Understanding structural defects in lithium-rich layered oxide cathodes

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Planar defects in lithium-rich layered oxides were examined by aberration-corrected scanning transmission electron microscopy (STEM) to understand their formation. Planar defects were found to form during the transition of the transition metal layer from a disordered R3̅m state to a lithium-ordered C2/m state. This disorder-to-order transition resulted in three orientation variants, namely [100], [110], and [110]. The fundamental mechanism behind the observed defects is a shear of ±b/3[010] on the (001) transition metal planes, which is equivalent to the point group operations lost during the disorder-to-order transition. These displacements also produced twins and single unit cells with P312 symmetry. Lithium-rich layered oxides with and without nickel show the presence of these three orientation variants.

Introduction

During the past decade, Li-ion batteries have revolutionized the portable electronics market. Due to this recent success, there has been a wide interest to develop lithium-ion technology for transportation uses, and for applications such as stationary storage of electricity produced by renewables like solar and wind. However, the limited energy density, high cost, and safety concerns associated with the currently used layered LiCoO2 cathode material have posed serious challenges for the adoption of lithium-ion technology for large-battery applications.

In this regard, Li-rich layered oxide cathode materials, with the general formula Li[Li1−xMx]O2 (M = transition metal), have become appealing as they exhibit much higher capacities (~250 mA h g⁻¹) relative to that of the LiCoO2 cathode (140 mA h g⁻¹). The high reversible capacity has been claimed to result from the presence of two phases, a parent trigonal LiMnO2 phase (space group R3̅m) and a monoclinic Li2MnO3 phase (space group C2/m). However, other researchers have argued that only one phase exists and thus the improved performance of Li[Li1−xMx]O2 should not be attributed to the presence of the two phases. As a result, there has been much debate over the structure of these materials. Recently, we found that one of these Li-rich layered oxides, namely Li[Li0.2Mn0.6Ni0.2]O2 (capacity of ~250 mA h g⁻¹ on first charge), is indeed a single-phase solid solution with long-range lithium ordering resulting in C2/m symmetry. From this work, it is clear that the enhancement in capacity does not result from the presence of two phases. Another source of debate has arisen from the fact that lithium-rich layered oxides with C2/m symmetry have been shown to contain multiple thin planar defects along the transition metal layers, which result in crystal rotations of the monoclinic structure. Several groups have reported these defects as stacking faults while others report the presence of a P312 phase. However, at present, a fundamental understanding of the origin of these defects and the mechanism by which the C2/m monoclinic structure transitions into various crystal orientations has not yet been achieved.

To address this issue and to develop a better understanding of the structure of the Li-rich layered oxides, we examine here the origin and formation of multiple planar defects for particles showing long-range lithium ordering in the transition metal layer for two samples with different overall compositions.

Experimental procedure

The Li2MnO3 and Li[Li0.2Mn0.6Ni0.2]O2 oxides were synthesized by a combined citric acid and ethylenediaminetetraacetic acid (EDTA) complexation route. EDTA and citric acid were first dissolved in NH4OH, and an aqueous solution containing the required amounts of lithium, manganese, and nickel acetates were added to this solution. The molar ratio of citric acid : EDTA : metal ions was optimized to be around 1.5 : 1 : 1. The mixed solution was then heated at ~120 °C under stirring until a viscous gel was obtained, which was then heated first at ~250 °C and then at 850 °C for 5 h to get the final oxide powder. Subsequently, the samples were sonicated or ground with a mortar and pestle in methanol and deposited onto lacy carbon TEM grids. Several particles were analyzed for both compositions. The atomic structure images in these samples were recorded with a JEOL 2200FS TEM/STEM, equipped with a CEOS corrector (CEOS GmbH, Heidelberg, Germany) for the illuminating lenses, and a high-angle annular dark-field (HAADF) detector. The instrument, located in the Advanced Microscopy...
Laboratory at Oak Ridge National Laboratory, was made available through the High Temperature Materials Laboratory’s national user program.

Models were made according to XRD results by Strobel and Lambert-Andron for Li$_2$MnO$_3$ and Jarvis et al. for Li$_2$Mn$_{0.6}$Ni$_{0.4}$O$_2$.

### Results and discussion

It has been reported that planar defects in Li[Li$_{0.2}$Mn$_{0.6}$Ni$_{0.2}$]O$_2$ result from crystal rotations leading to three orientations of the C2/m monoclinic structure, namely [100], [110], and [100]. To understand the origin of these defects and the mechanism by which the C2/m monoclinic structure changes to these orientations, we will first consider that a disorder-to-order transition occurs in the transition metal layer sub-lattice during cooling the sample from elevated temperatures to room temperature. For this initial discussion, we will consider the general case of any layered oxide that undergoes lithium ordering in the transition metal layer.

Layered oxides with disorder in the transition metal layer sub-lattice have a R3m structure that contains 12 symmetry groups. However, when ordering between Li$^+$ and Mn$^{4+}$ ions in the transition metal layer sub-lattice occurs, the symmetry reduces to C2/m, which contains only four symmetry groups. These four symmetry groups of the C2/m structure are part of the symmetry groups of the R3m structure (Table 1), which indicates that C2/m is a subgroup of R3m. In fact, the only symmetries lost during the transition from R3m to C2/m are point groups (Table 1). As a result, the transition metal layers will form three orientation variants upon going through the disorder-to-order transition, thus explaining the three orientations reported in the literature for this material. In addition, each variant must be transformed into the other variant by one of the point groups lost in the disorder-to-order transition.

To understand the effect of these lost point groups, we first consider a monoclinic unit cell of Li[Li$_{0.2}$Mn$_{0.6}$Ni$_{0.2}$]O$_2$ (Mn, Ni) that exhibits Li ordering in the M layer and no defects viewed perpendicular to the transition metal plane (Fig. 1a) and viewed parallel to the transition metal plane (Fig. 1b). When the top layer rotates about a three-fold clockwise axis (indicated with a solid triangle in Fig. 1c), the orientation of the crystal remains unchanged (Fig. 1d). The same will hold true for a three-fold anticlockwise rotation as well. However, if the top layer is subsequently inverted after the three-fold rotation (indicated with a white circle inscribed inside the solid triangle in Fig. 1e), the crystal orientation changes to the [110] orientation (Fig. 1f).

<table>
<thead>
<tr>
<th>Disorder (R3m)</th>
<th>Order (C2/m)</th>
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<tbody>
<tr>
<td>3; 0,0,z</td>
<td>1</td>
</tr>
<tr>
<td>3; 0,0,z</td>
<td>2 0,0,z</td>
</tr>
<tr>
<td>2 x,x,0</td>
<td>1 0,0</td>
</tr>
<tr>
<td>2 x,0,0</td>
<td>m x,0,z</td>
</tr>
<tr>
<td>2 0,y,0</td>
<td>0,0</td>
</tr>
<tr>
<td>1 0,0,0</td>
<td>m x,y,z</td>
</tr>
<tr>
<td>3; 0,0,z; 0,0,0</td>
<td>m x,y,z</td>
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<tr>
<td>3; 0,0,z; 0,0,0</td>
<td>m x,y,z</td>
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<tr>
<td>m x,x,z</td>
<td>m x,y,z</td>
</tr>
<tr>
<td>m x,x,z</td>
<td>m x,x,z</td>
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The crystal is rotated and inverted about an adjacent M
atom (indicated with the white circle inscribed inside the solid triangle in Fig. 1g), a [110] orientation is achieved (Fig. 1h).

While it is now clear that these three orientations result from the tendency of the crystal to maintain symmetry during the disorder-to-order transition, we do not know which atomic displacements take place to form these crystal rotations. Clearly, physical crystal rotations such as those shown in Fig. 1 are energetically unfavorable due to the large number of atoms involved, and thus atomic displacements are typically the operating mechanism for changes in crystal orientation.

As previously stated, the Li[Li$_{0.2}$Mn$_{0.6}$Ni$_{0.2}$]O$_2$ composition contains planar defects on the transition metal layer planes, where the plane being displaced is the monoclinic (001) plane. However, determining the displacement vector is not trivial. The presence of multiple planar defects, which result in crystal rotations in the material, and the fact that the image is a projection of the atomic structure make determining the displacement direction from the image and/or diffraction pattern challenging. Moreover, monoclinic structures have different shear systems depending on their atomic arrangements, and a shear system for this Li-rich layered oxide material has not been reported.

Fortunately, layered-oxides can be represented by the rock-salt NaCl-type structure, which has a well-known shear system. In the NaCl structure, the Li and M atoms occupy the Na sites, and O occupies the Cl sites. As a result, we can inscribe a layered oxide with lithium ordering in the transition metal layers (monoclinic $C2/m$ unit cell of Li[Li$_{1-x}$M$_x$]O$_2$ (M = Mn, Ni)), inside a $2\times2\times2$ NaCl-type structure (Fig. 2) with a lattice parameter $a = 4.00$ Å. In this case, the (001)$_M$ plane of the monoclinic $C2/m$ cell corresponds to the (111)$_{\text{NaCl}}$ plane of the cubic cell and the [010]$_M$ direction of the $C2/m$ cell corresponds to the [110]$_{\text{NaCl}}$ direction of the cubic cell (Table 2).

Table 2  Equivalent planes and directions in the cubic and monoclinic structures of Li[Li$_{1-x}$M$_x$]O$_2$ (M = Mn, Ni)

<table>
<thead>
<tr>
<th>System</th>
<th>Plane</th>
<th>Directions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl (cubic)</td>
<td>(111)</td>
<td>[110]</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>(001)</td>
<td>[010]</td>
</tr>
</tbody>
</table>

Fig. 3  HAADF/STEM image (left) and corresponding model (right) of Li[Li$_{0.2}$Ni$_{0.2}$Mn$_{0.6}$]O$_2$ observed on the [112]$_{\text{NaCl}}$ zone axis (which is equivalent to the [100]$_M$ monoclinic zone axis). The dashed lines guide the reader to the Li/Ni sites positioned above each other, while the arrows at the top show that the Li/Ni sites in the top layer are displaced relative to the Li/Ni sites in the other layers by 2.8 Å.

Fig. 4  Schematic of Li[Li$_{1-x}$M$_x$]O$_2$ (M = Mn, Ni) showing the result of (a) a displacement of $b/3[010]_M$ (indicated with the arrow), viewed perpendicular to the transition metal layer. (b) The result of a three-fold anticlockwise rotation and then inversion viewed perpendicular to the transition metal layer. The operations shown in (a) and (b) are thus equivalent.
occur along the (001)M plane of the monoclinic $C2/m$ cell, which thus correspond to displacements on the (111)$_{NaCl}$ plane of the cubic NaCl-like cell. To find the displacement vector in the monoclinic $C2/m$ structure, we looked into the preferred shear vector $\vec{s} = a/2[110]_{NaCl}$. To observe this shear vector edge on and to stack like atoms on top of like atoms, the NaCl-like crystal should be viewed along the [112]$_{NaCl}$ zone axes. Fig. 3 shows such an image projected along the [112]$_{NaCl}$ zone axis. The bright spots are columns of Mn atoms in the transition metal layer, while the dark intensity in-between the bright spots in the transition metal layer are Li/Ni columns. Clearly, each Li/Ni column lines up from one transition metal layer to another until the top most transition metal layer, where a displacement is observed. This displacement was measured to be 2.8 Å, which matches well the magnitude (2.83 Å) and direction of the $a/2[110]_{NaCl}$ shear vector in the NaCl-like structure. This confirms that the shear system is indeed (111)[110]$_{NaCl}$. In the monoclinic cell, this corresponds to a shear of $\vec{s} = b/3[010]_M$ on the (001)$_M$ plane. This displacement is equivalent to the three-fold anticlockwise rotation plus inversion ($\bar{3}$) point group lost during the disorder-to-order transition (Fig. 4).

We now examine the general implications brought about by these atomic displacements. To begin, assume five transition metal layers of monoclinic crystal viewed along the [100]$_M$ zone axis (Fig. 5a), which allows us to image the shear vector $b/3[010]_M$ perpendicular to the beam direction. We call this orientation $\varphi_1$. Assume now a shift of $+1/3[010]_M$ in one of the layers (Fig. 5b). This produces a change in orientation. Effectively, this means a crystal rotation from the [100]$_M$ orientation ($\varphi_1$) to the [110]$_M$ orientation, which we call orientation $\varphi_2$. Further shifts of $+1/3[010]_M$ in subsequent layers will thicken the region with orientation $\varphi_2$ (Fig. 5c). A different orientation from $\varphi_2$ is achieved when one of the layers of the crystal in the $\varphi_1$ orientation is displaced by $-1/3[010]_M$, which is a negative shift with respect to the origin. In this case, a new orientation is formed, [110]$_M$ (Fig. 5d). We call this orientation $\varphi_3$. Additional shifts of $-1/3[010]_M$ in subsequent layers will thicken the region with orientation $\varphi_3$ (Fig. 5e). In total, three crystal orientations are expected for the $R3m$ to $C2/m$ disorder-to-order transition. Furthermore, a combination of positive and negative $1/3[010]_M$ displacements may produce additional changes in the structure of this material. For example, if two layers are displaced by $1/3$

![Fig. 5](https://example.com/fig5.png)  
Schematic of a Li[Li$_{1-x}$M$_x$]O$_2$ ($M = Mn, Ni$) crystal tilted down the [100]$_M$ zone axis with (a) no defects and (b–g) varying levels of planar defects on the (001) planes.

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[010]M, while the adjacent region above these layers is displaced by two subsequent 1/3[010]M shears, a twin domain is formed (Fig. 5f). In addition, if a positive 1/3[010]M shear occurs only every third layer, a screw axis is formed resulting in a P3121 unit cell (Fig. 5g).

Not surprisingly, as shown in the aberration-corrected HAADF/STEM image of Fig. 6a, the three orientation variants $\varphi_1$, $\varphi_2$ and $\varphi_3$, twin domains, and a unit cell of P3121 symmetry are all present within Li[Li$_0.2$Mn$_0.6$Ni$_0.2$]O$_2$. We are now left to address whether stacking faults and the P3121 phase exist, as these continue to be debated in the literature.

Regarding the presence of stacking faults, consider again the NaCl-type structure. The stacking sequence of the {111} planes in NaCl-type crystal is abc, which can be easily interpretable when viewed down the [110]$_{NaCl}$ zone axis. A stacking fault is the result of atoms in a plane occupying sites that are not typically occupied for that layer. We can now consider the Li[Li$_0.2$Mn$_0.6$Ni$_0.2$]O$_2$ compositions observed along the [110]$_{NaCl}$ zone axis (Fig. 6b). Here we see that abc stacking is maintained throughout the crystal, showing that the atomic sites remain unchanged, and only the types of atoms at those sites change. Reverting to the monoclinic C2/m unit cell, we can conclude that the stacking of the (001)$_M$ transition metal planes remains unaltered across the structure and thus not related with the planar defects found, which is consistent with the report by Bareño et al.$^9$

With respect to the existence of the P3121 phase, the STEM image of the Li[Li$_0.2$Mn$_0.6$Ni$_0.2$]O$_2$ shows regions where a unit cell with P3121 symmetry exists, but no long-range P3121 ordering was found (Fig. 6a). Therefore, we do not consider that P3121 exists as a separate phase. Instead, the P3121 symmetry forms as a result of isolated 1/3[010]$_M$ displacements, which bring the three orientation variants adjacent to each other (Fig. 5).

It has been proposed that multiple planar defects are the result of the presence of Ni in the material.$^9$ Therefore, we must examine a composition without nickel, such as Li$_2$MnO$_3$, to confirm if the formation of planar defects holds true for other layered oxides with lithium ordering. Fig. 7a shows multiple planar defects, resulting in three orientation variants and twins in Li$_2$MnO$_3$. No evidence of long-range P3121 symmetry was found. Furthermore, when Li$_2$MnO$_3$ is viewed down [110]$_{NaCl}$ the stacking also remains unchanged for this material, confirming that the displacements are not stacking faults. From this analysis, we can conclude that the presence of Ni is not necessary to cause multiple planar defects in lithium-rich layered oxides. In fact, as we have shown, the planar defects can be predicted from the disorder-to-order transition occurring in these materials. This type of transformation is typically temperature and cooling rate dependent. Bréger et al.$^{12}$ confirmed that the synthesis temperature strongly affects the formation of planar defects. Therefore, we conclude that the greatest factor impacting the formation of planar defects in lithium-rich layered oxides is the synthesis temperature.

**Conclusions**

We have shown that as the transition metal layers in lithium-rich layered oxides change from a disordered $R3\overline{3}m$ state to a lithium-ordered $C2/m$ state, planar defects are produced and result in three crystal orientation variants, namely [100], [110], and [110]. These crystal orientation variants may exist with various thicknesses, may produce twin domains, and may lead to single unit cells of P3121 symmetry. The fundamental mechanism behind the appearance of these defects is a shear of $\pm b/[010]_M$ on the (001)$_M$ transition metal planes, which is equivalent to the point group operations lost during the disorder-to-order transition. We also show that planar defects can be present with or without the presence of Ni. As a result, the greatest factor impacting planar defect formation is the synthesis process.

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Notes and references