound velocity ($\bar{v}$ in m/s), and Debye temperature ($\Theta_D$) for Li$_2$MnSiO$_4$ polymorphs. Subscript $V$ indicates the Voigt bound, $R$ indicates the Reuss bound and VRH indicates the Hill average.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Li$_2$MnSiO$_4$</th>
<th>Li$_2$CoSiO$_4$</th>
<th>Li$_2$NiSiO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase</td>
<td>Pmn2$_1$</td>
<td>Pbn2$_1$</td>
<td>I222</td>
</tr>
<tr>
<td>$C_{11}$</td>
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<td>124</td>
<td>312</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>66</td>
<td>65</td>
<td>165</td>
</tr>
<tr>
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<td>55</td>
<td>141</td>
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<td>157</td>
<td>320</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>42</td>
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<tr>
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<tr>
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<tr>
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<td>208</td>
</tr>
<tr>
<td>$\nu_{T}$</td>
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<td>88</td>
<td>181</td>
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<tr>
<td>$\nu_{L/P}$</td>
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<td>88</td>
<td>195</td>
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</tr>
<tr>
<td>$\nu_{E}$</td>
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<td>589</td>
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<td>621</td>
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<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>Ductility</td>
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<td>0.5</td>
<td>1.64</td>
</tr>
<tr>
<td>Lamé constant</td>
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<td>61</td>
<td>−19</td>
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<tr>
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<td>−0.03</td>
</tr>
<tr>
<td>$\tau_{L}$</td>
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<td>13709</td>
</tr>
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<td>3643</td>
<td>9841</td>
</tr>
<tr>
<td>$\tau$</td>
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<td>10646</td>
</tr>
<tr>
<td>$\phi_{D}$</td>
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<td>1485</td>
<td>4038</td>
</tr>
</tbody>
</table>

3.3. Dynamical Stability

The total phonon density of states are calculated at the equilibrium volumes for different polymorphs of Li$_2$MnSiO$_4$ (shown in Figure 8). For the I222 modifications, the PhDOS are calculated at the phase transition point. The calculated PhDOS of Li$_2$MnSiO$_4$ polymorphs are displayed in Figure 8. Similarly, the total PhDOS of Li$_2$CoSiO$_4$ and Li$_2$NiSiO$_4$ are shown in Figure S5. For all the considered structures, imaginary frequencies were not observed (with the only exception of the I222 structure), indicating that all the structures dynamically stable at ambient conditions. The soft phonon modes observed for the I222 modification at the equilibrium volume disappear at pressures above 8.2 GPa for Li$_2$MnSiO$_4$ and 20.2, and 15.9 GPa for Li$_2$CoSiO$_4$ and Li$_2$NiSiO$_4$, respectively (see Figure 8 and Figure S4). Hence, these phases are predicted to be stable at the corresponding pressures (above the phase transition point). All the polymorphs of Li$_2$MnSiO$_4$, including the high-pressure phase, exhibit a similar phonon density of states. It is interesting to note that for the Li$_2$MnSiO$_4$ phase the energy difference between the $Pmn2_1$, $Pmn2_1$-mod., $Pc$, $P2_1/n$, and $Pmnb$ phases are very small and, hence, one can easily modify one polymorph into another by application of temperature or pressure. Because of the similarity in the phonon spectra, we have displayed in Figure 9 only the partial phonon DOS for $Pmn2_1$ polymorphs. In the $Pmn2_1$ phase, the site projected phonon DOS is plotted in Figure 9 for Li, Fe, Si, and O atoms Figure 9. Because of the heavier mass of the Mn atom, the lower frequency modes in the phonon spectra are mainly originated from the Mn contribution. Due to their similar atomic arrangement, of the O atoms exhibit similar phonon density, even though they are located at different crystallographic sites, labelled O1, O2 and O3. The calculated zero-point energy (ZPE) for the Li$_2$MnSiO$_4$ polymorphs varies from 0.48 to 0.68 eV/f.u. (see Table S1). Among the studied phases, the $Pbn2_1$-Li$_2$CoSiO$_4$ and $Pmn2_1$-Li$_2$NiSiO$_4$ phases have the minimum ZPE value and I222-Li$_2$CoSiO$_4$ has the maximum value. However, the calculated ZPE for the ambient phases (for example $Pmn2_1$, $Pmn2_1$-modi, $Pbn2_1$ modifications in Li$_2$MnSiO$_4$) are very close to each other. This finding suggests that...
the exclusion of the temperature effect is not expected to significantly affect our conclusion regarding the transition pressures reported in the present study.

![Graph](image)

**Figure 8.** Calculated total phonon density of states for Li$_2$MnSiO$_4$ in different modifications. The modifications are noted in the corresponding panel.

![Graph](image)

**Figure 9.** Calculated site projected phonon density of states for Li$_2$MnSiO$_4$ in $Pmn2_1$ modification. The corresponding sites are noted in the panel. The oxygen atoms are occupied in three different sites O1(4a), O2(2a), and O3(2a) are marked as O1, O2, and O3 in the figure.

### 3.4. Single-Crystal Elastic Constants and Mechanical Stability

The absence of imaginary phonon frequencies is not sufficient to validate the overall stability of a certain crystal, as it indicates its stability with respect to positional coordinates, without considering the lattice degrees of freedom. Our study is this completed by evaluating the mechanical stability by computing the single-crystal elastic constants. A set of strains is applied to the crystal cell, and the stress tensor is calculated. The elastic constants are then evaluated by linear fitting of the stress-strain curve.
The elastic constants describe the linear response of a material to an applied deformation, usually described in terms of tensile and shear components. Following the Voigt notation, we write the elastic constants as a $6 \times 6$ symmetric matrix, having in principle 27 independent components. The stress/strain relation is then written as $S_{ij} = C_{ij} \varepsilon_j$ for small stresses, $\sigma$, and strains, $\varepsilon$ for $i, j = 1, 2, \ldots, 6$ [68].

\[
\begin{pmatrix}
  S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\
  S_{21} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\
  S_{31} & S_{32} & S_{33} & S_{34} & S_{35} & S_{36} \\
  S_{41} & S_{42} & S_{43} & S_{44} & S_{45} & S_{46} \\
  S_{51} & S_{52} & S_{53} & S_{54} & S_{55} & S_{56} \\
  S_{61} & S_{62} & S_{63} & S_{64} & S_{65} & S_{66}
\end{pmatrix} =
\begin{pmatrix}
  C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
  C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
  C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
  C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
  C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
  C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66}
\end{pmatrix} \begin{pmatrix}
  \varepsilon_{11} \\
  \varepsilon_{22} \\
  \varepsilon_{33} \\
  2\varepsilon_{23} \\
  2\varepsilon_{13} \\
  2\varepsilon_{12}
\end{pmatrix}
\]

Structural symmetries simplify the general formula, as the response of the system to different deformation is the same. A cubic crystal, for example, has only three independent elements ($C_{11}$, $C_{12}$ and $C_{44}$), each of which represents three equal elastic constants ($C_{11} = C_{22} = C_{33}$; $C_{12} = C_{23} = C_{31}$; $C_{44} = C_{55} = C_{66}$). A single strain with non-vanishing first and fourth components can be used to calculate stresses relating to all three of these coefficients, yielding a very efficient method for obtaining elastic constants. A full account of the symmetry of stress, strain and elastic constants is given by Nye [69].

The elastic constants contain all the information regarding deformation of the crystal, and can be used to evaluate average properties such as the bulk modulus (response to an isotropic compression), the Poisson coefficient, and the Lamé constants. Within the Voigt approximation, the bulk and shear moduli can be written in terms of the elastic constants as:

\[
B_{\text{Voigt}} = \frac{1}{9} [(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{23} + C_{13})] 
\]

and:

\[
G_{\text{Voigt}} = \frac{1}{15} \left( C_{11} + C_{22} + C_{33} - 2(C_{12} + C_{23} + C_{13}) + \frac{1}{5} (C_{44} + C_{55} + C_{66}) \right) 
\]

alternatively, the Reuss approximation can be used, which relies on the elements of the compliance tensor $S_{ij}$ (the inverse of the stiffness tensor). The bulk modulus is given by:

\[
\frac{1}{B_{\text{Reuss}}} = \left[ (S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{23} + S_{13}) \right] 
\]

and the shear modulus is:

\[
\frac{15}{G_{\text{Reuss}}} = 4[(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{23} + S_{13}) + 3(S_{44} + S_{55} + S_{66})] 
\]

In general, for polycrystalline materials, the Voigt approximation gives the upper bound on the elastic moduli, while the Reuss approximation gives the lower bound [70]. The two approximations can be averaged in the Voigt-Reuss-Hill (VRH) form for the bulk modulus:

\[
B_{\text{VRH}} = \frac{B_{\text{Voigt}} + B_{\text{Reuss}}}{2} 
\]

the shear modulus:

\[
G_{\text{VRH}} = \frac{G_{\text{Voigt}} + G_{\text{Reuss}}}{2} 
\]

and the Young’s modulus ($E$):

\[
E_{\text{VRH}} = \frac{9B_{\text{VRH}} \times G_{\text{VRH}}}{3B_{\text{VRH}} + G_{\text{VRH}}} 
\]
The Poisson ratio $\sigma$ is then obtained by:

$$\sigma = \frac{3B_{VHR} - 2G_{VHR}}{6B_{VHR} + 2G_{VHR}}$$  \hspace{1cm} (8)

Using Poisson’s ratio, ductility and brittleness of materials may be tested as suggested in reference [71]. For brittle material, $\sigma$ is below 0.33, while for a ductile material, $\sigma = 0.33$.

Lamé constant ($\lambda$):

$$\lambda_{VHR} = B_{VHR} - \frac{2G_{VHR}}{3}$$  \hspace{1cm} (9)

The quantities can also be used to compute the speed of sound for the transverse and longitudinal waves, using the relations [72] for the speed of sound for the longitudinal waves:

$$v_L = \sqrt{\left(\frac{B + \frac{4}{3}G}{\rho}\right)}$$  \hspace{1cm} (10)

and for the transverse waves

$$v_T = \sqrt{\left(\frac{G}{\rho}\right)}$$  \hspace{1cm} (11)

where $\rho$ is the mass density of the material. The average speed of sound is then evaluated by

$$\dot{v} = \left[\frac{1}{3} \left(\frac{2}{v_T^3} + \frac{1}{v_L^3}\right)\right]^{-\frac{1}{2}}$$  \hspace{1cm} (12)

The Debye temperature of a solid can be written as [53]:

$$\theta_D = \frac{h}{k_B} \left[\frac{6\pi^2 n}{V}\right]^{\frac{1}{3}} \dot{v}$$  \hspace{1cm} (13)

where $n$ is the number of atoms in the cell, $V$ is its volume, and $\dot{v}$ is the average speed of sound of Equation (12). In addition to the above mentioned parameters once can also calculate the compressibility of the materials defined as the inverse of the bulk modulus ($1/B_{VHR}$). The ductility i can be estimated by applying Pugh’s criteria [73]. According to Pugh, a material is ductile if $G_{H}/B_{H}$ is smaller than 0.5, otherwise the material is brittle. The linear fitting of the stress-strain curve has been successfully used to study the elastic response of a range of materials including simple metals (such as Al) [74], super hard nitrides [75], borides [76,77], oxides [78], silicates [79], and semiconductors [80]. The results of these studies show that the accuracy of DFT elastic constants is typically within 10% of the experiment. The calculated values of bulk moduli, shear moduli, Young’s moduli and Poisson’s ratio are tabulated in Table 3. All these compounds exhibit similar values of the bulk and Young’s modulus. The compressibility value of these polymorphs suggested that these compounds are very soft materials. A parameter B/G is also introduced, in which B indicates the bulk modulus and G represent the shear modulus. The bulk and shear moduli are calculated from the Voigt–Reuss–Hill approximations [81–83]. The high (low) G/B value is associated with ductility (brittleness) and the critical value which separates ductile and brittle materials is 0.5 [73]. The calculated G/B values for these compounds are lower than 0.5, implying the ductile characteristics of materials and the stable cycle performance.

In general, the elastic energy of a system subjected to an infinitesimal strain can be written as

$$U = \varepsilon_i C_{ij} \varepsilon_j.$$  \hspace{1cm} (14)

The system is defined to be stable if $U > 0$ for every arbitrary strain $\varepsilon$. The elastic constant matrix $C_{ij}$ is therefore required to be positive definite. This proposition is equivalent to any of the following [84]:

$$\varepsilon_i C_{ij} \varepsilon_j > 0.$$  \hspace{1cm} (15)
1) The eigenvalues of $C_{ij}$ are positive.
2) Every leading principal (or trailing) minor, including determinants of $C$ is positive.

The second condition if also known as Sylvester’s criterion. Analytical formula can be readily obtained from these conditions and are reported in literature for simple crystal structures. It is also possible to verify them numerically by means of computational linear algebra routines. This second approach has been followed in this work. The calculated eigenvalues and minors are reported in Table 4 and all are positive for the studied phases. Hence, the studied phases are mechanically stable polymorphs.

Table 4. The calculated eigenvalues and minors of elastic tensor for the studied phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Leading Minors (GPa$^a$)</th>
<th>Trailing Minors (GPa$^a$)</th>
<th>Eigenvalues (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnSiO$_4$-Pmn2$_1$</td>
<td>1.92 $\times$ 10$^2$ 2.02 $\times$ 10$^4$</td>
<td>2.09 $\times$ 10$^{11}$ 1.47 $\times$ 10$^9$</td>
<td>2.83 $\times$ 10$^2$ 8.64 $\times$ 10$^1$</td>
</tr>
<tr>
<td>Li$_2$MnSiO$_4$-Pmn2$_1$-mod</td>
<td>1.19 $\times$ 10$^2$ 1.51 $\times$ 10$^4$</td>
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<td>2.34 $\times$ 10$^2$ 7.92 $\times$ 10$^1$</td>
</tr>
<tr>
<td>Li$_2$MnSiO$_4$-Pbn2$_1$</td>
<td>1.24 $\times$ 10$^2$ 1.52 $\times$ 10$^4$</td>
<td>1.09 $\times$ 10$^{11}$ 1.20 $\times$ 10$^9$</td>
<td>2.67 $\times$ 10$^2$ 7.24 $\times$ 10$^1$</td>
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<tr>
<td>Li$_2$CoSiO$_4$-I222</td>
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<tr>
<td>Li$_2$CoSiO$_4$-Pmn2$_1$</td>
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<tr>
<td>Li$_2$CoSiO$_4$-Pmn2$_1$</td>
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<td>2.12 $\times$ 10$^{11}$ 1.21 $\times$ 10$^9$</td>
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<tr>
<td>Li$_2$CoSiO$_4$-I222</td>
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<td>Li$_2$NiSiO$_4$-P2$_1$/n</td>
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<td>1.38 $\times$ 10$^{13}$ 6.74 $\times$ 10$^10$</td>
<td>6.49 $\times$ 10$^2$ 6.74 $\times$ 10$^1$</td>
</tr>
</tbody>
</table>
3.5. Diffusion Coefficient and Ionic Conductivity

We describe here the diffusion pathways for the transport of Li$^+$ ions and the associated activation energies. The latter quantities are evaluated using the NEB method, and the diffusion coefficients $D$ are then obtained using the equation:

$$D = d^2 \vartheta_0 \exp\left(\frac{-E_a}{k_B T}\right)$$

where $d$ is the hopping distance, $E_a$ the activation energy, $k_B$ the Boltzmann constant, $T$ the temperature and the attempt frequency (assumed to be $10^{13}$ Hz). In our extensive work on the diffusion of Li/Na within electrolyte or electrode materials, we have always found that converged results are obtained with 5 intermediate images for the neb calculations, for a total of 7 images considering the starting and the final configurations. According to our experience, calculations using an odd number of images converge more rapidly to the correct activation energy. This is due to the fact that, if the initial and final minima are equivalent, the saddle point if often located in the middle position, corresponding to the $(n+1)/2$ position where $n$ is the total number of images. With this in mind, we have reproduced one of our calculations (the first hop within the Li$_2$MnSiO$_4$ structure) using seven intermediate images. The comparison between these simulations is reported in Figure S6. The cubic splines, computed using the forces resulting from the NEB calculations, are indicated with solid lines, while the energy of the minima and of intermediate configurations are indicated with dots. As can be noted, the two splines are nearly overlapping, and the position of the saddle point and the associated energy (i.e., the activation barrier) are in perfect agreement. Hence, in the rest of the configurations we have used only five intermediate images.

The structures of Li$_2$MSiO$_4$ materials obtained from different synthesis methods further affect the lithium intercalation behavior [85]. The calculated diffusion barriers for the low energy structures of the studied phases are listed in Table 5. In this section, we present only the low energy configurations of the Li$_2$MSiO$_4$ materials with more details. In the case of Li$_2$MnSiO$_4$, all the lithium ions are located at $4b$ Wyckoff sites. Two hops are found to regulate the diffusion along this network. These are labelled as (i) and (ii) and are indicated in Figure 10a using ball and stick models. These hops have length 3.12 and 3.18 Å respectively, and associated activation energies of 0.78 and 0.86 eV respectively (see Figure 11a). The associated energy curves along the MEP are displayed in Figure 11a, with yellow and green lines respectively. As clear from Figure 10a, the diffusion along the c direction is regulated only by type (i) hops, whereas diffusion along a by type (ii) segments. Diffusion along b is not considered within our model, as the hop required to form a percolating path along this direction would have a length larger than 4 Å, and it is therefore unlikely to occur. These calculation reveal Li$_2$MnSiO$_4$ as a mediocre 2D conductor of Li ions.

In the case Li$_2$CoSiO$_4$, two inequivalent Li atoms are found, both located at $4a$ Wyckoff positions, indicated in Figure 10b using yellow and green spheres. Sticks connecting spheres indicate the possible hops for a Li vacancy within a 4 Å cutoff. Only hops connecting inequivalent Li atoms are available. Three inequivalent hops are found, labelled (i), (ii), and (iii) in Figure 10b with respective lengths of 2.99, 3.08, and 3.26 Å. The activation barriers for vacancy hopping along these distances are calculated to be 0.42, 0.71, and 0.85 eV. The energy curve along the MEP is reported in Figure 10b for these hops in green, blue, and yellow, respectively. Note that the extrema of these curves are shifted with respect to each other, indicating that the formation of a vacancy at site 1 (green sphere) is more favourable by 0.17 eV. These segments are used to construct percolating paths, considered to model the diffusion of Li atoms along independent directions. Indeed, the activation energies are to be anisotropic. Diffusion along the a direction is described defining two distinct percolating paths, as clear from Figure 10b. The first path is comprised by hops (i) and (iii), and the second one by (ii) and (iii). Due to the fact that hop (iii) is included in both both and it is the one with largest associated diffusion barrier, we can conclude that the activation energy for diffusion along a is 0.85 eV. While diffusion along b is
regulated by the same processes, a third percolating path, comprised by (ii) hops only, best describes diffusion along the c direction. The associated activation energy in this case is found to be 0.71 eV (see Figure 11b). Taking all together, Li$_2$CoSiO$_4$ is found to be a mediocre conductor of Li ions.

Table 5. Calculated barrier height (in eV), Li-Li migration distance (in Å), and diffusion coefficient (D; cm$^2$ s$^{-1}$) for Li$_2$SiO$_4$ phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Barrier Height</th>
<th>Li-Li Distance</th>
<th>Diffusion Coefficient at 300 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnSiO$_4$-Pmn2$_1$</td>
<td>0.78</td>
<td>3.12</td>
<td>7.6 × 10$^{-16}$</td>
</tr>
<tr>
<td></td>
<td>0.86</td>
<td>3.18</td>
<td>3.6 × 10$^{-18}$</td>
</tr>
<tr>
<td>Li$_2$MnSiO$_4$-Pbn2$_1$</td>
<td>0.68</td>
<td>3.03</td>
<td>3.4 × 10$^{-15}$</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>3.09</td>
<td>1.6 × 10$^{-15}$</td>
</tr>
<tr>
<td></td>
<td>0.73</td>
<td>3.12</td>
<td>5.3 × 10$^{-16}$</td>
</tr>
<tr>
<td>Li$_2$MnSiO$_4$-I222</td>
<td>1.2</td>
<td>3.12</td>
<td>6.7 × 10$^{-24}$</td>
</tr>
<tr>
<td></td>
<td>1.23</td>
<td>3.20</td>
<td>2.2 × 10$^{-24}$</td>
</tr>
<tr>
<td>Li$_2$CoSiO$_4$-Pbn2$_1$</td>
<td>0.43</td>
<td>2.99</td>
<td>5.3 × 10$^{-10}$</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>3.08</td>
<td>2.4 × 10$^{-15}$</td>
</tr>
<tr>
<td></td>
<td>0.86</td>
<td>3.26</td>
<td>3.8 × 10$^{-17}$</td>
</tr>
<tr>
<td>Li$_2$CoSiO$_4$-Pmn2$_1$-mod</td>
<td>0.74</td>
<td>3.24</td>
<td>3.9 × 10$^{-16}$</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>3.33</td>
<td>5.9 × 10$^{-17}$</td>
</tr>
<tr>
<td>Li$_2$CoSiO$_4$-I222</td>
<td>1.1</td>
<td>3.03</td>
<td>3.0 × 10$^{-22}$</td>
</tr>
<tr>
<td></td>
<td>1.31</td>
<td>3.31</td>
<td>1.08 × 10$^{-25}$</td>
</tr>
<tr>
<td>Li$_2$NiSiO$_4$-P2$_1$</td>
<td>0.67</td>
<td>2.72</td>
<td>4.1 × 10$^{-15}$</td>
</tr>
<tr>
<td></td>
<td>0.74</td>
<td>3.09</td>
<td>3.5 × 10$^{-16}$</td>
</tr>
<tr>
<td></td>
<td>0.74</td>
<td>3.10</td>
<td>3.5 × 10$^{-16}$</td>
</tr>
<tr>
<td></td>
<td>0.77</td>
<td>3.24</td>
<td>1.2 × 10$^{-16}$</td>
</tr>
<tr>
<td>Li$_2$NiSiO$_4$-Pmn2$_1$</td>
<td>0.85</td>
<td>3.12</td>
<td>5.1 × 10$^{-18}$</td>
</tr>
<tr>
<td></td>
<td>0.89</td>
<td>3.27</td>
<td>1.2 × 10$^{-18}$</td>
</tr>
<tr>
<td>Li$_2$NiSiO$_4$-I222</td>
<td>1.07</td>
<td>3.12</td>
<td>1.0 × 10$^{-21}$</td>
</tr>
</tbody>
</table>
|                      | 1.12           | 3.27           | 1.6 × a10$^{-22}$             

Figure 10. Li ion migration in different possible pathways (represented as i, ii, etc.) in (a) Li$_2$MnSiO$_4$ (Pmn2$_1$), (b) Li$_2$CoSiO$_4$ (Pbn2$_1$), and (c) Li$_2$NiSiO$_4$ (P2$_1$) used for NEB simulation.
Figure 11. Li ion migration in different possible path ways in (a) Li$_2$MnSiO$_4$ ($Pmn2_1$), (b) Li$_2$CoSiO$_4$ ($Pbn2_1$), and (c) Li$_2$NiSiO$_4$ ($P2_1$) obtained from NEB method. The connected lines are just to give a visual help of the sequence of images. The symbols represent calculated data points.

In the case of Li$_2$NiSiO$_4$, the Li atoms are located at four inequivalent 2$a$ Wyckoff sites, indicated in Figure 10c with green, yellow, purple and brown spheres. The vacancy formation energies for these atoms are comparable, being within a 50 meV energy window, and diffusion along the whole network is possible. We have considered four hops within this Li frame connecting frame, with length smaller than 4 Å. The first one, labelled as (i) and indicated in Figure 10c using a stick connecting spheres, connects Li1 and Li3, indicated with green and purple spheres respectively. The hop length is 3.11 Å, and the associated activation energy 0.74 eV. The second hop, connects Li1 and Li4, the latter indicated with a brown sphere, and has an activation energy of 0.74 eV.
We then considered hop three, between Li3 and Li4, with a length of 2.72 Å and an activation energy of 0.67 eV and hop four, between Li4 and Li2, with a length of 3.10 Å an activation energy of 0.74 eV (see Figure 11c). The ensemble of these hops form a percolating path within this layered structure, as clear from Figure 10c. The activation energy for Li-ion diffusion is therefore calculated to be 0.74 eV. In Figure 12 the results obtained for the natural logarithm of the diffusion coefficient in the low energy structures of Li2MSiO4 phases are displayed as a function of 1/T. The activation barrier is proportional to the slope of each straight line. The diffusion coefficient calculated in Li2MSiO4 polymorphs at room temperature, ranges from $10^{-25}$ cm$^2$/s up to $10^{-16}$ cm$^2$/s. On the other hand, the diffusion coefficient in commercial materials (e.g., Li2CoO2) is typically ranging from $10^{-13}$ cm$^2$/s to $10^{-7}$ cm$^2$/s. It is then clear that Li2MSiO4 phases cannot provide at the moment better kinetics than the state-of-the-art materials. However, by tailoring the particle size of the Li2FeSiO4 one can reduce the diffusion coefficient below $10^{-7}$ cm$^2$/s [86]. A similar effect can be expected on these studied phases and the investigation is under progress.

![Figure 12](image_url)

**Figure 12.** Natural logarithm of the diffusion coefficient against 1/T for different possible path ways in Li2MnSiO4 ($Pmn\overline{2}1$), Li2CoSiO4 ($Pbn\overline{2}1$), and Li2NiSiO4 ($P2_1$) obtained from NEB method. For the clarity of the figure only equilibrium structures natural logarithm of the diffusion coefficient against 1/T are shown in the figure.

4. Conclusions

In summary, the relative stability of Li2MSiO4 ($M = \text{Mn, Co, and Ni}$), electronic, lattice dynamics, mechanical, and electrochemical properties have been investigated, using density functional theory within the GGA approximation plus on-site Coulomb energy correction (U). According to our theoretical simulation, at ambient condition, Li2MSiO4, Li2CoSiO4, and Li2NiSiO4 are stabilized in the $Pmm\overline{2}1$, $Pbn\overline{2}1$, and $P2_1$ structures, respectively. When an external pressure is applied, the ground state structure of Li2MnSiO4 in $Pmm\overline{2}1$ transforms into the $I222$ modification at 8.2 GPa. For Li2CoSiO4, the following phase transition sequence was identified; $Pbn\overline{2}1 \rightarrow Pmn\overline{2}1\text{-mod} \rightarrow Pmm\overline{2}1 \rightarrow I222$ at 1.4, 5.4 and 20.5 GPa respectively. Similarly, for Li2NiSiO4 phase the following path was identified $P2_1 \rightarrow Pmn\overline{2}1 \rightarrow I222$ and the involved pressures are 0.7, and 15.9 GPa, respectively. The calculated structural data for these known phases are fitted very well with the experimental as well as other theoretical reports available in the literature. For all these compounds, several structures coexist within a very small energy window.
This proximity in energy clearly indicates that, depending upon the method of synthesis, one can stabilise either of these phases at ambient conditions and it might be a very challenging task for the experimentalist to get a phase pure sample. Furthermore, our vibrational analysis and single crystal elastic constant study clearly indicates that all these phases are dynamically as well as mechanically stable phases. Hence, one is more likely to obtain -multiphase materials. This might be solvable by a proper annealing procedure. However, during the battery cycling process these multiphases may form and the quantities of the phases may vary by the internal potential as well as chemical environment. The electronic structure of these phases revealed that all these compounds exhibit a finite energy gap between the valance and the conduction band. Hence, these compounds exhibit a poor electronic conductivity. Once the materials’ get amorphization or structural collapse were inhibited during lithium ion insertion/extraction from the host lattice, reversible structural changes and good cycling performances could be attained. Hence, it is important to understand the role of ion-substitution (either by one of the M atom or partial substitution of other transition metal), for stabilizing the structures, is an effective way to achieve high-capacity Li$_2$MSiO$_4$ materials. The work is under progress and the result will be publish in the forth coming article. Material-coating and optimization of the particle size/morphology are also applied as exterior modifying methods to enhance the electrochemical performance. From NEB calculation we found that the diffusion coefficients in Li$_2$MSiO$_4$ at room temperature are ranging from $10^{-25}$ cm$^2$/s up to $10^{-10}$ cm$^2$/s. The ionics is therefore suboptimal with respect to the current generation of state-of-the-art materials. More work is therefore required in order to improve the Li-ion diffusion in this class of materials.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/1996-1073/12/2/224/s1, Figure S1: Calculated electronic up-spin [(a) and (c)] and down-spin [(b) and (d)] band structure of Li$_2$MnSiO$_4$ in $Pmn2_1$ phase with [(a) and (b)] and without GGA+U correction [(c) and (d)]. The Fermi level is set to zero and marked by dotted line. The band gap value is changed from 2.1 eV to 2.9 eV when we include the GGA+U correction, Figure S2: Calculated electronic up-spin and down-spin band structure of Li$_2$MnSiO$_4$ in $P2/n$, $P2_1$, and $I-42m$ phases. The Fermi level is set to zero and marked by dotted line, Figure S3: Calculated electronic up-spin and down-spin band structure of Li$_2$CoSiO$_4$ in $Pn$, $Pn2_1$, and $I-42m$ phases. The Fermi level is set to zero and marked by dotted line, Figure S4: Calculated electronic up-spin and down-spin band structure of Li$_2$NiSiO$_4$ in $P2/n$, $Pn2_1$, $P2_1$, and $I-42m$ phases. The Fermi level is set to zero and marked by dotted line, Figure S5: Calculated total phonon density of states for Li$_2$CoSiO$_4$ and Li$_2$NiSiO$_4$ in different modifications. The modifications are noted in the corresponding panel, Figure S6: Comparison between the energetics along the minimum energy path calculated using 5 and 7 intermediate images, Table S1: Computational details for the phonon calculation, Energies 2019, 12, 224.

**Author Contributions:** Conceptualization, P.V.; methodology, P.V.; formal analysis, P.V and F.B.; investigation, H.F.; funding acquisition, H.F.

**Funding:** This research was funded by Research Council of Norway, Grant agreement no.: Nano-MILIB-143732 and SELiNaB-255441.

**Acknowledgments:** P.V. acknowledges the Research Council of Norway for providing the computer time (under the project number NN2875k and NS2875k ) at the Norwegian supercomputer (UNINETT Sigma2 AS).

**Conflicts of Interest:** The authors declare no conflict of interest.

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