Crystal growth and neutron diffraction studies of Li_xCoO_2 bulk single crystals

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Abstract

The first successful growth of neutron-size single-crystal Li_xCoO_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_xCoO_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 $R\bar{3}m$, 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 || c and H $\perp$ c, and an antiferromagnetic transition was observed ~ 10K, with no magnetic impurities.

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

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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_xCoO_2 have enabled a technological revolution in portable products from iPods to mobile phones. To further develop the Li_xCoO_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_xCoO_2 crystallizes in α-$NaFeO_2$ layered structure with trigonal $R\bar{3}m$ 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_xCoO_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_xCoO_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_xCoO_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 Li_xCoO_2, for the determination of the Li ordering using neutron diffraction and, potentially, the dynamics using inelastic neutron scattering.

The poor electro-chemical properties of Li_xCoO_2 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 Li_xCoO_2. Hence, after the successful growth of large sized Li_xCoO_2 single crystals, efforts were made to study their basic properties using neutron scattering measurements.

2. Experimental methods

Single-crystal Li_xCoO_2 was grown using the four-lamp optical floating zone technique. Precursor powders of high purity Li_2CO_3 and Co_3O_4 were used as starting materials and mixed together in a stoichiometric ratio. During the growth of $LiCoO_2$ single crystals, considerable difficulties arose on account of volatilization of lithium. Therefore the precursor was synthesized with excess Li_2CO_3 (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 1Tesla in both the $H \parallel c$ and $H \perp c$ 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/O_2/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 Li_xCoO_2 requires specific atmosphere conditions to minimise lithium vapourisation. On careful review we found that the trigonal structure of Li_xCoO_2 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 Li_xCoO_2 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_xCoO_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, infering 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_xCoO_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 ~ 40K. 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 $R\bar{3}m$ 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 $Li_{0.87}CoO_2$ are very weak compared to polycrystalline material in which the Co_3O_4 magnetic impurity is dominant below 50K [15]. However, the presence of magnetic impurities such as Co_3O_4 and 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 ∼10 K for the as-grown single crystal of $Li_{0.87}CoO_2$, clearly demonstrating the occurrence of antiferromagnetic (AFM) ordering, as previously reported by Ou-Yang et al. [18].

4. Conclusion

Neutron sized high quality Li_xCoO_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 ~ 10 K.

Acknowledgement

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Table 1: Experimental and crystallographic data for $Li_{0.87}CoO_2$:

Structural formula	$Li_{0.87}CoO_2$
Crystal system	Trigonal
Space group	$R\bar{3}m$
a(Å)	2.812(2)
b(Å)	2.812(2)
c(Å)	14.071(4)
V(Å^3)	96.3672(4)
T(K)	40
Z	3
Crystal size (mm^3)	8 x 2 x 1
Absorption correction method	Gaussian integration
Measured reflections	595
Observed reflections	266
Number of variables	10
Goodness of fit, χ^2	7.18
R obs., all	0.0796
w R obs., all	0.1050

Table 2: Positional parameters for $Li_{0.87}CoO_2$:

Atom	Site	*x*	*y*	*Z*	U_{eq} (Å^2)	Occupancy
Li	3a	0	0	0	0.0028(17)	0.87(6)
O	6c	0.6667	0.3333	0.09333(12)	0.0008(3)	1
Co	3b	0.3333	0.6667	0.1667	0.0008(8)	1

Table 3: Anisotropic displacement parameters for $Li_{0.87}CoO_2$:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	0.002(2)	0.002(2)	0.005(3)	0.0009(10)	0	0
O	0.0006(3)	0.0006(3)	0.0013(4)	0.00030(17)	0	0
Co	0.0005(9)	0.0005(9)	0.0034(17)	-0.0002(4)	0	0

Figure 1: As-grown single crystal of $Li_{0.87}CoO_2$

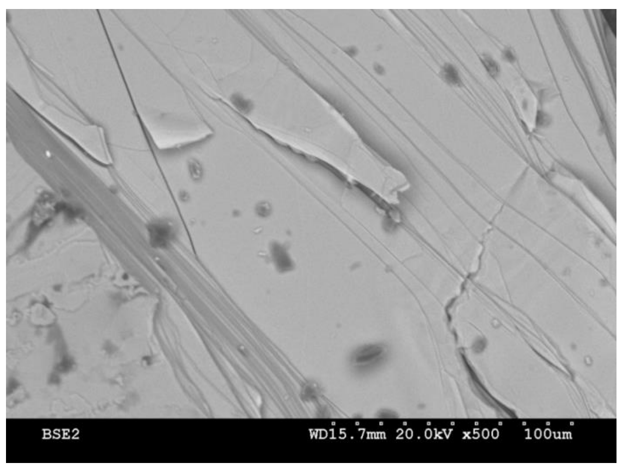

Figure 2: Extended layer growth pattern of $Li_{0.87}CoO_2$ showing very few cracks.

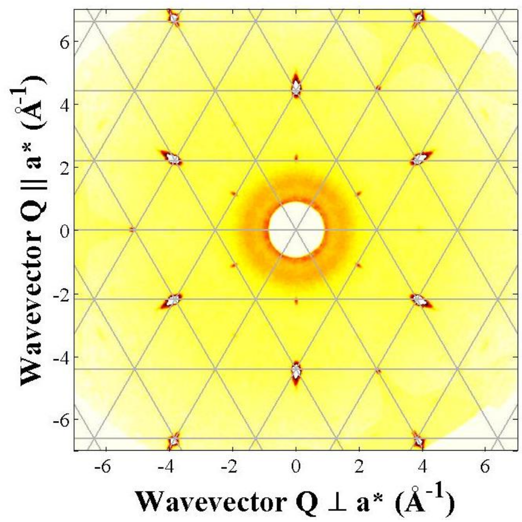

Figure 3: 2D cut of the x-ray diffraction pattern in the (h,k,0) plane for $Li_{0.87}CoO_2$. The weak extra peaks at the half positions are from higher order contamination.

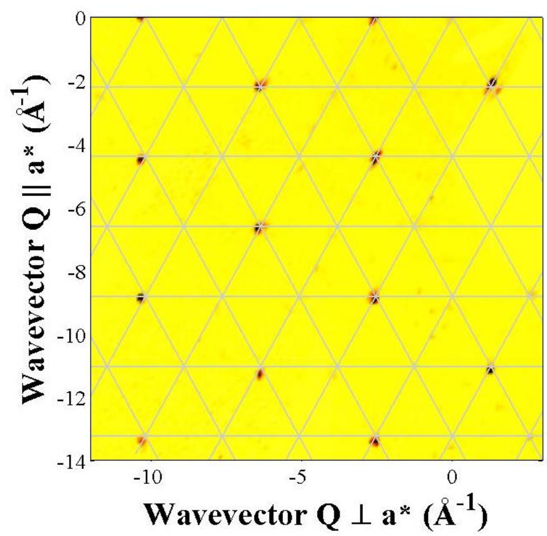

Figure 4: 2D cut of the neutron diffraction pattern in the (h,k,11) plane for $Li_{0.87}CoO_{2.}$ The neutron Laue diffraction technique does not have higher order contamination. There are no superlattice reflections.

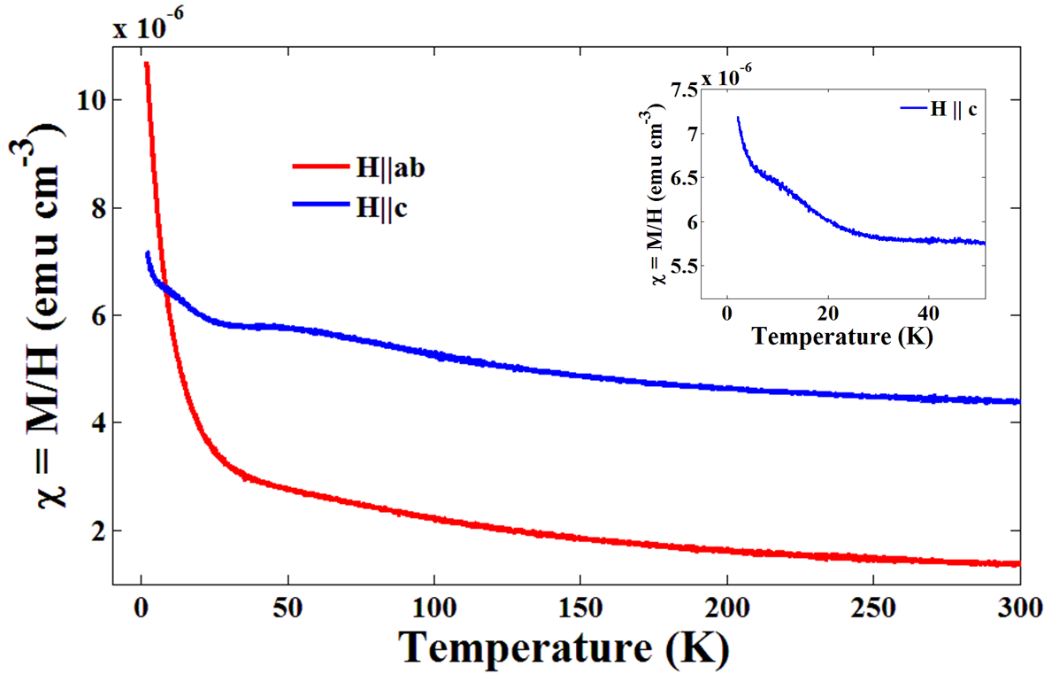

Figure 5: Magnetic susceptibilty of $Li_{0.87}CoO_2$ (H ∥ c and H $\perp$ c). The inset shows the antiferromagnetic transition at T ~ 10 K.

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