Single Crystal Growth, Structure and Physical Properties of $LiCoO_2$

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Lithium cobalt oxide, $LiCoO_2$, has the trigonal • – $NaFeO_2$ structure and is used industrially as the cathode material of lithium-ion rechargeable batteries. Since electrochemical deintercalation was first reported in $LiCoO_2$ by Mizushima *et al.* [1], the structural, physical, and electrochemical properties for $LiCoO_2$ and Li_xCoO_2 ($0 < x < 1$) have been widely investigated [2-7]. In all of the experimental studies reported to date, sintered or pressed powder samples are used. In an experiment using such samples, much of information on the anisotropy is lost, and in conductivity measurements in particular, the intrinsic properties of the material are sometimes masked by those of the grain boundaries or the impurities. To clarify the anisotropic nature of the physical properties of the cathode materials, well-characterized single-crystal specimens are highly desirable. In addition, it is expected that the precise structural properties such an ordering of lithium positions and a phase change in Li_xCoO_2 are confirmed by the single-crystal X-ray diffraction technique. Recently, we have succeeded in the synthesis of $LiCoO_2$ single crystals [8]. In the present study, we report crystal structures of as-grown $LiCoO_2$ and electrochemically deintercalated Li_xCoO_2, and physical properties measured using single crystal specimens.

$LiCoO_2$ single crystals was grown by a flux method of the slow cooling from 973 – 1173 K in a gold crucible, as mentioned recently [8]. The eutectic melting point of the optimal flux composition was estimated to be about 780 K. The products were easily separated from the frozen flux by rinsing the crucible in water for several hours. Black, hexagonal platelet crystals of about 1.5 × 1.0 × 0.3 mm^3 (maximum) were obtained. X-ray Laue and precession photographs confirmed the trigonal symmetry. The crystal structure was refined using the intensity data collected in the 2• -• scan mode at 300 K on a four-circle diffractometer. The experimental data and structural parameters were summarized in Tables I and II. The refined structural parameters are essentially consistent with the previous result [2], based on powder neutron diffraction data, but with higher accuracy. Single-crystal X-ray diffraction experiment revealed that the single-crystallinity in the electrochemically deintercalated Li_xCoO_2 specimens is maintained in the compositional range of $0 < x < 0.5$, as shown in Fig. 1.

References

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Table I Crystallographic and Experimental Data for $LiCoO_2$

Cell dimensions	a = 2.8156(6) Å
	c = 14.0542(6) Å
Cell Volume	V = 96.49(4) $Å^3$
Space group	R-3m
Measured reflections	2236
Independent reflections	250 (R_{int} = 2.01%)
Final R = 2.02%, Final wR = 2.09%	

Table II Structural Parameters of $LiCoO_2$

Atom	x/a	y/b	z/c	U_{eq} ($Å^2$)
Li	0	0	0	0.0120(15)
Co	0	0	1/2	0.00326(7)
O	0	0	0.23967(6)	0.00471(17)

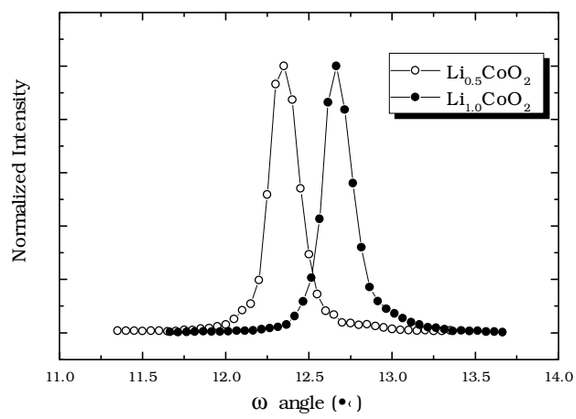

Fig. 1 The (009) peak profiles of as-grown $LiCoO_2$ and electrochemically deintercalated $Li_{0.5}CoO_2$ by single-crystal X-ray diffraction method using MoK• radiation.