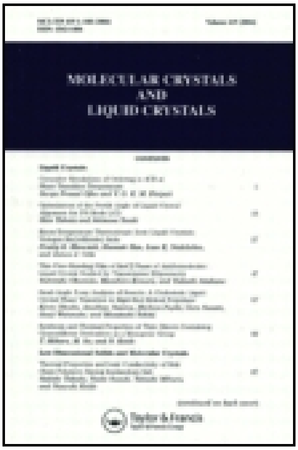

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Single Crystal Growth, Structure and Physical Property of $LiCoO_2$ and $LiNiO_2$

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Version of record first published: 27 Oct 2006

To cite this article: Junji Akimoto & Yoshito Gotoh (2000): Single Crystal Growth, Structure and Physical Property of $LiCoO_2$ and $LiNiO_2$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 143-146

To link to this article: http://dx.doi.org/10.1080/10587250008026131

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 143-146
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Single Crystal Growth, Structure and Physical Property of $LiCoO_2$ and $LiNiO_2$

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(In final form June 21, 1999)

Single crystals of $LiCoO_2$ and $LiNiO_2$ have been successfully grown for the first time by a flux method. A single-crystal X-ray diffraction study confirmed trigonal symmetry, and their lattice parameters were $a = 2.8161(5)$ Å and $c = 14.0536(5)$ Å for $LiCoO_2$, and $a = 2.8899(13)$ Å and $c = 14.1938(17)$ Å for $LiNiO_2$, respectively. The cation distribution in $Li_{0.92}Ni_{1.08}O_2$ was determined to be $(Li_{0.74}Ni_{0.26})_{3a}[Li_{0.18}Ni_{0.82}]_{3b}O_2$ with a final R value of 2.7% by a single-crystal X-ray structure analysis. $LiCoO_2$ proved to show a semiconducting behavior below room temperature by an in-plane electrical resistivity measurement using the single crystal specimen.

Keywords: single crystal growth; structure analysis; lithium-ion battery

INTRODUCTION

$LiCoO_2$ has the trigonal α–$NaFeO_2$ structure and is used industrially as the cathode material of lithium-ion rechargeable batteries. $LiNiO_2$ is isostructural with $LiCoO_2$, and is a promising potential cathode material. This compound is also of interest in connection with possible realization of a two-dimensional triangular lattice antiferromagnet with spin 1/2 [1]. Over the last two decades, the structural, physical, and electrochemical properties for $LiCoO_2$ and $LiNiO_2$ compounds have been widely investigated [2-11]. 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 grain boundaries or impurities. To clarify the anisotropic nature of the physical properties of $LiCoO_2$ and $LiNiO_2$, well-characterized single-crystal specimens are highly desirable. In addition, it is expected that precise structural properties such an ordering of lithium and phase changes in these compounds can be confirmed by the single-crystal X-ray diffraction technique. In the present study, we will report single crystal growth and characterization of $LiCoO_2$ and $LiNiO_2$.

EXPERIMENTAL

Single crystals of $LiCoO_2$ and $LiNiO_2$ were grown by a flux method of slow cooling from 973 – 1173 K in a gold crucible, as described before [12]. Starting $LiCoO_2$ and $LiNiO_2$ powder samples were kindly supplied by Nippon Chemical Industrial Co., Ltd., Japan. In order to find the best conditions to grow single crystals, we examined some flux materials, e.g., LiCl, LiF, Li_2O, Li_2CO_3, and $LiBO_2$. From the results, we chose an Li-O-Cl eutectic composition system, because of the stability of the solution at high temperatures. 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 minutes. EDX analyses showed that the crystals thus obtained were free from gold which was fed from the crucible. The structures of $LiCoO_2$ and $LiNiO_2$ were investigated by single-crystal X-ray diffraction.

RESULTS AND DISCUSSION

Lithium Cobalt Dioxide

Black, hexagonal platelet $LiCoO_2$ crystals of about 2 × 2 × 0.3 mm^3 at maximum were obtained at the bottom of frozen flux in the crucible. Single-crystal X-ray diffraction confirmed the trigonal symmetry. We could not find any superstructures in the present as-grown $LiCoO_2$ single crystal specimens. The refined hexagonal lattice parameters are a = 2.8161(5) Å and c = 14.0536(5) Å. These values agree quite well with reported powder data for $LiCoO_2$; e.g., a = 2.8179(1) Å and c = 14.0597(8) Å [5]. Structural parameters were refined using single-crystal X-ray diffraction data and reported elsewhere [12].

The in-plane electrical resistivity was measured using the single crystal specimen by a standard four-probe method. $LiCoO_2$ showed semiconducting behavior below room temperature. The in-plane resistivity at room temperature was considerably smaller than those reported in the literature using sintered samples [4,11].

Lithium Nickel Dioxide

Black, triangular platelets of $LiNiO_2$ with dimensions of about 0.5 × 0.5 × 0.3 mm^3 at maximum were obtained by cooling from 1173 K. Single-crystal X-ray diffraction confirmed the trigonal symmetry of the as-grown single crystal. The refined hexagonal lattice parameters are a = 2.8899(13) Å and c = 14.1938(17) Å. It is well established that the stoichiometric $LiNiO_2$ sample is very difficult to obtain even in the case of polycrystalline samples, because the high-temperature treatment of $LiNiO_2$ leads to decomposition from $LiNiO_2$ to $Li_{1-x}Ni_{1+x}O_2$ [9]. The present single-crystal structure analysis revealed that the chemical composition of the as-grown single crystal was $Li_{0.92}Ni_{1.08}O_2$, which corresponded to $Li_{1-x}Ni_{1+x}O_2$ with $x = 0.08$. The cation distribution in the present $Li_{0.92}Ni_{1.08}O_2$ was determined as $(Li_{0.74}Ni_{0.26})_{3a}[Li_{0.18}Ni_{0.82}]_{3b}O_2$ with final R values of $R = 2.7\%$ and $wR = 2.0\%$ for 202 observed reflections (Table 1). The refined coordinate for oxygen was $z = 0.2442(1)$, which is slightly shifted from 0.2411(2) in $Li_{0.996}Ni_{1.006}O_2$ [9] to the ideal oxygen packing value of 0.25. This fact is explained as the partly disordering of cation distribution between the *3a* and the *3b* sites in $Li_{1-x}Ni_{1+x}O_2$. The lattice parameters and the cation distribution in the present compound, $Li_{0.92}Ni_{1.08}O_2$, are well consistent with those in $Li_{0.9}Ni_{1.1}O_2$ reported by Gummow and Thackeray [6].

TABLE 1 Atomic coordinates, Equivalent isotropic displacement parameter U_{eq}, and site occupancy factor g for $Li_{0.92}Ni_{1.08}O_2$.

Atom	Position	x	y	z	U_{eq} (Å^2)	g
Li1	*3a*	0	0	0	0.0072(2)	0.744(4)
Ni1	*3a*	0	0	0	= U_{eq} (Li1)	=1-g(Li1)
Li2	*3b*	0	0	1/2	0.0056(1)	0.18(1)
Ni2	*3b*	0	0	1/2	= U_{eq} (Li2)	=1-g(Li2)
O	*6c*	0	0	0.2442(1)	0.0157(4)	1

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