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

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Version of record first published: 27 Oct 2006

To cite this article: Mikio Shimode, Makoto Sasaki & Ken-Ichi Mukaida (2000): Synthesis of Layered-Structure $LiFeO_2$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 183-188

To link to this article: http://dx.doi.org/10.1080/10587250008026137

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 183-188
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Synthesis of Layered-Structure $LiFeO_2$

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(In final form June 23, 1999)

$LiFeO_2$, with a layered rocksalt structure of α-$NaFeO_2$-type was prepared by ion exchange reaction from Na^+ ion to Li^+ ion using α-$NaFeO_2$. α-$NaFeO_2$-type $LiFeO_2$ was synthesized by using the mixture of LiI and KI in the temperature range 220 to 480 °C. The heat treatment temperature of 600 °C gave α-$LiFeO_2$-type $LiFeO_2$ as a main product. As a result of Rietveld analysis, the structure of $LiFeO_2$ which assigned to α-$NaFeO_2$-type by an XRD measurement, was the mixture of α-$NaFeO_2$-type and Li-intercalated spinel-type structures.

Keywords: α-$NaFeO_2$-type oxide; $LiFeO_2$; Ion exchange reaction; Structure refinement

INTRODUCTION

The oxides having both chemical formula of ABO_2 (A, monovalent metal; B, trivalent metal) and containing Li^+ ion in the " A" site, with a layered rocksalt α-$NaFeO_2$-type structure, have been studied on the property for cathode materials in Li^+ ion secondary battery [1, 2]. $LiCoO_2$ [3] has been used for a practical application, because it has high charge and discharge voltage and excellent cycling characteristics. On the other hand, $LiFeO_2$ with α-$NaFeO_2$-type, can be expected to have a great advantage in comparison with $LiCoO_2$ for commercial use, because of the low cost of Fe.

Figure 1 shows the structure field map for the various ABO_2 containing Li^+ ion and Na^+ ion in the " A" site[4, 5]. On the series with Li^+ ion in the " A" site, oxides contain ions with smaller ionic radii than V^{3+} ion (ionic radius: 0.640 Å) in the " B" site adopt α-$NaFeO_2$-type and the compounds with larger ionic radii

than V^{3+} ion in the " B" site have α-$LiFeO_2$-type structure. Therefore, it seems that α-$NaFeO_2$-type $LiFeO_2$ is not prepared by a conventional solid state reaction[6]. Tabuchi et al.[7] attempted to synthesize $LiFeO_2$ with α-$NaFeO_2$-type structure using various starting materials by solid state reaction. However, it was unsuccessful. Nalbandyan and Shukaev[8] prepared α-$NaFeO_2$-type $LiFeO_2$ from α-$NaFeO_2$ which is stable in α-$NaFeO_2$-type structure, by ion exchange reaction from Na^+ ion to Li^+ ion in molten $LiNO_3$. Fuchs and Kemmler-Sack[9] prepared using the mixture of $LiNO_3$ and LiCl, and Shirane et al.[10] employed the mixed salt of LiCl and KCl.

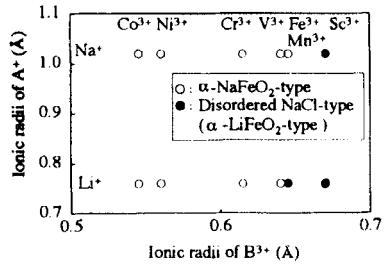

FIGURE 1 Structure field map for various ABO_2 compounds.
Structural data were taken from Refs. [4] and [5].

The present work has focused on the reaction condition for preparing α-$NaFeO_2$-type $LiFeO_2$ by using the mixture of LiI and KI.

EXPERIMENTAL

α-$NaFeO_2$ was prepared by solid state reaction. Na_2O (Wako Pure Chemical Ind., Ltd.; 85 %) and γ-Fe_2O_3 (Kojundo Chemical Lab. Co., Ltd.; 99%) were mixed in N_2 filled glove box (mixing ratio, Na: Fe= 55: 45 at%), and shaped by CIP method (pressure, 60 MPa; pressing time, 60 sec). Shaped specimens were heated at 600 °C for 30 h in O_2 (heating rate, 250 °C• h^{-1}; flowing rate, 200 SCCM). α-$NaFeO_2$ obtained was mixed with various Li-salts in a glove box. Reagents used for ion exchange reaction were $LiNO_3$ (Kishida Chemical Co., Ltd.; 98 %), LiCl (Kishida Chemical Co., Ltd.; 98 %), LiI (Kishida Chemical Co., Ltd.; 98 %) and KI (Kishida Chemical Co., Ltd.; 98 %). Ion exchange reaction was performed with $LiNO_3$, LiI, mixed salts of $LiNO_3$: LiCl= 88: 12 mol% and LiI: KI= 41: 59 mol%. To verify the effect of ion exchange from Na^+ ion to Li^+ ion, the mixing molar ratio was Na: Li= 1: 5. The mixed powder specimens were heated at 200- 600 °C for 4 h in Ar (heating rate, 250 °C• h^{-1}; flowing rate,

200 SCCM). After heat treatment, the reaction products were washed with distilled water then dried.

The powder specimens obtained were evaluated by an XRD (Rigaku Denki, RV-200) with CuK α_1 radiation. Intensity data were collected from 5 to 80 deg in 2 θ at room temperature; scan speed, 4 deg• min^{-1}; scan step, 0.04 deg. The structure and the lattice parameters were refined by Rietveld analysis using the computer program RIETAN-97 beta.

RESULTS AND DISCUSSION

The reaction conditions and their products are summarized in Table I. As a result of using $LiNO_3$ in the ion exchange reaction, α-$NaFeO_2$ was included in the specimens in spite of heating at the temperature above its melting point (255 °C). When LiI was used in the ion exchange reaction, no ion exchange reaction occurred at the heat treatment temperature below melting point of LiI (446 °C). However the phase obtained at the heat treatment temperature above the melting point, was only a cation disordered rocksalt-type (α-$LiFeO_2$-type) $LiFeO_2$ with

TABLE I Reaction conditions and products.

Salts	Reaction conditions	Reaction products
$LiNO_3$	300 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$, α-$NaFeO_2$
LiI	300 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$, α-$NaFeO_2$
	460 °C, 4h	α-$LiFeO_2$-type $LiFeO_2$
$LiNO_3$/ LiCl	200 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	300 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	340 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	380 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	460 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	500 °C, 4h	α-$LiFeO_2$-type $LiFeO_2$
LiI/ KI	220 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	300 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	380 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	380 °C, 8h	α-$NaFeO_2$-type $LiFeO_2$
	380 °C,12h	α-$NaFeO_2$-type $LiFeO_2$, α-$LiFeO_2$-type $LiFeO_2$
	440 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	480 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$
	540 °C, 4h	α-$NaFeO_2$-type $LiFeO_2$, α-$LiFeO_2$-type $LiFeO_2$
	600 °C, 4h	α-$LiFeO_2$-type $LiFeO_2$

cubic and a space group of Fm3m. Therefore, the result shows the complete occurrence of the ion exchange reaction from Na^+ ion to Li^+ ion. When only one Li-salt is used as starting material, it is suggested that the Li-salt reactivity on α-$NaFeO_2$ is not so good, by the formation of single phase product of α-$LiFeO_2$-type $LiFeO_2$ instead of α-$NaFeO_2$-type structure.

As a result of mixed salt ($LiNO_3$: LiCl = 88: 12 mol%) used by Fuchs and Kemmler-Sack[9], the sample synthesized at 200 °C under eutectic temperature of 260 °C, contained α-$NaFeO_2$-type $LiFeO_2$. The heating up to 460 °C resulted a main product of α-$NaFeO_2$-type $LiFeO_2$. However, higher temperature of 460 °C gave α-$LiFeO_2$-type $LiFeO_2$ as a main product. No diffraction peak of α-$NaFeO_2$ as starting material was observed in the products obtained by using the mixed salt of $LiNO_3$ and LiCl under any heat treatment conditions. Thus, it is indicated that the mixed salt has a role to promote ion exchange reaction from Na^+ ion to Li^+ ion.

Figure 2 shows the XRD patterns for the products prepared by the mixed salt of LiI and KI. The use of the mixed salt of LiI: KI with a composition of 41: 59 mol% (eutectic temperature of 260 °C) at a lower temperature of 220 °C than the melting point, resulted α-$NaFeO_2$-type $LiFeO_2$ same as the use of the mixture of $LiNO_3$ and LiCl. α-$NaFeO_2$-type $LiFeO_2$ and α-$LiFeO_2$-type $LiFeO_2$ as main phase were prepared in the temperature 220-480 °C, above 480 °C, respectively. The crystallization of $LiFeO_2$ was attempted at fixed heat treatment temperature of 380 °C with varying holding time, because of the lower diffraction intensities of the specimens. However, phase transformation from α-$NaFeO_2$-type to α-

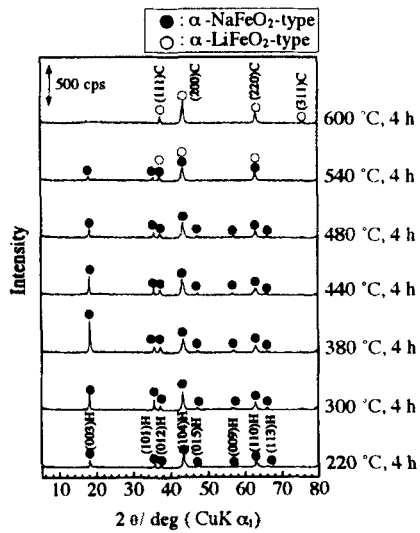

FIGURE 2 XRD patterns for $LiFeO_2$ obtained by ion exchange reaction using LiI/ KI at various temperatures.
(h k l) H as the hexagonal cell
(h k l) C as the cubic cell

$LiFeO_2$-type occurred without increasing the diffraction intensities. Therefore, these results indicate the difficulty of crystallization of α-$NaFeO_2$-type $LiFeO_2$ obtained by ion exchange from Na^+ ion to Li^+ ion in α-$NaFeO_2$.

The structure of $LiFeO_2$ synthesized by the mixed salt of LiI and KI was refined by Rietveld analysis. The Rietveld analysis performed on the specimen prepared at 380 °C for 4 h with the highest diffraction intensities, and used with α-$NaFeO_2$-type structure. For this analysis, all atom occupations were fixed in 1. The refinement results and the lattice parameters are listed in Table II. Judging from the results of S value in Table II, higher S value of 1.5136 was obtained in the α-$NaFeO_2$-type structure model. Thus, $LiFeO_2$ obtained in this work, can not be only α-$NaFeO_2$-type structure because of the higher S value than 1.3.

As shown in Figure 2, the diffraction peaks around 38, 43 and 63 in 2 θ (

TABLE II Rietveld refinement results for $LiFeO_2$.

Structure model	S	a (Å)	c (Å)
α-$NaFeO_2$-type (R-3m)	1.5136		
Two phases of α-$NaFeO_2$ type (R-3m) and α-$LiFeO_2$ type (Fm3m)	1.7215		
Two phases of α-$NaFeO_2$ type (R-3m) and Li-intercalated spinel type (Fd-3m)	1.2789	2.958(8)	14.57(8)

(S: goodness of fit between observed and calculated data)

deg) were assigned to (111), (200) and (220) for α-$LiFeO_2$-type $LiFeO_2$, respectively. Thus, the structure refinement was done with two-phase model of α-$NaFeO_2$-type and α-$LiFeO_2$-type structures. However, the result with two-phase model still showed a higher S value of 1.7215.

$LiFeO_2$ prepared by Fuchs and Kemmler-Sack[9] and by Shirane et. al.[10] has the mixed structure of α-$NaFeO_2$-type $LiFeO_2$ and Li-intercalated spinel-type $Li_2Fe_2O_4$. Then, Rietveld analysis was carried out by another two-phase model of α-$NaFeO_2$-type $LiFeO_2$ with a space group of R-3m and Li-intercalated spinel-type $Li_2Fe_2O_4$ with cubic and a space group of Fd-3m. As a result of S= 1.2789, it was better fit between observed and calculated data. The lattice parameters after Rietveld analysis, agree nearly with the values reported by Fuchs and Kemmler-Sack[9] (a= 2.960(5) Å, c= 14.55(1) Å) and by Shirane et al. [10] (a= 2.9466(5) Å, c= 14.521(4) Å).

Table III gives the lattice parameters of $LiFeO_2$ prepared in this work compared with other ABO_2-type compounds with α-$NaFeO_2$ structure containing Li^+ in the "A" site. The length of the a axis extends a little, whereas the c axis greatly increases with increasing ionic radii in the "B" site.

TABLE III Lattice parameters for various α-$NaFeO_2$-type compounds.

Compounds	a (Å)	c (Å)	References
$LiCoO_2$	2.805(2)	14.203(4)	[11]
$LiVO_2$	2.841(1)	14.751(1)	[11]
$LiNiO_2$	2.885(1)	14.203(4)	[11]
$LiCrO_2$	2.896(2)	14.34(3)	[11]
$LiFeO_2$	2.958(8)	14.57(8)	This work

CONCLUSIONS

$LiFeO_2$ with α-$NaFeO_2$-type structure was prepared by ion exchange reaction from Na^+ ion to Li^+ ion in α-$NaFeO_2$. Application of the mixture of LiI and KI produced α-$NaFeO_2$-type $LiFeO_2$ as a main phase in the temperature range from 220 to 480 °C. α-$LiFeO_2$-type $LiFeO_2$ was obtained at 600 °C by this method. Rietveld refinement resulted that $LiFeO_2$ obtained was the mixed structures of α-$NaFeO_2$ type and Li-intercalated spinel type.

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