The effect of Ni-doping on the stability of Li$_2$MnO$_3$ cathode material: a DFT study

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Abstract. The density functional theory with Hubbard parameter (DFT+U) incorporated within the Vienna Ab Initio Simulation Package was utilized to investigate the structural, electronic, elastic, and dynamical properties of pristine and Ni-doped Li$_2$MnO$_3$. The cluster expansion technique was used to generate the doped phases of Li$_2$MnO$_3$. The binary phase diagram predicted Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ as the most stable phase with the lowest heat of formation. The study shows that Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ is more thermodynamically stable than Li$_2$MnO$_3$ with a lower heat of formation. Additionally, the density of states showed that Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ has a narrower band gap of 1.54 eV compared to the undoped structure with a band gap of 1.89 eV which leads to a higher electrical conductivity of the material. The elastic constants show that both structures are mechanically stable and lastly the phonon dispersions showed that these structures are vibrationally stable with no presence of imaginary vibrations. Finally, based on the results, Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ can be proposed as potential cathode materials for use in lithium-ion batteries.

1 Introduction

Layered Li$_2$MnO$_3$ has attracted significant attention as a potential cathode material for lithium-ion batteries due to its excellent capacity, affordability, and environmental friendliness [1]. Despite these advantages, the material has limitations that make it impractical for widespread use. When the material is electrochemically activated at around 4.5 V, lattice oxygen redox occurs, which results in additional capacity. However, this process also causes irreversible free oxygen release and migration of transition metal ions, leading to low Coulombic efficiency and poor cycle stability [2, 3]. Moreover, the layer-to-spinel structural transition, characteristic of Mn migration into the Li layer, is believed to be directly related to the performance degradation of Li$_2$MnO$_3$[4]. Various techniques have been used to overcome these challenges, and doping with transition metals is the most effective approach.

A density functional theory (DFT) [5] showed that the movement of Mn atoms, facilitated by a sequence of MnO$_6$ distortions, leads to the breaking of existing Mn-O bonds and the formation of new bonds. By stabilizing MnO$_6$, the spinel-type transition can be suppressed.
Alternatively, transition-metal atoms can compensate for the Li$^+$ removal charge variation or contribute extra electrons to O during the discharge/charge process. Consequently, MnO$_6$ distortion is alleviated, and O vacancies are suppressed. It may also be possible to fix the O ions by doping atoms that form stronger bonds with O.

Various studies have been done on Ni doping [6, 7, 8]. In previous studies, this material was doped with transition metals at either the Mn or Li site. The substitutional doping method was employed, wherein other elements are used to replace either oxygen or transition metal atoms. This process stabilizes the material's structure and enhances its electrochemical performance [9]. A study by T. Matsunaga revealed that a partially Ni-doped Li$_2$MnO$_3$ contain a large number of stacking faults and exhibits significant cation mixing in the transition-metal layers which promotes the formation of smooth Li percolation paths, thus increasing the number of active Li ions and improving the charge–discharge capacity [10]. A study by A. Lanjan showed that doping with Ni improves Li$_2$MnO$_3$ stability by preventing the removal of oxygen [11].

In this paper, we explore various structural configurations of doped Li$_2$Mn$_{1-x}$Ni$_x$O$_3$ derived from the unique cluster expansion (CE) code and investigate the structural, electronic, elastic and dynamic properties of the most stable phase.

## 2 Method

### 2.1 Cluster expansion

The cluster expansion calculations in the paper were performed using the Universal Cluster Expansion (UNCLE) code developed by Müller et al. [12]. The code can perform a complete CE fit using a genetic algorithm and predict the ground states of systems containing up to three or more elements. UNCLE continues to increase the number of clusters included in the cluster expansion until the desired accuracy is achieved. This method was used to determine the ground-state structure and thermodynamic properties of Li$_2$Mn$_{1-x}$Ni$_x$O$_3$. For exploring the configurational, 4-unit cells were taken into account. The fitting scheme ran for a maximum of 10 iterations, adding a maximum of 5 structures in each iteration and starting from an initial set of 5 structures. The fitness of every figure set was evaluated using the cross-validation score (CVS), which quantifies the predictive accuracy of the figure set for an unknown structure. A CE can be considered accurate if the CVS is less than 5 eV/pos.

### 2.2 First-principles calculations

The density functional theory (DFT) framework was employed to perform calculations on the structural, electronic, elastic, and dynamic properties. For all the calculations, the Vienna ab-initio simulation package (VASP) [13] was utilized with the projector augmented wave (PAW) pseudopotentials. To determine the ground-state properties of Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$, the spin-polarized generalized gradient approximation (GGA) proposed by Perdew and Wang was used. In order to accurately describe the localization of strongly correlated transition metal 3d-electrons, the Hubbard parameter (U) introduced by Liechtenstein and Zaanen within the local density approximation (LDA + U) was applied, with $U_{\text{Mn}}=5.0$, $U_{\text{Ni}}=6.4$ eV and $J=1$ eV as the chosen numerical values [14]. The number of plane waves was determined by setting a kinetic cut-off energy of 500 eV, and the Brillouin zone sampling scheme of Monkhorst-Pack with a $4 \times 4 \times 4$ for Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ and $5 \times 5 \times 5$ for Li$_2$MnO$_3$ k-points mesh were used. The densities of states were computed using the Methfessel-Paxton smearing width of 0.2 eV for both spin-up and spin-down orientations. The elastic properties were calculated by performing a Taylor expansion of the total energy.
with a strain of 0.005. Phonon dispersion spectra were evaluated using the PHONON code developed by Parlinski [15] as embedded in the MedeA program [16].

3 Results

3.1 Cluster Expansion

Figure 1 shows the results of formation energies $\Delta E_f (\sigma)$ plotted against the concentration of Ni and Mn. The green squares represent DFT enthalpies of formation of the training set, green crosses CE predicted enthalpies of formation of the training set and grey the CE predicted enthalpies of formation of all other structures considered by the cluster expansion. The cluster expansion generated 73 new structures for Li$_2$Mn$_{1-x}$Ni$_x$O$_3$. Among the 73 newly generated structures, only 3 lie along the red ground state line and are listed in table 1. These are considered as the most important phases. The most stable phase, with the lowest enthalpy was found at $x$=0.17. The cross-validation score (CVS) was used to examine the predictive power of the cluster expansion, CVS value was found to be 3.70 meV/pos < 5 meV/pos, indicating good cluster expansions.

![Ground state line for Li$_2$Mn$_{1-x}$Ni$_x$O$_3$ system highlighting calculated enthalpy of formation values against the concentration of Ni.](image)

**Table 1.** Stable structures of Li$_2$Mn$_{1-x}$Ni$_x$O$_3$ along the ground state line.

<table>
<thead>
<tr>
<th>Structural formula</th>
<th>Space group</th>
<th>Formation energy (eV/atom)</th>
<th>a(Å)</th>
<th>b(Å)</th>
<th>c(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$NiO$_3$</td>
<td>C2/m</td>
<td>-32.91</td>
<td>4.87</td>
<td>8.42</td>
<td>4.98</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.25}$Ni$_{0.75}$O$_3$</td>
<td>C2/m</td>
<td>-32.30</td>
<td>4.90</td>
<td>8.48</td>
<td>18.94</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.625}$Ni$_{0.375}$O$_3$</td>
<td>C2</td>
<td>-36.37</td>
<td>12.61</td>
<td>8.55</td>
<td>9.88</td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{0.83}$Ni$_{0.17}$O$_3$</td>
<td>C2</td>
<td>-37.88</td>
<td>9.66</td>
<td>8.59</td>
<td>8.18</td>
</tr>
</tbody>
</table>
3.2 Structural and thermodynamic properties

Lattice parameters describe the physical dimension of unit cell in a crystal lattice. Lattices in three-dimension have the lattice constants a, b and c. Full lattice parameters consists of the three lattice constants and the three angles between them. Figure 2 shows the structures of Li₂MnO₃ and Li₂Mn₀.₈₃Ni₀.₁₇O₃ both structures are monoclinic with space group C2/m and C2 respectively. Table 2 presents the cell parameters, volume at equilibrium and the enthalpies of formation for the fully relaxed structures of Li₂MnO₃ and Li₂Mn₀.₈₃Ni₀.₁₇O₃. The lattice parameters were obtained by minimizing the structures of the unit cells. The calculated cell parameters for Li₂MnO₃ show a 95% agreement with the experimental data, noted in parentheses, indicating that the employed approach is validated. There is no experimental data that can be used to compare the ones for Li₂Mn₀.₈₇Ni₀.₁₇O₃.

To assess the thermodynamic stabilities of Li₂MnO₃ and Li₂Mn₀.₈₃Ni₀.₁₇O₃, we calculated the enthalpies of formation using Equation 1:

$$\Delta H_f = E_c - \sum x_i E_i$$  \hspace{1cm} (1)$$

where $E_c$ is the calculated total energy of the compound and $E_i$ is the calculated total energy of element $i$ in the compound. The enthalpies of formation were used to determine the thermodynamic stability of the systems. It is worth noting that the heat of formations are negative, indicating thermodynamic stability in all the systems. This implies good cycling performance, safety, and experimental feasibility.

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Fig. 2. Structures of (a) Li₂MnO₃ and (b) Li₂Mn₀.₈₃Ni₀.₁₇O₃
3.2 Structural and thermodynamic properties

Fig. 2. Structures of (a) Li$_2$MnO$_3$ and (b) Li$_2$Mn$_{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$.

Lattice parameters describe the physical dimension of unit cell in a crystal lattice. Lattices in three-dimensional have the lattice constants $a$, $b$ and $c$. Full lattice parameters consists of the three lattice constants and the three angles between them. Figure 2 shows the structures of Li$_2$MnO$_3$ and Li$_2$Mn$_{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$. Both structures are monoclinic with space group C2/m and C2 respectively. Table 2 presents the cell parameters, volume at equilibrium and the enthalpies of formation for the fully relaxed structures of Li$_2$MnO$_3$ and Li$_2$Mn$_{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$.

The lattice parameters were obtained by minimizing the structures of the unit cells. The calculated cell parameters for Li$_2$MnO$_3$ show a 95% agreement with the experimental data, noted in parentheses, indicating that the employed approach is validated. There is no experimental data that can be used to compare the ones for Li$_2$Mn$_{\text{0.87}}$Ni$_{\text{0.17}}$O$_3$.

To assess the thermodynamic stabilities of Li$_2$MnO$_3$ and Li$_2$Mn$_{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$, we calculated the enthalpies of formation using Equation 1:

$$
\Delta \mathcal{H}_f = E_c - \sum E_i
$$

where $E_c$ is the calculated total energy of the compound and $E_i$ is the calculated total energy of element $i$ in the compound. The enthalpies of formation were used to determine the thermodynamic stability of the systems. It is worth noting that the heat of formation are negative, indicating thermodynamic stability in all the systems. This implies good cycling performance, safety, and experimental feasibility.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lattice parameters (Å)</th>
<th>Δ$\mathcal{H}_f$ (KJ/mol)</th>
<th>Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MnO$_3$ (C2/m)</td>
<td>a: 4.99 (4.87)$^a$</td>
<td>-874.42</td>
<td>204.80</td>
</tr>
<tr>
<td></td>
<td>b: 8.61 (8.53)$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c: 5.07 (5.03)$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li$<em>2$Mn$</em>{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$ (C2)</td>
<td>a: 9.66</td>
<td>-20622.89</td>
<td>609.37</td>
</tr>
<tr>
<td></td>
<td>b: 8.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c: 8.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ [17]

3.3 Electronic properties

3.3.1 Band structures

Electronic band structures are plots of energy against wave-vectors for a number of bands. They help in determining if a material is a semiconductor, insulator or metal. Figure 3 shows electronic band structures for Li$_2$MnO$_3$ and Li$_2$Mn$_{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$, figure 3(a) shows the band structure of Li$_2$MnO$_3$ with an energy band gap of 1.89 eV. The valence maximum is located along the Z direction at -0.025 eV and the conduction band minimum is located at 1.91 eV with respect to the Fermi level. Figure 3(b) shows the band structure for Li$_2$Mn$_{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$ with an energy band gap of 1.54 eV, the valence band gap maximum is located at -0.10 eV and the conduction band minimum at 1.53 eV with respect to the Fermi level. Both of these have indirect band gaps and are semiconductors. However, since the energy band gap of Li$_2$Mn$_{\text{0.83}}$Ni$_{\text{0.17}}$O$_3$ is narrower than that of Li$_2$MnO$_3$, it is expected to have improved conductivity than the pristine structure.
3.3.2 Density of states

The Density of States (DOS) refers to the energy levels available for electrons to occupy across different states. Figure 4 illustrates the total and partial density of states for Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$. These DOS calculations were conducted using the spin-polarized local density approximation. The positive scale of the total DOS displays the spin-up states, while the negative scale displays the spin-down states. The total DOS provides an overview of the collective electronic contribution of the entire system, whereas the partial DOS showcases the individual atom contributions. Additionally, the energy zero (E-E$_F$=0) is set at the Fermi energy in all the plots, allowing for a consistent reference point. The DOS are used to determine whether the structures are metallic, semi-conductors or insulators by measuring the band gaps. It was found that Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ have band gaps of 1.89 and 1.54 eV respectively which indicate that both structures are semi-conductors. Figure 4(a) shows that the states near the Fermi energy are mainly contributed by O $p$-states and minimal contribution is from Mn 3d and Li 2p states. From figure 4(b) The largest contribution to the states near the Fermi energy level is made by O 2p states, and Li 2p states and the minimal contribution is made by the Mn 3d and Ni 3d states.
The Density of States (DOS) refers to the energy levels available for electrons to occupy across different states. Figure 4 illustrates the total and partial density of states for \( \text{Li}_2\text{MnO}_3 \) and \( \text{Li}_2\text{Mn}_{0.83}\text{Ni}_{0.17}\text{O}_3 \). These DOS calculations were conducted using the spin-polarized local density approximation. The positive scale of the total DOS displays the spin-up states, while the negative scale displays the spin-down states. The total DOS provides an overview of the collective electronic contribution of the entire system, whereas the partial DOS showcases the individual atom contributions. Additionally, the energy zero \((E-E_F=0)\) is set at the Fermi energy in all the plots, allowing for a consistent reference point. The DOS are used to determine whether the structures are metallic, semiconductor or insulators by measuring the band gaps. It was found that \( \text{Li}_2\text{MnO}_3 \) and \( \text{Li}_2\text{Mn}_{0.83}\text{Ni}_{0.17}\text{O}_3 \) have band gaps of 1.89 and 1.54 eV respectively which indicate that both structures are semiconductors. Figure 4(a) shows that the states near the Fermi energy are mainly contributed by \( \text{O}p \) states and minimal contribution is from \( \text{Mn} \) 3d and \( \text{Li}2p \) states. From figure 4(b) The largest contribution to the states near the Fermi energy level is made by \( \text{O}2p \) states, and \( \text{Li}2p \) states and the minimal contribution is made by the \( \text{Mn} \) 3d and \( \text{Ni}3d \) states.

### 3.4 Elastic constants

The elastic constants and moduli for \( \text{Li}_2\text{MnO}_3 \) and \( \text{Li}_2\text{Mn}_{0.87}\text{Ni}_{0.13}\text{O}_3 \) structures were investigated within the density functional theory (DFT) in the framework of GGA with a strain of 0.005. The plane-wave cut-off energy was 500 eV, and the convergence of the calculations is 1meV. Elastic constants determine the response of crystal to external forces. They play an important role in determining the strength of the material. The elastic properties of solids are important hence they are related to various fundamental properties, equation of state, phonon spectra etc. The monoclinic systems have 13 independent elastic constants \((C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}, C_{66}, C_{15}, C_{25}, C_{35}, C_{46})\). The Born mechanical stability criteria for a monoclinic system [18] is given by:

\[
C_{ij} > 0 \quad (2)
\]

\[
[C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})] > 0 \quad (3)
\]

\[
(C_{33}C_{55}-C_{23}C_{25}) > 0 \quad (4)
\]

\[
(C_{44}C_{66}-C_{24}C_{26}) > 0 \quad (5)
\]

\[
(C_{22}+C_{33}+2C_{23}) > 0 \quad (6)
\]

\[
[C_{22}(C_{33}C_{55}-C_{23}C_{25})+2C_{23}C_{25}C_{35}-C_{23}C_{55}-C_{23}C_{35}] > 0 \quad (7)
\]

\[
\{2[C_{15}C_{25}(C_{33}C_{12}-C_{13}C_{23})]+C_{15}C_{35}(C_{22}C_{13}-C_{12}C_{23})+C_{25}C_{15}(C_{11}C_{23}-C_{12}C_{13})]-[C_{25}C_{35}(C_{12}C_{13}-C_{12}C_{13})+C_{12}C_{25}C_{35}]+gC_{55}\} > 0 \quad (8)
\]
The calculated elastic constants showed mechanical stability for both systems since they satisfied the necessary Born stability criterion for monoclinic crystals. The cluster expansion technique was used to generate Ni doped phases of these structures showed no availability of soft modes indicating vibrational instability, whereas their phonon dispersion curves for Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ exhibits promising characteristics as a potential candidate for cathode material in lithium ion batteries.

Table 3. Elastic constants (GPa) for Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>Li$_2$MnO$_3$</th>
<th>Li$<em>2$Mn$</em>{0.83}$Ni$_{0.17}$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{11}$</td>
<td>271.51(269)$^a$</td>
<td>214.67</td>
</tr>
<tr>
<td>C$_{12}$</td>
<td>67.75(48)$^a$</td>
<td>39.85</td>
</tr>
<tr>
<td>C$_{13}$</td>
<td>38.22(35)$^a$</td>
<td>41.46</td>
</tr>
<tr>
<td>C$_{15}$</td>
<td>16.19</td>
<td>0.02</td>
</tr>
<tr>
<td>C$_{22}$</td>
<td>275.93(274)$^a$</td>
<td>278.97</td>
</tr>
<tr>
<td>C$_{23}$</td>
<td>39.96(34)$^a$</td>
<td>63.71</td>
</tr>
<tr>
<td>C$_{25}$</td>
<td>-9.90</td>
<td>3.93</td>
</tr>
<tr>
<td>C$_{33}$</td>
<td>213.87(220)$^a$</td>
<td>260.40</td>
</tr>
<tr>
<td>C$_{35}$</td>
<td>2.61</td>
<td>20.28</td>
</tr>
<tr>
<td>C$_{44}$</td>
<td>52.13(79)$^a$</td>
<td>107.67</td>
</tr>
<tr>
<td>C$_{46}$</td>
<td>-12.19</td>
<td>-0.05</td>
</tr>
<tr>
<td>C$_{55}$</td>
<td>55.11(81)$^a$</td>
<td>84.42</td>
</tr>
<tr>
<td>C$_{66}$</td>
<td>103.02(105)</td>
<td>48.82</td>
</tr>
</tbody>
</table>

Table 4. The bulk (B), shear (G), Young’s (E) moduli and Pugh's ratio (B/G) (GPa) for Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$

<table>
<thead>
<tr>
<th></th>
<th>Li$_2$MnO$_3$</th>
<th>Li$<em>2$Mn$</em>{0.83}$Ni$_{0.17}$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>115.51(113)$^b$</td>
<td>114.54</td>
</tr>
<tr>
<td>G</td>
<td>78.04 (83)$^b$</td>
<td>84.77</td>
</tr>
<tr>
<td>E</td>
<td>219.56</td>
<td>227.57</td>
</tr>
<tr>
<td>$\frac{B}{G}$</td>
<td>1.48 (1.36)$^b$</td>
<td>1.35</td>
</tr>
</tbody>
</table>

3.5 Phonon Dispersion

To determine the dynamical stability of Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$, we evaluated their lattice vibrational phonon dispersions along symmetry lines (Γ, Z, M, A, V). Figure 5 shows phonon dispersion curves for the Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ structures. Phonon modes can be classified into two types: optical modes and acoustic modes. Optical phonons occur at higher frequencies and can be determined through Raman scattering techniques. In contrast, acoustic phonons occur at lower frequencies and are typically measured using Brillouin scattering techniques. The presence of negative acoustic (soft) modes in a material indicates vibrational instability, whereas their absence suggests stability. The phonon dispersions for Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ show no imaginary vibrations, suggesting that both these structures are vibrationally stable.

![Fig. 5. Phonon dispersions for (a) Li$_2$MnO$_3$ and (b) Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$.](image)

4 Conclusions

The cluster expansion technique was used to generate Ni doped phases of Li$_2$MnO$_3$ cathode material, and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ was found to be the most thermodynamically stable with the lowest heat of formation. DFT+U calculations showed that the Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ has a smaller band gap than the pristine material, suggesting that it will have better conductivity. The calculated elastic constants showed mechanical stability for both systems since they satisfied the necessary Born stability criterion for monoclinic crystals. The phonon dispersion curves for Li$_2$MnO$_3$ and Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ structures showed no availability of soft modes along the high symmetry zone suggesting dynamic stability. The findings suggest that Li$_2$Mn$_{0.83}$Ni$_{0.17}$O$_3$ exhibits promising characteristics as a potential candidate for cathode materials in lithium-ion batteries.
References