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Crystallographic Evidence for the Formation of a Continuous Series of Mixed Crystals between NiO and $LiNiO_2$

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The system NiO − $Li_{1-x}Ni_{1+x}O_2$, with $0 \leq x \leq 1$ has to be considered as a continuous series of mixed crystals of one structure type (structure of α-$NaFeO_2$). The substitution of one Ni^{2+} ion in NiO by a Li^+ ion is accompanied by the oxidation of another Ni^{2+} ion to Ni^{3+}. In the series NiO − $Li_{1-x}Ni_{1+x}O_2$ the Vegard rule holds true for both lattice constants “a” and “c”. The literature statements on the formation of different phases in the system NiO − $Li_{1-x}Ni_{1+x}O_2$ are obviously misinterpretations of the X-ray data. A very simple low-temperature solution combustion technique was adopted in this study to prepare different samples of this mixed crystal series. The samples were characterized by inductively coupled plasma for elemental analysis and by X-ray powder diffraction and Rietveld refinement for structural analysis.

I. Introduction

Metal oxides, such as $LiNiO_2$, $LiCoO_2$, and $LiMn_2O_4$, have been proposed as cathode materials for 4 V rocking chair lithium-ion secondary batteries.[1,2] In view of these applications, the structure and electrochemistry of lithium nickelate in nonaqueous electrolytes has been very-often studied. Although $LiCoO_2$ has been practically utilized as the cathode material for lithium-ion batteries, $LiNiO_2$ is more attractive because of its lower cost and the possibility of higher discharge capacity. However, this compound shows structural and compositional changes depending on its preparation conditions.[3] The stoichiometric $LiNiO_2$ is difficult to obtain, because a high-temperature treatment of $LiNiO_2$ leads to the lithium deficient products Li_{1-x} $Ni_{1+x}O_2$ ($x > 0$), which have a disordered cation distribution at the lithium sites.[4]

It has been reported that the stoichiometric lithium nickelate crystallizes in the rhombohedral lattice mode of the trigonal symmetry (*SG:R*-3*m*). The lithium and nickel ions occupy the octahedral sites of the *fcc* oxygen packing. Depending upon the value of x in $Li_{1-x}Ni_{1+x}O_2$, various authors report distortions in structure of the compound.[5,6] If $x < 0.56$, the structure of lithium nickelate is that of disordered rock salt type, whereas for $x > 0.6$, partial cation ordering occurs, culminating in the formation of the layered $LiNiO_2$ (α-$NaFeO_2$) structure at $x = 0$. Ohzuku et al. reported that $Li_{1-x}NiO_2$ forms different phases depending on the x values.[7] They observed four distinct regions with three single-phase regions and one two-phase coexistence region (a hexagonal phase H1 for $0 < x < 0.25$, a monoclinic phase M1 for $0.25 < x < 0.55$, a hexagonal phase H2 for $0.55 < x < 0.75$, and a two-phase coexistence region H2 + H3 for $0.75 < x < 1$). Li et al.[8] reported three hexagonal phases and one monoclinic phase within the composition range $0 \leq x \leq 0.82$. Hirano et al.[9] reported that on deintercalation from the nearly stoichiometric $Li_{1-x-y}NiO_2$ ($x = 0.01$), a monoclinic phase appeared for $0.3 \leq y \leq 0.6$. In contrast, no symmetry change from *R*3*m* was observed on deintercalation from the nonstoichiometric hosts of $0.05 \leq y$.

The Inorganic Crystal Structure Database (ICSD) contains a few entries for lithium nickel oxides.[10] In these crystal structures all the lithium, nickel, and oxygen atoms are arranged on regular lattice positions. Goodenough et al.[5] investigated the compound $Li_{0.3}Ni_{0.7}O$. Davidson et al.[11] studied the structure of $Li_{0.4}Ni_{1.6}O_2$. Both compositions are described to crystallize in the NaCl structure-type with the space group

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$Fm\bar{3}m$ (no. 225). Ni and Li occupy the 4a Wyckoff position with different site occupation factors (SOF). Oxygen is on the 4b Wyckoff position with SOF = 1. $Li_{0.99}NiO_2$ crystallizes in the space group $R\bar{3}m$ (no. 166). Li and small amounts of Ni are on the 3a position, Ni occupies the 3b position, and O occupies the 6c position.[12] The Powder Diffraction File (PDF) edited by the International Center of Diffraction Data contains X-ray patterns of the cubic NiO,[13] a rhombohedral NiO,[14] a rhombohedral $LiNiO_2$,[15] and a hexagonal $Li_2Ni_8O_{10}$.[16] All these data and reports give contradictory descriptions of the structure of nonstoichiometric lithium nickel oxides.

The objectives of this study are (i) to show that NiO and $Li_{1-x}Ni_{1+x}O_2$ could be considered as one structure type with $0 \le x \le 1$; (ii) to demonstrate the synthesis of $Li_{1-x}Ni_{1+x}O_2$ with various compositions using a solution combustion technique; and (iii) to check the structure type model of these samples by means of XRD and ICP results.

II. Experimental Section

Preparation of $Li_{1-x}Ni_{1+x}O_2$ by Solution Combustion Method. To prepare different stoichiometric compounds of $Li_{1-x}Ni_{1+x}O_2$ ($0 \le x \le 1$), a series of experiments were carried out by keeping the Ni content (1 mol) constant and varying the Li content. We investigated samples with Li/Ni mole ratios of 0.6 (LiNi1), 0.8 (LiNi2), 1.0 (LiNi3), 1.2 (LiNi4), 1.5 (LiNi5), and 2.0 (LiNi6). The required amounts of reactants viz. $LiNO_3$, $Ni(NO_3)_2$, and urea were dissolved in a minimum amount of distilled water in a quartz beaker. The beaker with solution was subjected to heating in a muffle furnace at 500 °C. After a few minutes the solution boiled, solidified, and ignited with flame temperature of 1100−1200 °C to yield a gray-black fine powder.

X-ray Diffraction Studies. Powder diffraction data of the samples were obtained using an X-ray diffractometer HZG 4 (Seifert-FPM) with Bragg−Brentano geometry, Cu Kα radiation (40 kV, 30 mA), fixed slits, and a graphite secondary monochromator GSM-6. The samples were scanned in the 2θ range of 10−80° in 0.02° steps, counting for 4 s/step. The measurements were carried out at room temperature. The crystal structures were solved on the basis of the transformation model in the space group $R\bar{3}m$ (166). Structure analysis and refinement procedures were performed using the Rietveld method (Wyriet).

ICP Analysis. Lithium and nickel contents in the samples were measured using ICP−OES. A 10−14-mg portion of each sample was dissolved in HCl, and the measurements were carried out on a spectrometer UNICAM 701 at the wavelengths of 670.784 nm (Li1) and 231.604 nm (Ni3). Quantitative analysis was done using the calibration-curve method with Merck standard solutions.

III. Results

Unit Cell Transformation. Unit cell transformations are frequently used in determining the crystal structures of compounds. A cubic face centered cell (*fcc*) with the coordinates *x*, *y*, *z*, + [0,0,0; 0,1/2,1/2; 1/2,0,1/2; 1/2,1/2,0] can be transformed into a triple-hexagonal cell (*th*) with *x*, *y*, *z*, + [0,0,0; 1/3,2/3,2/3; 2/3,2/3,1/3]. For calculating lattice constants and volume of the unit cell, the following relationships are used

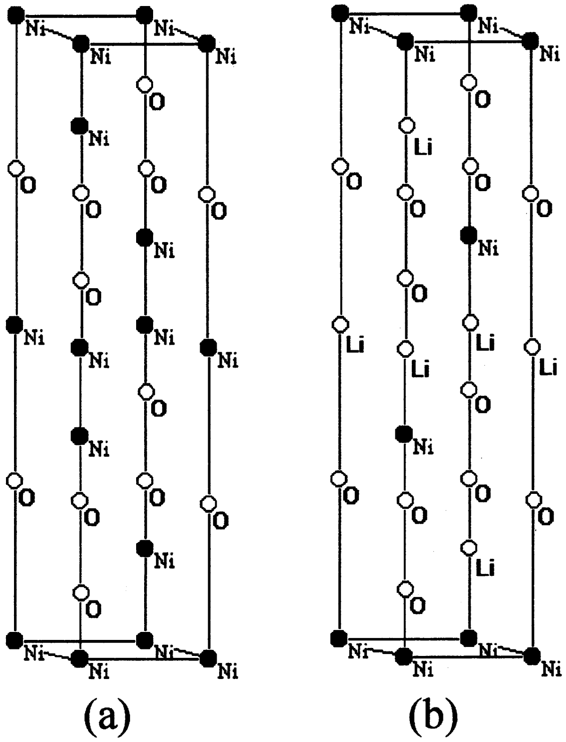

Figure 1. Crystal structures of (a) NiO[17] and (b) transformed $LiNiO_2$.[12]

$$a_{th} = \sqrt{2}a_c/2 \qquad (1)$$

$$c_{th} = \sqrt{3}\cdot a_c \qquad (2)$$

$$V_{th} = 3/4V_c \qquad (3)$$

NiO was reported to crystallize in the NaCl structure type.[13,17] Transformation and doubling the *c*-axis of the triple hexagonal unit cell leads to the same atomic arrangement as that in $LiNiO_2$, which has the structure of α-$NaFeO_2$.[12] From a pure crystallographic point of view a complete mixed crystal formation between Ni_2O_2 and $LiNiO_2$ should be occurring. The replacement of one Ni^{2+} ion by one Li^+ ion is accompanied by a simultaneous change of valency from Ni^{2+} to Ni^{3+}. Figure 1a and b shows the crystal structures of NiO[17] and transformed $LiNiO_2$.[12] Both unit cells contain 12 atoms: 6 Ni and 6 O (Figure 1a) in case of NiO; and 3 Li, 3 Ni, and 6 O (Figure 1b) in case of $LiNiO_2$.

Table 1 contains the calculated X-ray data for NiO[18] having the lattice constants a = 0.2954 nm and c = 1.4462 nm, and also for $LiNiO_2$ with the lattice constants as a = 0.288 nm and c = 1.4195 nm. It is clear that the calculated X-ray pattern of NiO is identical with the observed X-ray powder pattern.[13]

The idea of mixed crystal formation of $Li_{1-x}Ni_{1+x}O_2$ with $0 \le x \le 1$ is also supported by the calculated values of the lattice constants "a" and "c" from the references.[5,10−17] Figure 2 shows that the Vegard rule holds good. A linear fit gives *R* values of 0.999 for the a axes and 0.991 for the c axes. With increasing Li content (1

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Table 1. Calculated X-ray Data for NiO and $LiNiO_2$

			NiO: $a = 0.2954$ nm; $c = 1.4462$ nm			$LiNiO_2$: $a = 0.2880$ nm; $c = 1.4195$ nm			
hkl			*d* (nm)	*I*/rel.	|F(hkl)|	*d* (nm)	*I*/rel.	|F(hkl)|	Mu
0	0	3	0.4821	0.00	0.000	0.4732	100.00	71.030	2
1	0	1	0.2520	0.00	0.000	0.2457	49.10	58.302	6
0	1	2	0.2412	56.56	98.762	0.2366	6.25	37.596	6
0	0	6	0.2410	18.82	98.747	0.2353	17.79	36.864	2
1	0	4	0.2089	100.0	155.211	0.2041	84.81	95.048	6
0	1	5	0.1916	0.00	0.000	0.1874	18.46	49.108	6
1	0	7	0.1607	0.00	0.000	0.1577	2.97	42.126	6
0	0	9	0.1607	0.00	0.000	0.1573	15.54	55.835	2
1	1	0	0.1477	28.84	127.065	0.1446	23.44	76.067	6
0	1	8	0.1476	28.78	127.015	0.1440	23.65	76.792	6
1	1	3	0.1412	0.00	0.000	0.1378	16.77	48.216	12
0	2	1	0.1274	0.00	0.000	0.1242	5.07	42.067	6
2	0	2	0.1260	7.16	76.181	0.1234	3.17	33.514	6
1	1	6	0.1260	14.31	76.171	0.1230	5.99	32.666	12
1	0	10	0.1259	7.14	76.151	0.1228	2.91	32.239	6
0	2	4	0.1206	13.32	108.578	0.1183	3.52	63.666	6
0	0	12	0.1205	4.43	108.510	0.1177	10.86	64.867	2
2	0	5	0.1170	0.00	0.000	0.1146	5.41	46.749	6
0	1	11	0.1169	0.00	0.000	0.1142	3.37	36.996	6
0	2	7	0.1088	0.00	0.000	0.1063	4.87	32.756	6
1	1	9	0.1088	0.00	0.000	0.1062	3.93	41.626	12
2	0	8	0.1044	8.60	95.572	0.1020	7.11	56.386	6
1	0	13	0.1020	0.00	0.000	0.1000	1.91	29.184	6
2	1	1	0.0965	0.00	0.000	0.0946	1.33	41.123	12
0	0	15	0.0964	0.00	0.000	0.0941	5.29	33.354	2
1	2	2	0.0959	7.30	61.379				12
0	2	10	0.0958	3.65	61.359				6
0	1	14	0.0958	3.65	61.340				6

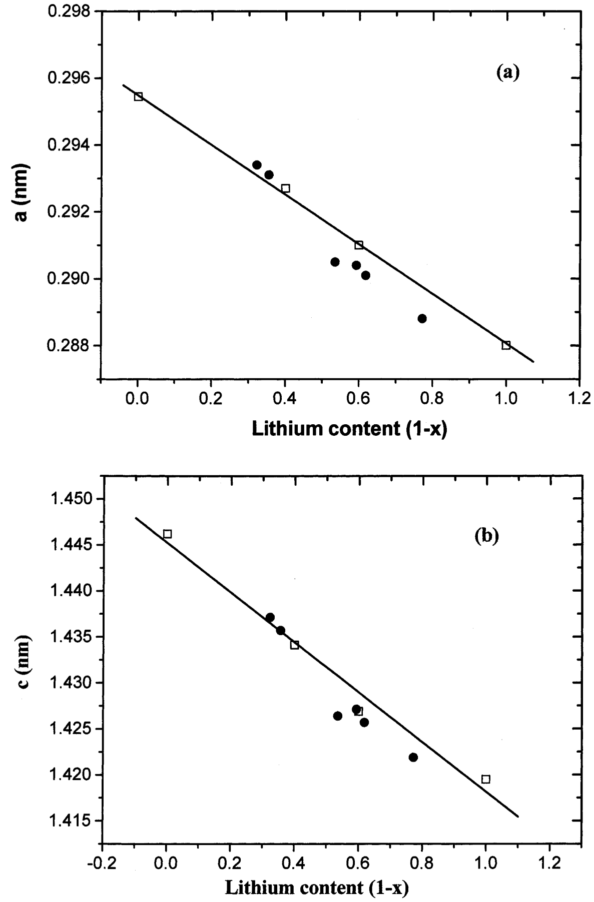

Figure 2. Comparison of the lattice parameters obtained from ICP results (black circles) with reference data (hollow squares) (a) lithium content $(1 - x)$ vs lattice constant "a"; (b) lithium content $(1 - x)$ vs lattice constant "c".

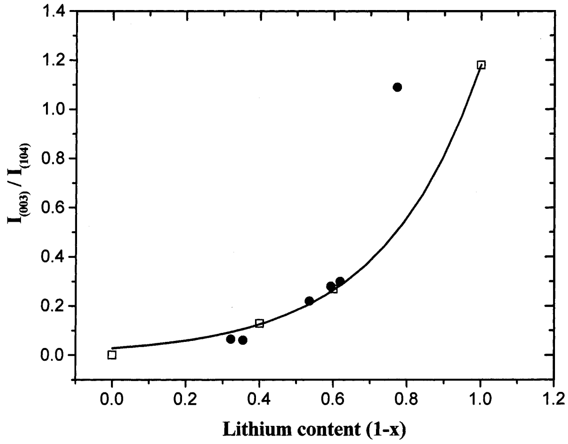

Figure 3. Comparison of the integral intensities $I_{(003)}/I_{(104)}$ obtained from ICP results (black circles) with reference data (hollow squares).

$-\ x)$ the lattice constants decrease. The ionic radii of octahedral coordinated Ni^{2+}, Ni^{3+}, and Li^+ are 0.069, 0.056, and 0.076 nm, respectively.[19] The sum of two Ni^{2+} radii is 0.138 nm and the sum of Li^+ and Ni^{3+} is 0.132 nm. The ratio of these two sums is 1.04, and this value corresponds to the ratios of the lattice constants of NiO and $LiNiO_2$. The ratios of lattice constants of NiO and $LiNiO_2$ are 1.03 for the a axes and 1.02 for the c axes. Many authors[7,20] characterize the prepared samples by means of X-ray integral intensity ratio of the reflections (003)/(104). A high value (>1) suggests the existence of nearly stoichiometric $LiNiO_2$. On the basis of references[5,10−17] we have calculated the ratio of $I_{(003)}/I_{(104)}$ for $Li_{1-x}Ni_{1+x}O_2$ in the range of $0 \le x \le 1$. The *z*-values for oxygen in the 6c position vary between $z = 0.25$ (Ni_2O_2) and $z = 0.244$ ($LiNiO_2$). The graph in Figure 3 shows a steady rise of these intensity ratios. Also, these

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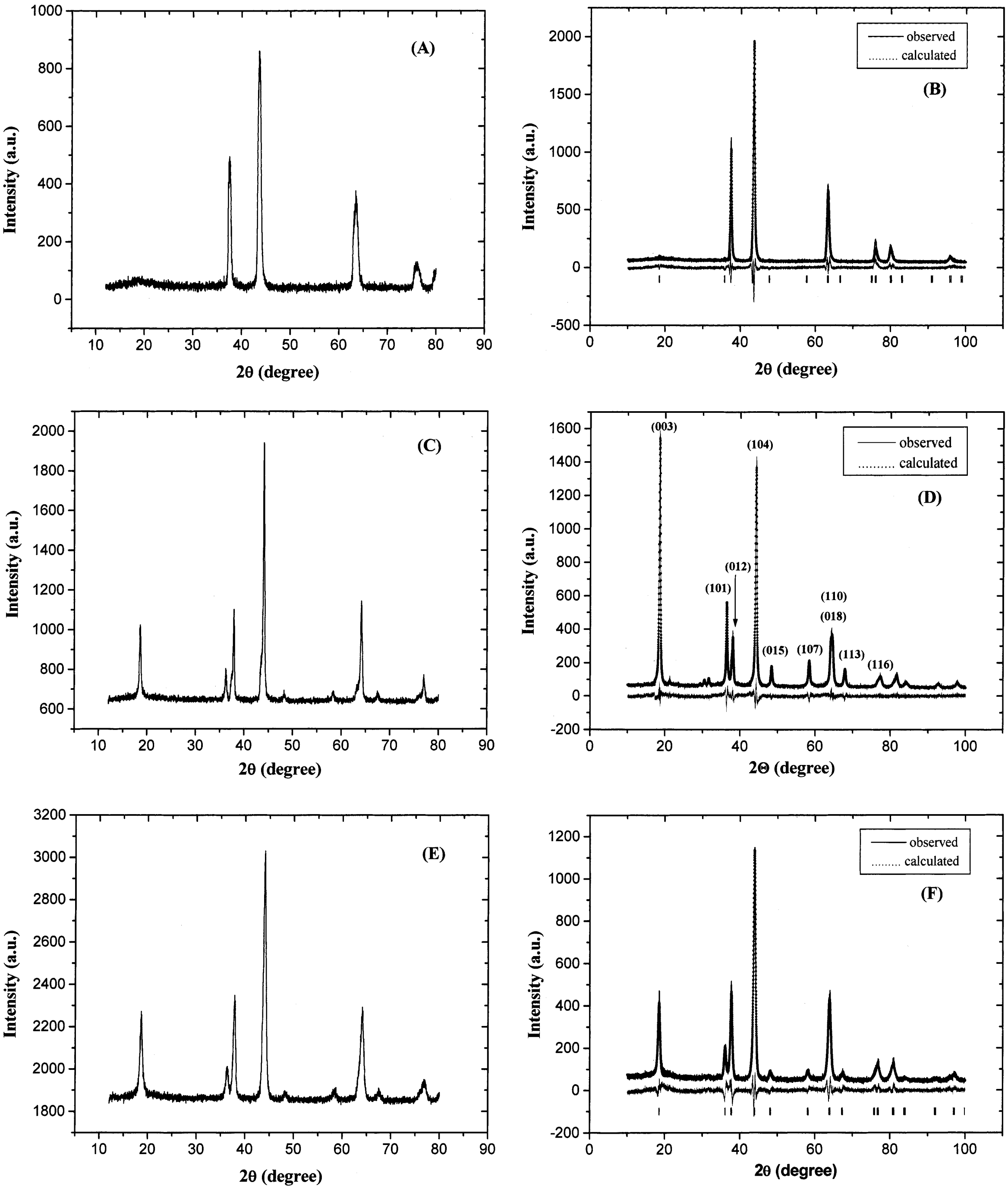

Figure 4. X-ray patterns of samples prepared with Li/Ni ratio of (A) 0.6 (LiNi1); (B) 0.8 (LiNi2); (C) 1.0 (LiNi3); (D) 1.2 (LiNi4); (E) 1.5 (LiNi5); (F) 2.0 (LiNi6).

calculations support the theory of complete mixed crystal formation.

Analysis of Samples

Figure 4 shows the X-ray patterns of all six samples. The patterns of Li/Ni with 0.6 and 0.8 ratios are similar to that of NiO and the pattern of Li/Ni with 1.2 ratio resembles the diffractogram of $LiNiO_2$. The XRD patterns of samples with Li/Ni ratios 1.0, 1.5, and 2.0 show the formation of mixed crystals $Li_{1-x}Ni_{1+x}O_2$, i.e., of NiO and $LiNiO_2$. Peak positions and intensities, as well as line profiles, are influenced by the composition of the initial mixture. All these data run through a maximum or a minimum (Table 2).

The stoichiometry of lithium nickel oxide samples was investigated by ICP. The Li and Ni contents in the samples were obtained in wt % and by means of the relation

$$R = \frac{m_{\mathrm{Li}}}{m_{\mathrm{Ni}}} = \frac{(1-x)M_{\mathrm{Li}}}{(1+x)M_{\mathrm{Ni}}} \tag{4}$$

where m = mass, x = mole fraction, and M = atomic weight.

We have calculated R for a series of x values in $Li_{1-x}Ni_{1+x}O_2$. From these reference R values the lithium nickel ratios were interpolated from the experimental R values. The values of lattice constants, the integral

Table 2. Values of Lattice Constants (a and c), Integral Intensities ($I_{(003)}/I_{(104)}$), Full Width at the Half Maximum (FWHM), and ICP[a]

sample	Li/Ni	ICP $R = m_{Li}/m_{Ni}$	*a* (nm)	*c* (nm)	$Li_{1-x}Ni_{1+x}O_2$	FWHM (104)	$I_{(003)}/I_{(104)}$
refs 15,16,19	0.0		0.2954	1.4462	Ni_2O_2		0.0[b]
refs 13,18	0.4		0.2927	1.4341	$Li_{0.4}Ni_{1.6}O_2$		0.129[b]
ref 4	0.6		0.2910	1.4269	$Li_{0.6}Ni_{1.4}O_2$		0.27[b]
refs 17,14	1.0		0.2880	1.4195	$LiNiO_2$		1.18[b]
LiNi1	0.6	0.025	0.2931	1.4357	$Li_{0.355}Ni_{1.645}O_2$	0.74	0.06
LiNi2	0.8	0.023	0.2934	1.4371	$Li_{0.322}Ni_{1.678}O_2$	0.48	0.065
LiNi3	1.0	0.053	0.2901	1.4257	$Li_{0.618}Ni_{1.382}O_2$	0.32	0.30
LiNi4	1.2	0.075	0.2888	1.4219	$Li_{0.772}Ni_{1.228}O_2$	0.35	1.09
LiNi5	1.5	0.050	0.2904	1.4271	$Li_{0.593}Ni_{1.407}O_2$	0.60	0.28
LiNi6	2.0	0.044	0.2905	1.4264	$Li_{0.535}Ni_{1.465}O_2$	0.77	0.22

[a] The compositions of $Li_{1-x}Ni_{1+x}O_2$ calculated using the ICP data are also given. [b] Calculated.

intensities $I_{(003)}/I_{(104)}$, the full width at the half-maximum (fwhm), and the ICP results are given in Table 2. The compositions of $Li_{1-x}Ni_{1+x}O_2$ compounds determined by ICP are also given in Table 2. It is observed that an increasing amount of Li (Li/Ni > 1.2) in the initial mixture leads to a decrease of Li amount in the compounds. The ICP results are in agreement with the lattice constants of the compounds. The lattice parameters "a" and "c" increase again if the initial mixtures contain greater amounts of Li (Li/Ni > 1.2). The broadening of reflection profiles (fwhm) in the X-ray pattern is an indication either for small domain sizes or micro strains or both.[21] It is obvious that the compounds with higher lithium content have smaller lattice defects.

The lattice constants "a" and "c" obtained from the ICP results of the samples were compared with the reference data in Figure 2. The coherence between lithium content and lattice constants is clearly demonstrated, but the lattice constants deviate significantly to smaller unit cell parameters with increasing lithium amount in the compounds. The X-ray integral intensity ratios $I_{(003)}/I_{(104)}$ show an astonishing accordance between calculated (line curve) and observed data (●). Only the sample with $(1 - x) = 0.772$ deviates to a smaller extent, but the values are in the calculated range (Figure 3).

Discussion

It is clear from the reference curve (Figure 2) that the Li contents of $Li_{1-x}Ni_{1+x}O_2$ determine the lattice constants. The small deviations in lattice constants and integral intensities of the samples from the reference curves could be due to a systematic error in the ICP measurements, because the differences in values *a*, *c*, and $I_{(003)}/I_{(104)}$ increase with increasing Li content in the final product. If we assume that the lattice constants from the reference curve are absolutely true, the lithium contents in the samples can be estimated using the reference curve in Figure 2 and in such case the lithium content in samples (LiNi3 to LiNi6) would be higher than those listed in Table 2. The same is the case with the X-ray integral intensity ratio $I_{(003)}/I_{(104)}$ for sample LiNi6.

The results of Rietveld refinement data for samples LiNi2, LiNi4, and LiNi6 are given in Table 3 and Figure 4. The observed XRD patterns coincide well with the calculated ones, and their pattern differences shown in the lower part of the Figure 4B,D, and F show a good refinement quality. The R_p and R_{wp} values ranging from 7.5 to 10.0 and 9.7 to 12.8 respectively, are in agreement with that reported by Bianchi et al.[22] The Goodness of fit (Gof) is <1.3, which is considered to be quite satisfactory. Rietveld refinement analysis also showed that the Li^+ ions occupy preferably the 3a positions. Statistical distributions on the 3a and 3b atomic position clearly show deviations from the experimental results.[22]

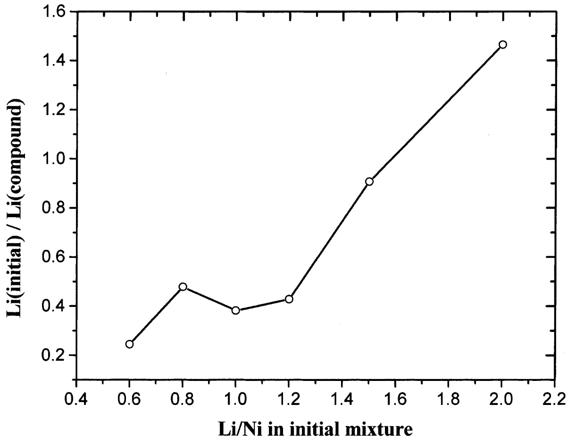

Figure 5. Plot showing change in lithium content in the initial mixture to that of sample as revealed by ICP analysis.

Table 3. Results of Rietveld Refinement of XRD Patterns

sample	R_p	R_{wp}	Gof	*z*
LiNi2	10.02	12.85	1.18	0.256
LiNi4	7.55	9.76	1.10	0.240
LiNi6	9.47	11.55	1.04	0.244

Independent of the above considerations, the main observations of the experimental part of this study are as follows: (i) in all the samples the lithium content is lower than the lithium content taken in the initial mixture; (ii) the lithium content in $Li_{1-x}Ni_{1+x}O_2$ passes through a maximum with increasing Li/Ni ratio; and (iii) the difference in the Li contents of the initial mixture and the sample increases with increasing Li/Ni ratio (Figure 5). It seems that the lithium deficiency in the samples depends on the amount of $LiNO_3$ taken in the initial mixture. The chemical equation for the formation of stoichiometric $LiNiO_2$ in the SPHTC technique can be written as

$$LiNO_3 + Ni(NO_3)_2 + 3CO(NH_2)_2 + O_2 \rightarrow LiNiO_2 + 6H_2O + 4.5N_2 + 3CO_2$$

In all the experiments only the initial concentration of

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$LiNO_3$ is changed from 0.6 to 2.0 mol, and the molecular amounts of the other constituents are kept constant. It is known that the SPHTC synthesis produces a very high temperature (1100−1200 °C). At this higher temperature, there is every possibility that the decomposition of $LiNO_3$ at higher concentrations (samples LiNi5 and LiNi6) may lead to the formation of Li_2O. We have not detected the Li_2O in final product by XRD. From this observation, we conclude that the evaporation of Li_2O might have occurred during the combustion as reported earlier.[20] The evaporation temperature of Li_2O at atmospheric pressure is reported to be around 1200 °C.[23]

Conclusions

The results of this study underline the importance of a careful interpretation of X-ray data. It is obvious that all reports on the formation of different phases in the system NiO − $Li_{1-x}Ni_{1+x}O_2$ are wrong, because a simple unit cell transformation and doubling of the *c*-axis of the triple hexagonal unit cell leads, in the case of NiO, to the same atomic arrangement as in $LiNiO_2$. The fact that the Vegard rule holds true for the entire system NiO − $Li_{1-x}Ni_{1+x}O_2$ when understood as a series of mixed crystals of the α-$NaFeO_2$ structure, is sufficient proof for the soundness of this interpretation. At this point it has to be made clear that our results do not concern the phase transitions observed when a $Li_{1-x}Ni_{1+x}O_2$ phase is undergoing lithium intercalataion/deintercalation processes in electrochemical reactions. This is another branch of reactions, as there is no substitution of nickel ions taking place but only their reduction/oxidation accompanying the lithium ion uptake/expulsion.

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