Crystal growth and neutron diffraction studies of Li$_x$CoO$_2$ bulk single crystals

S. Uthayakumar$^{a*}$, M. S. Pandiyam$^a$, D. G. Porter$^a$, M. J. Gutmann$^b$, R. Fan$^c$, J. P. Goff$^a$

$^a$Department of Physics, Royal Holloway, University of London, Egham, Surrey TW20 0EX, United Kingdom
$^b$ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, United Kingdom
$^c$Diamond Light Source, Harwell Science and Innovation Campus, Didcot OX11 0DE, United Kingdom

Abstract

The first successful growth of neutron-size single-crystal Li$_x$CoO$_2$ by the optical floating-zone technique is reported. Structural properties have been studied using the time-of-flight neutron Laue diffraction technique. Our experiment is the first report of a Li$_x$CoO$_2$ single-crystal neutron study. The neutron diffraction profile yields sharp, strong Bragg reflections, indicating a single grain of high crystalline quality. The structural refinement from the single-crystal neutron diffraction data indicated a trigonal structure of space group R$ar{3}$m, and a Li concentration $x = 0.87$. No superlattice reflections were detected. The surface morphology analysed by scanning electron microscopy revealed the absence of cracks. The magnetic susceptibility was measured in a field of 1Tesla with H $\parallel$ c and H $\perp$ c, and an antiferromagnetic transition was observed $\sim 10$K, with no magnetic impurities.

Keywords: Floating zone technique; A2. Single crystal growth; A2. Lithium compounds; B1. Crystal structure; A1.

*Corresponding author
1. Introduction

There has been a renaissance of research on alternative energy sources to decrease global warming and environmental pollution. Hence energy generation and storage are two of the biggest challenges modern science faces. Lithium ion batteries have been considered to be one of the most attractive technologies in recent years due to high energy density and long service life [1]. Such high performance batteries based on the movement of Li$^+$ ions in layered transition metal oxides such as Li$_x$CoO$_2$ have enabled a technological revolution in portable products from iPods to mobile phones. To further develop the Li$_x$CoO$_2$ system, it is imperative to understand the crystal structure in order to elucidate its material properties such as its power fade, capacity loss and cyclability. Structural changes during reaction are detrimental to those properties. Therefore understanding the structure plays a vital role in the practical use of lithium ion batteries.

Li$_x$CoO$_2$ crystallizes in α-NaFeO$_2$ layered structure with trigonal R̅3m symmetry which consists of three CoO$_2$ layers with an oxygen stacking sequence of ABCABC along the c-axis, and the Li$^+$ ions occupy the octahedral interstitial sites between them. The most common method of preparing Li$_x$CoO$_2$ is by the solid state reaction method. However, the results obtained from polycrystalline samples tend to lead to scattered results due to non-homogeneity and irregular morphology. In addition, upon prolonged calcinations at elevated temperature, it is difficult to control stoichiometry because of the high activation energy [2]. This in turn promotes grain growth and particle coarsening which significantly hampers the electrochemical properties of the material. Several groups have successfully grown single crystals of Li$_x$CoO$_2$ by the flux and floating zone methods [3-6]. Nevertheless, it is apparent from the literature that due to the small crystal size a detailed study by neutron scattering has not been made. To resolve such issues, immense efforts were made to grow Li$_x$CoO$_2$ single crystals by evolving appropriate synthesis techniques. In the present study we employed the optical floating-zone technique (FZ-T-10000-H-VI-VPO-PC, Crystal System) which favours improved morphological and chemical reactivity compared to flux and solid state reaction techniques. In addition the crystals obtained by this technique are large enough for
neutron scattering measurements [7]. This is the first time that it has been possible to
grow a large enough single crystal of Li₅CoO₂, for the determination of the Li ordering
using neutron diffraction and, potentially, the dynamics using inelastic neutron scattering.

The poor electro-chemical properties of Li₅CoO₂ are attributed to the weak
electronic conductivity and slow ionic diffusion of lithium ions [8]. To probe the
underlying mechanism and to improve electro-chemical properties, a complete
understanding of the crystal structure is essential. Through single crystal x-ray diffraction
(XRD) studies it is difficult to detect deficiency of lithium due to the low scattering
power of lithium. Single-crystal neutron diffraction (SXD) provides complementary
information due to its ability to localize light atoms and its high penetration depth
compared to that of XRD. Despite many studies using neutron diffraction on battery
materials, there has been no previous report on bulk single crystals of Li₅CoO₂. Hence,
after the successful growth of large sized Li₅CoO₂ single crystals, efforts were made to
study their basic properties using neutron scattering measurements.

2. Experimental methods

Single-crystal Li₅CoO₂ was grown using the four-lamp optical floating zone
technique. Precursor powders of high purity Li₂CO₃ and Co₃O₄ were used as starting
materials and mixed together in a stoichiometric ratio. During the growth of LiCoO₂
single crystals, considerable difficulties arose on account of volatilization of lithium.
Therefore the precursor was synthesized with excess Li₂CO₃ (30%) to compensate the
lithium loss and to decrease the cobalt impurities by increasing the Li to Co ratio. The
mixture was finely powdered in an agate mortar and calcined in air at 850–870°C for 24
h with intermediate grinding. The calcined powders were then pressed into cylindrical
feed rods of diameter 8-7 mm and length 10-12 cm in a hydrostatic press. Subsequently
the feed rod was sintered in air at 880-900°C for 15 hours. The crystal growth was
carried out by employing a four-mirror optical floating zone furnace in an argon/oxygen
atmosphere with a growth speed of 8-10 mm/h with feed and seed rod counter rotation at 10-15 rpm. The as-grown single crystal is shown in Figure 1. This single crystal was subjected to various characterisations.

Single-crystal x-ray diffraction (Xcalibur-E, Agilent Technologies) was used to check the quality of the as grown single crystal with samples of size <0.5mm. A much larger boule of about 7 cm in length was screened using neutron diffraction on SXD at the ISIS spallation neutron source. SXD combines the white beam Laue technique with area detectors covering a solid-angle of 2π steradians, allowing comprehensive surveys of 3D volumes of reciprocal space [9]. A large single crystal grain (>1cm) was cleaved from the boule and mounted on an aluminium pin and cooled to 40 K using a closed-cycle helium refrigerator. A typical data set required 5 orientations to be collected for 7 hours per orientation. Data were corrected for incident flux using a null scattering V/Nb sphere. These data were then combined to a volume of reciprocal space and sliced to obtain single planar and linear cuts. Besides the structural characterization, the surface morphology was analysed by scanning electron microscopy. Magnetic measurements were performed in a field of 1 Tesla in both the H || c and H ⊥ c configurations using a SQUID/VSM on the I10 beamline at the Diamond Light Source.

3. Results and discussion

It is well known that the molten zone is sensitive to atmosphere (Ar/O₂/Air), growth speed and feed-rod seed rod rotation [10]. To reach a better understanding and to optimize the growth conditions several growth attempts with different growth parameters were made. During the growth we observed that the choice of oxygen or air has no effect in stabilizing the molten zone. At the same time the growth of LiₓCoO₂ requires specific atmosphere conditions to minimise lithium vapourisation. On careful review we found that the trigonal structure of LiₓCoO₂ is stabilized when the crystal growth is performed in argon atmosphere instead of air or oxygen. Uniform diameter of the as-grown crystal is required for the stability of the molten zone (interface). The as-grown single crystals can easily be cleaved along the growth direction. The microstructure of the LiₓCoO₂ crystals
was studied using scanning electron microscopy (Hitachi S3000 SEM) in the backscattered electron mode for in-depth analysis. Figure 2 presents the extended layer growth pattern along the growth direction showing the absence of cracks. It is believed that such an absence of crack formation can be attributed to the appropriate pressure and growth rate [11].

X-ray diffraction measurements were performed on an as-grown bulk single crystal of Li$_x$CoO$_2$ of size 0.4x0.25x0.1 mm$^3$. A 2D cut through the reciprocal space volume in the (h, k, 0) plane is shown in Figure 3, superimposed with hexagonal grid lines. The resulting diffraction pattern has strong and sharp Bragg reflections, inferring the high quality single crystal with c/a ratio of 5.003Å. These values are in good agreement with those of existing reports [12]. The scattering of x-rays by lithium is small compared to higher atomic number elements in the periodic table; therefore the concentration of lithium could not be refined.

The neutron Laue diffraction for a single grain of Li$_x$CoO$_2$ of size 8 x 2 x 1 mm$^3$ was obtained using the single crystal diffractometer (SXD). A large area of reciprocal space was measured for the temperature $T \sim 40$K. Figure 4, shows a cut through the reciprocal lattice plane (h, k, 11). The strong and sharp Bragg reflections indicate a high quality single crystal. The crystal structure was determined using JANA2006 refinement software [13] and the trigonal space group symmetry R$3m$ and the lattice parameters a=b= 2.812(2) Å and c=14.071(4) Å were obtained. The composition of this compound determined from the refinement is Li$_{0.87(6)}$Co$_{(1)}$O$_{(2)}$. The full crystallographic parameters obtained from these refinements are provided in Tables 1, 2, and 3. No superlattice reflections were detected besides principal Bragg reflections, in agreement with the theoretical predictions from density-functional theory for this structure at high $x$ [14].

The magnetic susceptibility was measured as a function of temperature for the single crystal of Li$_{0.87}$CoO$_2$. The field-cooled (FC) and zero-field-cooled (ZFC) magnetisation measurements were performed using the SQUID/VSM with a magnetic field of H= 1Tesla. The magnetic susceptibility was measured for both the field parallel
and perpendicular to \(c\)-direction (see figure 5). The magnetic anomalies for the single crystals of \(\text{Li}_{0.87}\text{CoO}_2\) are very weak compared to polycrystalline material in which the \(\text{Co}_3\text{O}_4\) magnetic impurity is dominant below 50K [15]. However, the presence of magnetic impurities such as \(\text{Co}_3\text{O}_4\) and \(\text{CoO}\) is not obtained in single crystal form [16]. No magnetic transition at 175K was found unlike previous observations by Hertz et al. [17]. We found the anisotropic magnetic anomaly \(\sim 10\) K for the as-grown single crystal of \(\text{Li}_{0.87}\text{CoO}_2\), clearly demonstrating the occurrence of antiferromagnetic (AFM) ordering, as previously reported by Ou-Yang et al. [18].

4. Conclusion

Neutron sized high quality \(\text{Li}_x\text{CoO}_2\) single crystals were grown by the optical floating zone technique. Bulk measurements using neutron diffraction revealed for a single grain in the trigonal \(R\bar{3}m\) structure a composition \(x = 0.87(6)\), and no superlattice reflections were detected. Antiferromagnetic ordering was detected below \(\sim 10\) K.

Acknowledgement

We thank the EPSRC for financial support via grant EP/J011150/1.
### Table 1: Experimental and crystallographic data for Li$_{0.87}$CoO$_2$:

<table>
<thead>
<tr>
<th>Structural formula</th>
<th>Li$_{0.87}$CoO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal system</td>
<td>Trigonal</td>
</tr>
<tr>
<td>Space group</td>
<td>R$\bar{3}$m</td>
</tr>
<tr>
<td>a(Å)</td>
<td>2.812(2)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>2.812(2)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>14.071(4)</td>
</tr>
<tr>
<td>V(Å$^3$)</td>
<td>96.3672(4)</td>
</tr>
<tr>
<td>T(K)</td>
<td>40</td>
</tr>
<tr>
<td>Z</td>
<td>3</td>
</tr>
<tr>
<td>Crystal size (mm$^3$)</td>
<td>8 x 2 x 1</td>
</tr>
<tr>
<td>Absorption correction method</td>
<td>Gaussian integration</td>
</tr>
<tr>
<td>Measured reflections</td>
<td>595</td>
</tr>
<tr>
<td>Observed reflections</td>
<td>266</td>
</tr>
<tr>
<td>Number of variables</td>
<td>10</td>
</tr>
<tr>
<td>Goodness of fit, $\chi^2$</td>
<td>7.18</td>
</tr>
<tr>
<td>R obs., all</td>
<td>0.0796</td>
</tr>
<tr>
<td>w R obs., all</td>
<td>0.1050</td>
</tr>
</tbody>
</table>

### Table 2: Positional parameters for Li$_{0.87}$CoO$_2$:

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>Z</th>
<th>U$_{eq}$ (Å$^2$)</th>
<th>Occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0028(17)</td>
<td>0.87(6)</td>
</tr>
<tr>
<td>O</td>
<td>6c</td>
<td>0.6667</td>
<td>0.3333</td>
<td>0.09333(12)</td>
<td>0.0008(3)</td>
<td>1</td>
</tr>
<tr>
<td>Co</td>
<td>3b</td>
<td>0.3333</td>
<td>0.6667</td>
<td>0.1667</td>
<td>0.0008(8)</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 3: Anisotropic displacement parameters for Li$_{0.87}$CoO$_2$:

<table>
<thead>
<tr>
<th>Atom</th>
<th>U$_{11}$ (Å$^2$)</th>
<th>U$_{22}$ (Å$^2$)</th>
<th>U$_{33}$ (Å$^2$)</th>
<th>U$_{12}$ (Å$^2$)</th>
<th>U$_{13}$ (Å$^2$)</th>
<th>U$_{23}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.002(2)</td>
<td>0.002(2)</td>
<td>0.005(3)</td>
<td>0.0009(10)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>0.0006(3)</td>
<td>0.0006(3)</td>
<td>0.0013(4)</td>
<td>0.00030(17)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Co</td>
<td>0.0005(9)</td>
<td>0.0005(9)</td>
<td>0.0034(17)</td>
<td>-0.0002(4)</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 1: As-grown single crystal of Li$_{0.87}$CoO$_2$

Figure 2: Extended layer growth pattern of Li$_{0.87}$CoO$_2$ showing very few cracks.
Figure 3: 2D cut of the x-ray diffraction pattern in the (h,k,0) plane for Li$_{0.87}$CoO$_2$. The weak extra peaks at the half positions are from higher order contamination.

Figure 4: 2D cut of the neutron diffraction pattern in the (h,k,11) plane for Li$_{0.87}$CoO$_2$. The neutron Laue diffraction technique does not have higher order contamination. There are no superlattice reflections.
Figure 5: Magnetic susceptibility of Li$_{0.87}$CoO$_2$ (H || c and H ⊥ c). The inset shows the antiferromagnetic transition at $T \sim 10$ K.
References