

Topochemical Reactions of Li_xNbO_2

NOBUHIRO KUMADA, SUGURU MURAMATU, FUMIO MUTO,
AND NOBUKAZU KINOMURA*

*Institute of Inorganic Synthesis, Yamanashi University, Miyamae-cho 7,
Kofu 400, Japan*

AND SHINICHI KIKKAWA AND MITUE KOIZUMI

*Institute of Scientific and Industrial Research, Osaka University,
Mihogaoka 8-1, Ibaragi 567, Japan*

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Intercalation and deintercalation of lithium in Li_xNbO_2 were carried out by electrochemical and chemical methods. The hexagonal system for the compounds was retained over the whole range of x observed ($0.51 < x < 0.93$). The a parameter was increased with decrease of x , while the c parameter remained almost unchanged. This variation of the crystallographic parameters was explained by the deformation of NbO_6 trigonal prisms caused by weakening of Nb-Nb bonding in the $(\text{NbO}_2)_n$ sheets. Temperature-independent paramagnetism on the order of 10^{-5} emu/mole and semiconductive behavior were observed for Li_xNbO_2 . © 1988 Academic Press, Inc.

Introduction

Intercalation and deintercalation of lithium or sodium have been investigated extensively on inorganic compounds because of their potential use as cathode materials for a secondary battery (1) or in order to prepare metastable compounds which cannot be obtained by usual methods (2). The most attention has been directed to transition metal dichalcogenides having the general formula of MX_2 (M , transition metals of group VIB, VB, or VIB; X , S or Se). This group is characterized by van der Waals bonded layers between which various chemical species can be accommodated.

In addition to the dichalcogenides, many

attempts to prepare new metastable oxides by intercalation or deintercalation have been made by using layered or framework oxides such as rutile (3), spinel (4), ReO_3 , and $\alpha\text{-NaFeO}_2$ (5) type compounds. Among them, $\alpha\text{-NaFeO}_2$ type and its analogous compounds are the group which have been studied most numerously. A review by Delmas and Hagenmuller gives comprehensive understanding concerning structural changes on intercalation and deintercalation of these compounds (6).

Although LiNbO_2 , which was first reported by Meyer and Hoppe (7), has a similar formula to $\alpha\text{-NaFeO}_2$ -type compounds and its analogs, they are different in the structure of layer. The layer of LiNbO_2 is composed of edge-sharing of NbO_6 trigonal prisms and is similar to the 2H-type transi-

* To whom correspondence should be addressed.

tion metal dichalcogenides. Transition metal ions in the other group are surrounded by six oxygens octahedrally. In LiNbO_2 , the existence of Nb–Nb bonding is supposed by Burdett and Hughbanks (8).

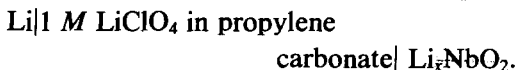
We will describe here electrochemical and chemical intercalation and deintercalation of lithium in Li_xNbO_2 and changes of the structure and magnetic properties of the products.

Experimental

Starting powder of Li_xNbO_2 was prepared by heating a mixture of powders of Li_3NbO_4 (9) and NbO (10) in a molar ratio of 1 : 2 in a vacuum silica tube at 1050°C for 60 hr. Li_3NbO_4 was obtained by heating a mixture of Li_2CO_3 (99.9%) and Nb_2O_5 in a molar ratio of 3 : 1 at 900°C in air for 48 hr, and NbO was prepared by firing a mixture of Nb_2O_5 and metallic Nb in a molar ratio of 1 : 3 in an evacuated silica tube at 1100°C for 72 hr. Weight gain on oxidation in air revealed that the Nb/O ratio for NbO prepared here was almost 1 : 1.

Chemical deintercalation was carried out by stirring the starting powder (1–2 g) in 0.1–2 M acetonitrile solution of iodine or bromine. A solution of *n*-butyllithium in hexane (6%) was used for chemical intercalation. The reaction temperature was room temperature or 60°C and the duration time ranged from 5 to 96 hr for both reactions. Products were separated by centrifugation and washed with acetonitrile or hexane several times and finally with ethanol. The amount of lithium released into the solution in the case of deintercalation was determined by the atomic absorption spectroscopy.

The cells for the electrochemical reaction were built up as follows:



The cell was discharged or charged at a constant current of 500 $\mu\text{A}/\text{cm}^2$.

Products thus obtained were identified by X-ray powder diffractometry with $\text{CuK}\alpha$ radiation. Lattice parameters were determined by least-squares refinement of powder data taken with a scanning speed of $\frac{1}{4}^\circ/\text{min}$. Silicon was used as an internal standard. The crystal structure of a deintercalated compound was refined using the Rietveld method (11). The powder data was collected by using $\text{CuK}\alpha$ radiation with a graphite monochromator for 20 sec at 0.05° intervals over 2θ angle from 10 to 100° . Magnetic susceptibilities were measured with a Faraday balance from 80 to 300 K at several magnetic field strengths up to approximately 1 T. Electric resistances were measured on powder samples pressed at approximately 40 MPa at room temperature by the two-probe method in the temperature range 80 to 300 K. Samples for the structure determination and magnetic measurement were produced by the chemical method.

Results

Preparation of the Starting Material

An X-ray powder pattern of the reddish brown product was very similar to that of LiNbO_2 (7). The lattice parameters were calculated to be $a = 2.912(1)$ and $c = 10.46(1)$ Å in the hexagonal system. The a parameter was slightly larger than the one reported for LiNbO_2 , while the c parameter coincided. The chemical analysis showed that the ratio of Li/Nb was 0.87. The weight gain of 11.5% on oxidation of the product at 900°C in air agreed well with the value of 11.4% calculated on the assumption that Nb ions in $\text{Li}_{0.87}\text{NbO}_2$ were oxidized to Nb^{5+} . The value of the a parameter is larger than that of LiNbO_2 and is generally observed for the deintercalated phase as mentioned later. These facts indicate that the

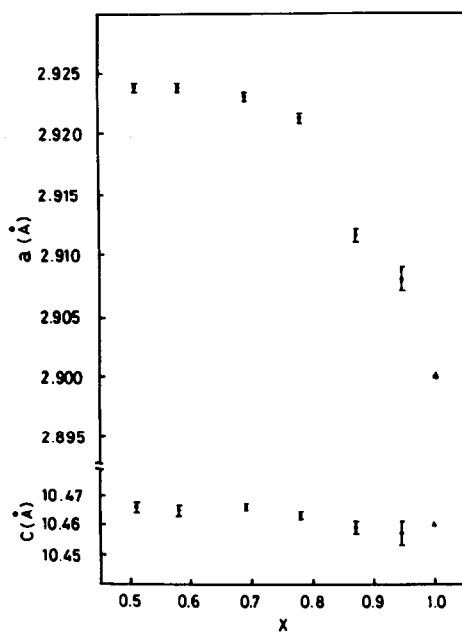


FIG. 1. Lattice parameters vs lithium content x in Li_xNbO_2 . Triangles represent values reported by Meyer and Hoppe (7).

compound used as the starting material was nonstoichiometric. The nominal composition of the starting powder implies that the average valence of Nb is 3.13, composed of Nb^{3+} and Nb^{4+} .

Chemical Treatment

Chemical deintercalation changed the color of the sample from reddish brown to black. The minimum value of x , corresponding to the maximum extraction of Li, was found to be $x = 0.51$, when deintercalation was carried out by using bromine as an oxidizing agent at 60°C for 72 hr. An X-ray powder diffraction pattern of the product showed a slight shift of peaks to lower 2θ angles from those of starting material except $00l$ reflections and was indexed with a hexagonal cell.

On the other hand, the color of the sample was not changed on lithiation by using n -butyllithium. The maximum value of x of

0.93 was attained at 60°C for 50 hr. The lattice parameters for the sample were calculated to be $a = 2.908(1)$ and $c = 10.46(1)$ Å. Contrary to the deintercalation, a slight decrease of the a parameter was observed, while the c parameter remained almost constant.

By intercalation or deintercalation of Li, extensive structural change does not seem to occur, except for a change of the a parameter. The evolution of lattice parameters on intercalation and deintercalation is shown in Fig. 1. The a parameter, which corresponds to the Nb–Nb distance in the $(\text{NbO}_2)_n$ layer, is strongly dependent on x in the region of $0.7 < x < 1$, and slightly increases in $x < 0.7$. The c parameter remains almost constant, independent of x . This behavior of the c parameter is unusual when compared with increase of the c parameter of other ABO_2 compounds with α - NaFeO_2 -type structure and its analogs on deintercalation.

Electrochemical Method

The open circuit voltage (OCV) vs the composition is shown in Fig. 2. Variation of OCV with x was continuous during deintercalation and intercalation, indicating that

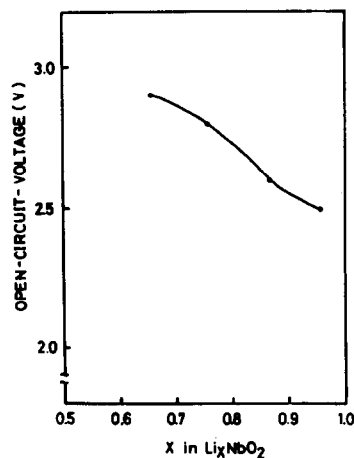


FIG. 2. Open-circuit voltage against lithium content x in Li_xNbO_2 .

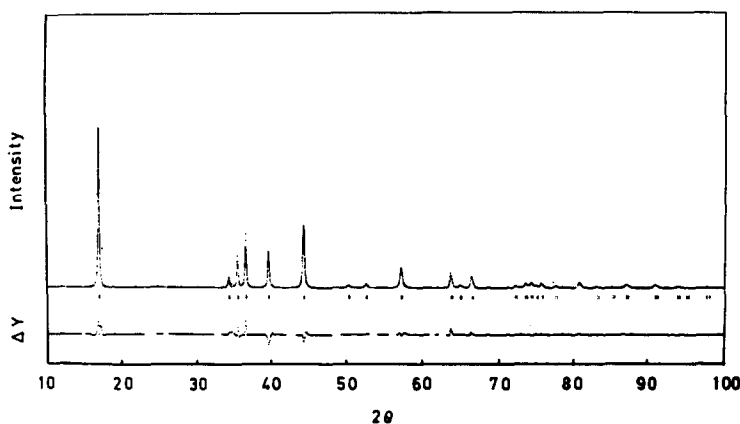


FIG. 3. Rietveld refinement patterns for Li_xNbO_2 . Observed data are shown by dots and calculated pattern is drawn by solid line in the upper portion of the figure. Positions of reflections calculated for $\text{CuK}\alpha_1$ and $\text{K}\alpha_2$ are marked by vertical bars in the middle part of the figure. The lower portions are plots of ΔY , the differences between observed and calculated intensities.

there is no region of multiple phases over the observed composition range and that the composition changes continuously. Deintercalation proceeded up to $x \approx 0.5$ with OCV of 2.95 V but further extraction was not carried out because of partial decomposition of the electrolyte. Intercalation was attained up to $x = 0.96$ with OCV of 2.5 V.

The lattice parameters of products obtained by the electrochemical method changed in the same way as those for products obtained by the chemical method, having similar magnitudes to the latter at the corresponding compositions. The change in color also agreed with the change by the chemical method.

Structure Refinement

As mentioned above, no structural change was observed on the intercalation or deintercalation of Li_xNbO_2 , but unusual dependence of the a and c parameters on x was observed. In order to estimate the interatomic distances, the structure refinement by the Rietveld method was carried out for a deintercalated product by supposing the same space group of $P6_3/mmc$ with LiNbO_2 (7). The sample was prepared by

the chemical method and its composition was $\text{Li}_{0.58}\text{NbO}_2$. The final R factors, R_{WP} , R_{P} , and R_{B} , defined in Ref. (12) were 14.9, 11.6, and 9.1%, respectively. Observed and calculated diffraction profiles are shown in Fig. 3 and the atomic coordinates and temperature factors are shown in Table I.

Electric and Magnetic Properties

In the whole measured composition range ($0.51 < x < 0.93$), Li_xNbO_2 showed temperature-independent paramagnetism and semiconductive behavior. The magnetic susceptibility increased slightly with decrease of x , while its magnitude ranged in the order of 10^{-5} emu/mol (Fig. 5). Unlike the result reported by Meyer and Hoppe

TABLE I
POSITIONAL AND THERMAL PARAMETERS FOR
 $\text{Li}_{0.58}\text{NbO}_2$ (ESTIMATED STANDARD DEVIATIONS
IN PARENTHESES)

Atom	Position	x	y	z	$B(\text{Å}^2)$
Li	2a	0	0	0	2(4)
Nb	4d	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	0.4(2)
O	4f	$\frac{1}{3}$	$\frac{2}{3}$	0.133(2)	6.4(7)

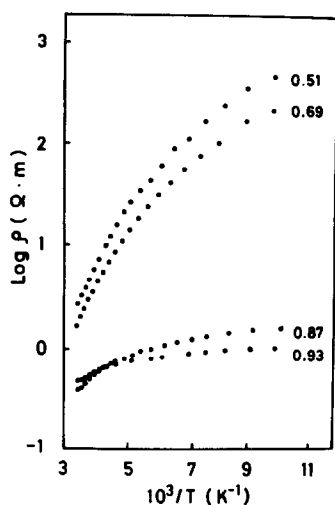


FIG. 4. Temperature dependence of electrical resistivity of Li_xNbO_2 .

(13), clear dependence of the susceptibility on magnetic field strength was not observed. As seen in Fig. 4, positive dependence on temperature was observed for the electric resistivities of Li_xNbO_2 . In the region of high x , near the stoichiometric composition, the temperature dependence of resistivity is slight, while it is much larger at low x . The resistivities increased with a decrease of x .

Discussion

By extraction of alkali ions from interlayer spaces of AMoO_2 ($A = \text{Li, Na; } M = \text{Cr,}$

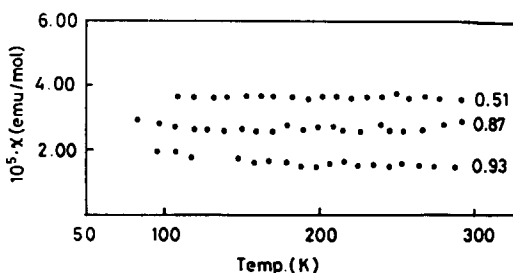


FIG. 5. Magnetic susceptibilities of Li_xNbO_2 .

Ni, Co), the structures of which are $\alpha\text{-NaFeO}_2$ -type or are related to it, a decrease of the a parameter and an increase of the c parameter are generally observed on extraction of A (14). This change in the crystallographic axes is considered to result from a decrease of ionic radius of the transition metal ion in the layer and an increase of repulsive force between layers. The a parameter corresponds to the metal-metal distance in the $(\text{MO}_2)_n$ layer, therefore contraction of part of the transition metal ion by oxidation causes the decrease of the a parameter. The partial oxidation results in decrease of negative charge on the sheet and positive charge in the interlayer spaces, and the attractive force between the sheet and alkaline ions is weakened and repulsive force between O^{2-} and the opposite sheets increases. Then, the c parameter increases.

As an exception, a contraction of the c parameter was observed for LiVO_2 and NaTiO_2 (15, 16). In these compounds, migration of the transition metal ions from intralayer to interlayer octahedra was supposed on deintercalation, and therefore the transition metal ions in the interlayer spaces was considered to fasten a connection between sheets and decrease the c parameter.

On the other hand, expansion of the a parameter and the almost constant c parameter were observed on extraction of Li^+ ions from interlayer spaces in the system of Li_xNbO_2 . The interatomic distances in $\text{Li}_{0.58}\text{NbO}_2$ as well as those for LiNbO_2 (7) are listed in Table II. Expansion of LiO_6 and the larger separation of sheets are clearly seen in $\text{Li}_{0.58}\text{NbO}_2$ when compared with the stoichiometric compound. At the same time, the NbO_6 trigonal prism deformed so that it contracted along the c -axis and its basal plane was enlarged.

In spite of the almost constant c parameter for Li_xNbO_2 , its interlayer spacing is increased on partial oxidation as $\alpha\text{-NaFeO}_2$ -type and related compounds due to the repulsion between layers. However, the

TABLE II
INTERATOMIC DISTANCES AND THICKNESSES OF THE
SHEET AND INTERLAYER SPACE

Distances (Å)	LiNbO ₂ ^a	Li _{0.58} NbO ₂ ^b
Li–O	2.13	2.19
Nb–O	2.11	2.09
(LiO ₂) _n ^c	2.64	2.78
(NbO ₂) _n ^d	2.59	2.46

^a Ref. (7).

^b This work.

^c Thickness of interlayer space was estimated from the position of oxygen.

^d Thickness of the (NbO₂)_n sheet was estimated from the position of oxygen.

contraction of the NbO₆ trigonal prism along the *c*-axis compensates the expansion of interlayer spacing. As a result, the *c* parameter seems to remain unchanged. The expansion of the interlayer spacing by 0.17 Å for Li_{0.58}NbO₂ from the stoichiometric compound is comparable to the increase of the *c* parameter by 0.22 Å for Li_{0.49}Co_{1.01}O₂ (5).

The reason why the NbO₆ prism deforms in the above-mentioned way on partial oxidation should be interpreted by taking account of the bond scheme of Nb in the trigonal prismatic environment. Burdett and Hughbanks (8) proposed the stabilization of this structure by the metal–metal bonding similar to that for MoS₂, although the stability range for the trigonal prism is narrow around *d*² configuration. This means that a two-dimensional Nb network linked by the metal–metal bonding is formed parallel to the basal plane. By partial oxidation, the electron density in metal–metal bonding is reduced and consequently the metal–metal bonding is weakened. This leads to an expansion of Nb–Nb distance. At the same time, the oxygen–oxygen distance (length of shared edge perpendicular to the Nb network) is considered to be shortened in order to reduce the repulsion between Nb ions which have more effective positive

charge. A similar shortening of the shared edge is observed for VO₂, when the metal–metal bonding is broken (17). The magnitude of shortening is calculated to be 0.12 Å for VO₂ and 0.13 Å for Li_xNbO₂.

Burdett and Hughbanks (8) also predicted stoichiometric LiNbO₂ to be a diamagnetic semiconductor. We could not prepare the stoichiometric compound, only nonstoichiometric compounds, Li_xNbO₂. All of them showed the temperature-independent paramagnetism with very low susceptibility. The magnitude of susceptibility depended slightly on *x*, and at *x* = 0.93, which is closest to the stoichiometry among the observed compositions, the susceptibility was minimum, but still not diamagnetic. Because the electric resistivity was measured on the pressed body of a powder sample, we could not positively determine if the compound near stoichiometry was a semiconductor. The fact that the electric resistivity increased with degree of deviation from the stoichiometry and the low temperature-independent susceptibility might indicate that the nonstoichiometric compounds, Li_xNbO₂, prepared here are semiconductors with the van Vleck paramagnetism. The stability range of the trigonal prism is so narrow that oxidation of Li_xNbO₂ extended beyond our range might result in formation of NbO₆ octahedra from the trigonal prism.

Summary

(1) Li_xNbO₂ (0.51 < *x* < 0.97) was prepared topochemically from Li_{0.87}NbO₂ by means of electrochemical and chemical methods.

(2) In all composition ranges, the compounds showed semiconductive behavior with weak van Vleck paramagnetism.

(3) The *c* parameter remained almost unchanged, while the *a* parameter increased with decreasing *x*.

(4) The change of crystallographic pa-

rameters was related to the slight deformation of the NbO_6 trigonal prism.

(5) The deformation of the NbO_6 prism was considered to be caused by a weakening of the Nb–Nb bonding in $(\text{NbO}_2)_n$ sheets.

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