JOURNAL OF SOLID STATE CHEMISTRY 97, 105–114 (1992)

# Li-inserted $Nb_3O_7F$ and Its Thermal Decomposition Products Studied by High-Resolution Electron Microscopy and X-ray Powder Diffraction

LOTTA PERMÉR

*Department of Inorganic Chemistry, Arrhenius Laboratory,*
*Stockholm University, S-106 91 Stockholm, Sweden*

Received June 7, 1991; in revised form September 6, 1991

Li has been chemically inserted into $Nb_3O_7F$, obtained by thermal decomposition of $NbO_2F$. The $Li_{3x}Nb_3O_7F$ ($0 < x \leq 1.5$) products have been investigated by X-ray powder diffraction and high-resolution electron microscopy techniques. Three different phases, one of orthorhombic, one of triclinic, and one of hexagonal symmetry, could be identified, although none of them were pure. Chemical delithiation was performed by reacting the Li-containing samples with DDQ in acetonitrile. The delithiation results depended on the total Li content of the starting material, but lithium could never be fully extracted. Thermal decomposition of $Li_{3x}Nb_3O_7F$ ($0 \leq x \leq 1.4$) was studied by differential scanning calorimetry. The samples were heated to 950 K, and the thermograms revealed that the starting temperature of the decomposition decreased with increasing Li content. The following phases were obtained: LiF, $NbO_2$, $LiNb_3O_8$, and $LiNbO_3$.

## Introduction

The compounds formed by chemical insertion of lithium into $NbO_2F$ have recently been characterized by X-ray powder diffraction and high-resolution electron microscopy (HREM) (*1*). With increasing Li content the $NbO_2F$ structure, isomorphous with that of $ReO_3$, gradually transforms into an approximately hexagonally close-packed structure of the $LiNbO_3$ type plus an amorphous product. An extension of (*1*) includes an investigation of the thermal stability of the insertion products ($Li_xNbO_2F$). The thermal decomposition resulted in a variety of phases mainly with close-packed anion arrangements, in contrast to that of $NbO_2F$ (*2*).

An interesting question following from these results is whether the introduction of crystallographic shear planes into the $NbO_2F$ structure type will affect its ability of incorporating Li. The structure of $Nb_3O_7F$ is built up of slabs of the $NbO_2F$ type (three octahedra wide) linked by common edges so that crystallographic shear planes running parallel to (100) are formed (see Ref. (*8*) and Fig. 6). Therefore this structure was chosen as a host for Li insertion. The products were examined by X-ray powder diffraction and by HREM methods. The thermal decomposition of the insertion products was also investigated. The results are compared with those obtained for $Li_xNbO_2F$ and with those concerning Li-inserted $Nb_3O_7F$ published earlier by Cava *et al.* (*3*).

0022-4596/92 $3.00

## Experimental

$Nb_3O_7F$ was synthesized by thermal decomposition of $NbO_2F$ (obtained from Nb metal (*1*)) in argon at about 970 K (*4*). The product was identified by X-ray powder diffraction and ascertained to be a single phase sample before the insertion reactions were started.

Lithium was inserted chemically by treating $Nb_3O_7F$ with *n*-butyllithium dissolved in *n*-hexane (Merck-Schuchardt, 1.6 *M*, zur Synth.). Approximately 190 mg of $Nb_3O_7F$ was mixed with 2–4 ml of 1.6 *M* *n*-Bu-Li in *n*-hexane and 10–30 ml of pure *n*-hexane, and the mixtures were stirred for 1–16 days. All reactions were carried out at 295 K in a drybox filled with $N_2$ (g). The resulting dark blue or black crystals were washed three times in *n*-hexane and dried in vacuum for about 1 hr.

All insertion products were analyzed for Li content by atomic absorption spectrometry (AAS) according to the method described in (*1*).

Delithiation was carried out by reacting the Li-containing products with 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) dissolved in acetonitrile. Approximately 30 mg of the samples were mixed with 25 ml of 0.1 *M* DDQ in acetonitrile, and the mixtures were stirred for 4 days at room temperature in sealed flasks. The resulting products were washed three times with acetonitrile, and then dried in vacuum for about 1 hr.

Thermal decomposition of the Li-inserted samples was studied by differential scanning calorimetry (DSC, Perkin–Elmer DSC-2, equipped with a thermal analytical data system). Approximately 5 mg of a sample was heated in an argon atmosphere in the DSC equipment, from 600 to 950 K at a rate of 10 K/min, followed by a rapid cooling to room temperature.

X-ray powder diffraction photographs were taken with a Guinier–Hägg camera using $CuK\alpha_1$ radiation, and with Si as an internal standard. The powder patterns were indexed, and the unit-cell parameters were refined with the program PIRUM (*5*).

Electron-microscope specimens were prepared as described in (*1*). These were examined at 200 kV using a JEM-200CX electron microscope equipped with a high-resolution top-entry goniometer stage with tilt angles of ±10°, and with a liquid nitrogen cooled sample holder. The objective aperture used corresponds to 0.41 $Å^{-1}$ in reciprocal space. Theoretical ED patterns were calculated with a modified version of the program DIFPAT (*6*), and simulated images were calculated by the multislice method, using a locally modified version of the SHRLI suite of programs (*7*).

## Results

### *1. Synthesis of $Nb_3O_7F$*

The synthesis of $Nb_3O_7F$ by thermal decomposition of $NbO_2F$ resulted in a white, microcrystalline specimen for which the unit-cell parameters obtained from Guinier X-ray powder diffraction data were refined to the values given in Table I (in good agreement with those given in (*8*)). The ED patterns contained weak extra reflections belonging to the superstructure previously observed (*2*). HREM studies showed the crystals to be well-ordered, but intergrowths of small amounts of the high-pressure form of $Nb_3O_7F$ were frequently found (*9*).

### *2. Li-inserted Samples of $Nb_3O_7F$*

*2.1. Li-inserted samples studied by X-ray powder diffraction.* Insertion of Li into the crystal structure of $Nb_3O_7F$ resulted in black or dark blue powders of $Li_{3x}Nb_3O_7F$ ($0 < x \leq 1.5$), where $x$ corresponds to the number of lithium atoms per niobium atom. All Li-insertion products were examined by X-ray powder diffraction. The lines became a little

TABLE I

UNIT CELL PARAMETERS DERIVED FROM X-RAY POWDER DIFFRACTION DATA

| Compound | $a$(Å) | $b$(Å) | $c$(Å) | $\alpha$ | $\beta$ | $\gamma$ | $V$(Å$^3$) | Ref. |
|---|---|---|---|---|---|---|---|---|
| $Nb_3O_7F$ | 20.67 | 3.833 | 3.927 | — | — | — | 311.13 | (*8*) |
| $Nb_3O_7F$ (subcell) | 20.676(1) | 3.8316(2) | 3.9264(2) | — | — | — | 311.06 | — |
| $Li_{3x}Nb_3O_7F$ ($x$ = 0.4) orthorhombic | 20.71(2) | 3.844(5) | 3.945(5) | — | — | — | 314.09 | — |
| $Li_{3x}Nb_3O_7F$ ($x$ = 0.7) triclinic | 9.884(3) | 3.838(1) | 3.762(1) | 94.57(1) | 94.14(3) | 86.57(5) | 141.7 | — |
| $LiNb_3O_8$ (pure) | 15.262(2) | 5.033(1) | 7.457(1) | — | 107.34(1) | — | 546.8 | (*11*) |
| "$LiNb_3O_8$" (from $x$ = 0.4) | 15.248(5) | 5.043(2) | 7.447(2) | — | 107.29(5) | — | 546.7 | — |
| $NbO_2$ (pure) | 13.70 | — | 5.987 | — | — | — | 1124 | (*10*) |
| "$NbO_2$" (from $x$ = 0.4) | 13.645(1) | — | 5.991(3) | — | — | — | 1115.5 | — |

*Note.* Standard deviations are given in parantheses.

less sharp as Li was introduced, and the diffuseness increased with increasing Li content.

From the powder patterns it was obvious that as soon as some lithium had entered the host structure, the samples consisted of more than one phase. However, at low $x$ values ($0 < x \leq 0.4$) the diffraction lines of the predominant phase could be associated with the original orthorhombic structure type. The cell parameters of this phase were refined, and it was found that the unit cell volume increased approximately linearly with the total Li content from 311 Å$^3$ ($x$ = 0) to 314 Å$^3$ ($x$ = 0.4) (see Table I). It was therefore concluded that the orthorhombic structure can accomodate some Li without changing its symmetry.

Some diffraction lines originating from a new phase appeared in the powder films together with those of the expanded orthorhombic cell. At Li contents exceeding $x$ = 0.4 the orthorhombic phase gradually disappeared, and for $x$ = 0.7 the new compound was almost a single phase. The $d$ values of this phase agreed fairly well with those of the unidentified phase obtained by Li-insertion of $Nb_3O_7F$, by Cava *et al.* (*3*) (see Table II). The lines from the sample with $x$ = 0.7 could be indexed on the basis of a triclinic unit cell with the parameters shown in Table I.

For $x > 1.0$ a phase of the $LiNbO_3$ type was formed coexisting with the triclinic phase, which gradually disappeared as the Li content was increased. For $x$ = 1.4 the X-ray powder diffraction lines originating

TABLE II

X-RAY POWDER DIFFRACTION DATA OF THE TRICLINIC FORM OF Li-INSERTED $Nb_3O_7F$

| $h$ | $k$ | $l$ | Values from this work | | | $d_{obs}$ from Cava *et al.* (*3*) |
|---|---|---|---|---|---|---|
| | | | $2\theta_{obs}$ | $\Delta 2\theta$ | $d_{obs}$ | |
| 1 | 0 | 0 | 8.930 | −0.046 | 9.894 | 10.037 |
| 2 | 0 | 0 | 17.991 | −0.016 | 4.926 | 4.962 |
| 0 | 1 | 0 | 23.258 | −0.011 | 3.821 | 3.832 |
| 0 | 0 | 1 | 23.760 | −0.003 | 3.742 | 3.746 |
| 1 | 1 | 0 | 24.555 | 0.039 | 3.622 | 3.641 |
| 1 | −1 | 0 | 24.850 | −0.009 | 3.580 | 3.587 |
| −1 | 1 | 0 | 25.439 | −0.008 | 3.498 | 3.520 |
| 1 | 0 | 1 | 26.010 | −0.015 | 3.423 | 3.431 |
| 3 | 0 | 0 | 27.143 | −0.010 | 3.283 | 3.302 |
| −2 | 1 | 0 | 30.378 | 0.013 | 2.940 | 2.950 |
| 2 | 0 | 1 | 30.970 | 0.007 | 2.885 | |
| 0 | −1 | 1 | 32.178 | 0.007 | 2.780 | |
| −1 | −1 | 1 | 32.625 | −0.021 | 2.742 | |
| 0 | 1 | 1 | 34.816 | 0.031 | 2.575 | |
| 3 | 0 | 1 | 35.086 | −0.017 | 2.556 | |
| 2 | −1 | 1 | 38.549 | −0.018 | 2.334 | |
| 2 | 1 | 1 | 39.574 | −0.033 | 2.275 | |
| −3 | −1 | 1 | 40.571 | 0.005 | 2.222 | |
| 3 | −1 | 1 | 44.527 | −0.005 | 2.033 | |
| 3 | 1 | 1 | 44.920 | −0.014 | 2.016 | |

*Note.* $M(20) = 31$, $F(31) = 22.(0.015352, 93)$.

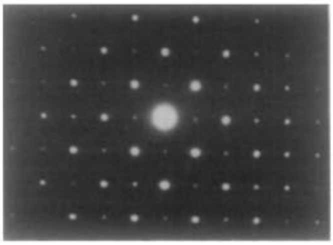

FIG. 1. ED pattern recorded from triclinic $Li_{3x}Nb_3O_7F$ in the [100] direction. Note the weak extra reflexions.

from the $LiNbO_3$ structure type were the only recognizable ones. However, the lines were very diffuse and could therefore not be indexed.

*2.2. Li-inserted samples studied by electron microscopy.* Four samples with different amounts of Li were examined by electron microscopy, vis. $x = 0.4, 0.7, 1.0$, and 1.5. ED and HREM studies revealed the same overall tendencies as did the X-ray powder diffraction studies. For $x = 0.4$ the main part of the crystals investigated consisted of the orthorhombic $Li_{3x}Nb_3O_7F$ phase, although some of the diffraction spots were diffuse, indicating that the structure was disordered.

In the samples with $x = 0.7$ and 1.0 the triclinic phase was frequently found, mixed with a few crystals of the orthorhombic phase and a large number of amorphous fragments. The fact that they were amorphous could mean that they had been damaged in the electron beam, that they contained more Li than the well-ordered crystal fragments, or even that they were formed during the TEM specimen preparation. The ED patterns of the triclinic $Li_{3x}Nb_3O_7F$ exhibited relatively sharp diffraction spots, and it was observed (see Fig. 1) that they all contained the same type of superstructure spots as the patterns of pure $Nb_3O_7F$. An example of an HREM image along [010] of a crystal fragment of the triclinic form is shown in Fig. 2. As can be seen, the crystal consists of domains of a well-ordered, triclinic structure interrupted by narrow disordered parts, possibly present due to one of the reasons mentioned above. It is obvious from Figs. 1 and 2 that this new structure is very similar to and built up in the same manner as the $Nb_3O_7F$ structure, but with a smaller cell volume per formula unit.

The phases identified in these first three samples appeared to be stable in the electron beam. The last sample ($x = 1.5$), however, containing mostly crystals of the $LiNbO_3$ structure type, was very unstable. After approximately 20–30 sec in the beam the crystals were destroyed, and the sharp diffraction spots had coalesced into diffuse rings. It was therefore very difficult to image this phase in the high resolution mode. There were some doubts about the identification of the $LiNbO_3$ structure type from the X-ray powder diffractograms, but the comparison of the experimental and the calculated ED patterns showed the assumption to be correct. However, the recorded ED patterns deviated from the extinction rule ($-h+k+l \neq 3n$) of rhombohedral $LiNbO_3$, i.e., the $LiNbO_3$ obtained had hexagonal symmetry. This was also observed for the $LiNbO_3$ obtained by Li insertion into $NbO_2F$ (*1*).

## 3. The Delithiation of $Li_{3x}Nb_3O_7F$

Chemical delithiation was achieved by reacting $Li_{3x}Nb_3O_7F$ ($x = 0.3, 0.5, 0.6, 1.0$, and 1.5) with DDQ in acetonitrile. All the starting materials were black, but after the reaction with DDQ the three samples with the lowest Li contents had become almost white, and the last two were light and dark grey, in that order, which signified that Li had not been completely extracted. Guinier powder diffractograms were recorded from all five delithiated specimens. The three white samples yielded relatively sharp diffraction lines corresponding to orthorhom-

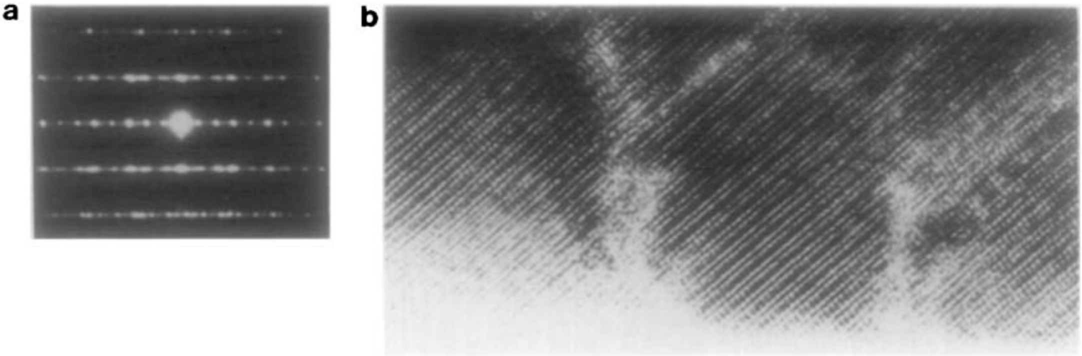

FIG. 2. (a) ED pattern of triclinic $Li_{2.1}Nb_3O_7F$ in the [010] direction. (b) Corresponding HREM image of a crystal fragment exhibiting well-ordered domains of the triclinic form, interrupted by amorphous strings.

bic $Li_{3x}Nb_3O_7F$, whereas the light grey one gave more diffuse lines and appeared to contain orthorhombic $Li_{3x}Nb_3O_7F$ mixed with traces of the triclinic modification. The diffraction pattern of the dark grey specimen was very diffuse, and no discrete lines could be recognized. The powder diffractograms from the four most light-colored samples were of a high enough quality to allow indexing, but it was not possible to refine the cell parameters with any accuracy. The unit cell volume of the orthorhombic $Li_{3x}Nb_3O_7F$ varied between 311.0 and 311.5 Å$^3$, indicating that the samples contained almost no Li.

When the orthorhombic $Li_{3x}Nb_3O_7F$ in the delithiated specimen with an original $x$ value of 0.5 was studied by HREM, stacking faults were found. They were of the type sometimes, but not frequently, seen in "undisturbed" $Nb_3O_7F$ (as mentioned in (9)), i.e., the single row of octahedra between the shear planes was absent. An example of this type of defect can be seen in Fig. 3.

### 4. *The DSC Thermograms*

Thermal decomposition of 10 samples of $Li_{3x}Nb_3O_7F$ ($0 \leq x \leq 1.4$) was investigated by the DSC technique. All samples remained black after the DSC experiments, indicating that the amount of oxygen in the argon gas used was small enough not to oxidize them to any noticeable extent. Pure $Nb_3O_7F$ was shown not to decompose in the temperature range investigated (≤950 K). With increasing Li contents, however, the temperature at which the decomposition started was decreased stepwise. For values of $x$ up to 0.6 the first peak appeared at approximately 740 K, for $x = 0.7$ the decomposition temperature decreased to about 690 K, and for $x > 0.7$ to about 640 K. The peaks in the thermograms were broad, and their shapes generally suggested that the transformation produced more than one phase. Attempts were made to associate some of the peaks with particular transformations by interrupting the heating procedure immediately after the appearance of a peak and recording a powder photograph. This did not give any information, however, since the diffraction lines in most cases were so diffuse that the patterns were unrecognizable.

*4.1. The thermal decomposition products studied by X-ray and EM.* The decomposition products after the heat treatment to 950 K were all characterized by their Guinier powder photographs, and the results

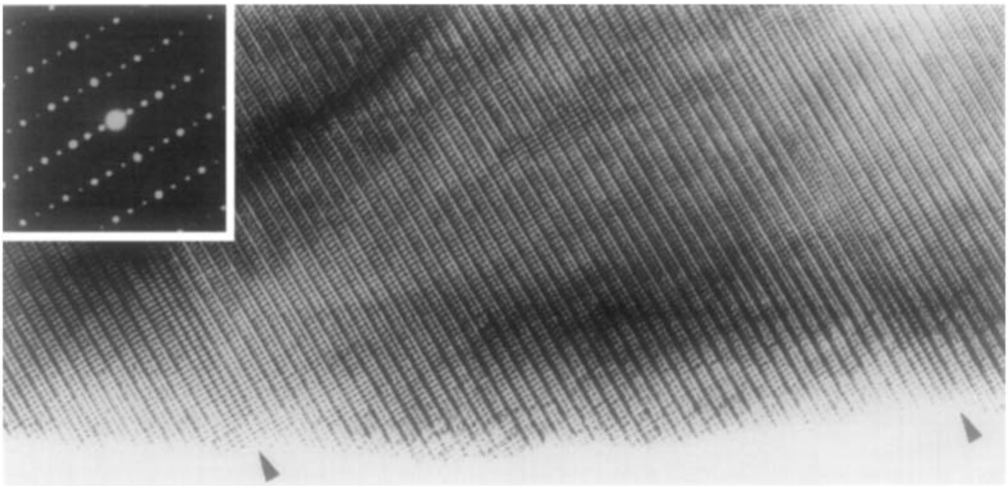

FIG. 3. HREM micrograph of desintercalated $Li_{1.5}Nb_3O_7F$ of orthorhombic symmetry, seen along [010]. The stacking faults are pointed out. The inset shows the corresponding ED pattern.

are summarized in Table III. It is obvious that none of the Li-inserted samples became single phase and also that the kinds of products obtained depended on the amount of lithium in the bulk material.

Three of the nine samples were also investigated by electron microscopy methods. The results from the X-ray experiments were in this way confirmed (see Table III), except for the fact that small amounts of the triclinic $Li_{3x}Nb_3O_7F$ were detected by ED.

LiF was clearly identified as one of the components in all samples. It can therefore be presumed that the Li content, above the stoichiometric amounts, was small in all the other phases except $LiNbO_3$ (see below).

A phase of the $NbO_2$ structure type was also formed in all samples. The unit-cell pa-

TABLE III

PRODUCTS OBTAINED AT 950 K BY THERMAL DECOMPOSITION OF $Li_{3x}Nb_3O_7F$

| $x$ | Orthorhombic $Li_{3x}Nb_3O_7F$ | $LiNb_3O_8$ | LiF | "$NbO_2$" | "$LiNbO_3$" | Triclinic $Li_{3x}Nb_3O_7F$ |
|---|---|---|---|---|---|---|
| 0 | X | | | | | |
| 0.3 | X | X | X | (X) | | |
| 0.4 | | X,E | X,E | X,E | (X),E | |
| 0.5 | | (X) | X | X | X | |
| 0.6 | | | X | X | X | |
| 0.7 | | | X,E | X,E | X,E | (E) |
| 0.8 | | | (X) | X | X | |
| 0.9 | | | (X) | X | X | |
| 1.4 | | | (X),E | (X) | X,E | (E) |

*Note.* X: X-ray powder diffraction; E: electron microscopy. The parantheses indicate small amounts of the product.

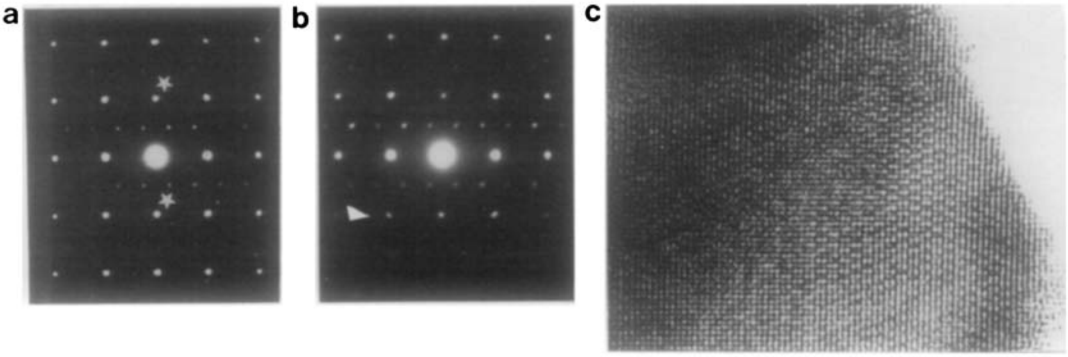

FIG. 4. (a) ED pattern in the [100] direction, recorded from a "$NbO_2$" crystal obtained by thermal decomposition of $Li_{1.2}Nb_3O_7F$. The indicated reflections should be absent according to the X-ray structure determination. (b) Diffractogram of the same crystal as in (a), tilted through a small angle. The reflections marked in (a) have weakened more than the rest of the spots. (c) HREM image in the [100] direction, showing a well-ordered crystal.

rameters of this structure were shown to vary somewhat with the Li content of the bulk materials (see Table I) in approximately the same way as described in (*2*). It was therefore assumed to have accomodated some Li and is labeled "$NbO_2$". Some of the ED patterns exhibited a few strong reflections which, according to the calculated patterns of pure $NbO_2$, are accidentally absent or very weak (a phenomenon mentioned in (*2*) as well). The same extra reflections have also been seen for pure $NbO_2$. An example of this is shown in Fig. 4a, which is an ED pattern of "$NbO_2$" along [100] (where the two reflections which should be absent are pointed out). As the crystal was tilted through a small angle around the *b*-axis, the extra reflections became weaker compared to the rest of the spots (Fig. 4b), and therefore they may perhaps be interpreted as arising from dynamic scattering. This phenomenon will be further studied by convergent beam electron diffraction. Figure 4c is an HREM image of a well-ordered crystal fragment of "$NbO_2$" oriented in the [100] direction.

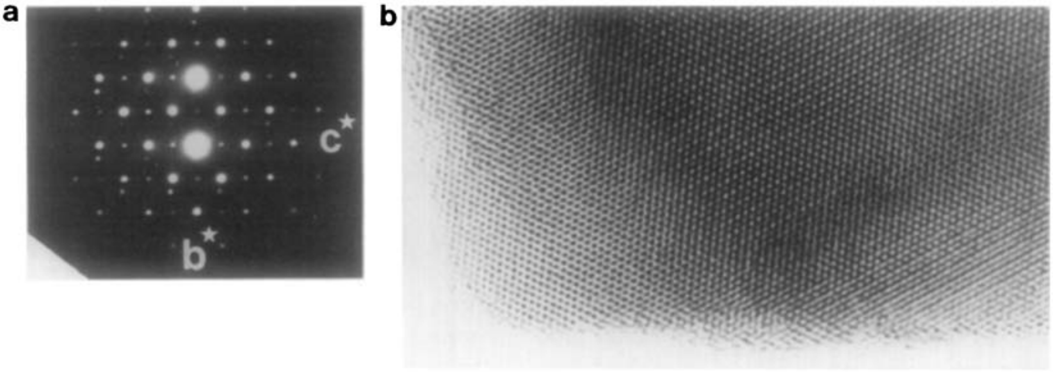

FIG. 5. (a) ED pattern, in the [100] direction, of a $LiNb_3O_8$ crystal found in the sample of thermally decomposed $Li_{1.2}Nb_3O_7F$. (b) The corresponding high-resolution electron micrograph.

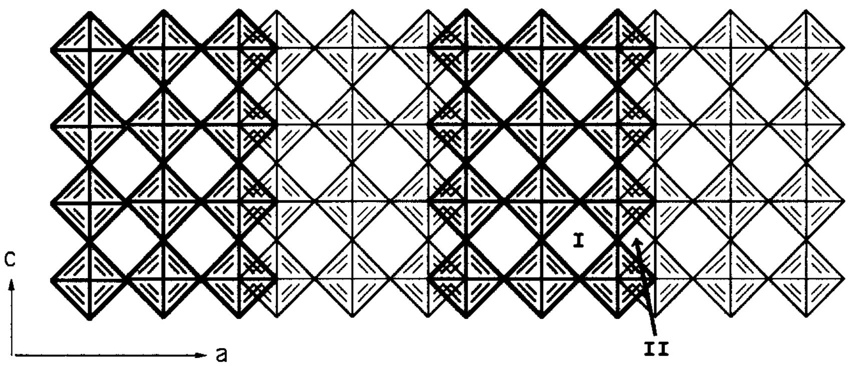

FIG. 6. The ideal structure model of $Nb_3O_7F$ projected along the *b*-axis. I: the perovskite holes; II: the distorted, six-coordinated interstices in the shear planes.

For low Li contents a phase of the $LiNb_3O_8$ type was formed in comparatively large amounts. The powder diffraction lines of this phase were relatively sharp, and the cell parameters could be refined to a good agreement with the monoclinic unit cell given in (*11*) (see Table I). Figure 5 shows an HREM image in the [100] direction of a well-ordered crystal of $LiNb_3O_8$.

The disordered $LiNbO_3$ structure type formed during the insertion reactions seemed to be stable to the heat treatment and was not decomposed. On the contrary, it became more well-ordered and therefore more stable under the electron beam, i.e., behaved in the same way as the $LiNbO_3$ formed by decomposition of $Li_xNbO_2F$ (*2*). In Table III it is designated "$LiNbO_3$" since it can, and is assumed to, host more than one Li per Nb atom (as discussed in (*2*)).

## Discussion

The insertion of lithium into the structure of $Nb_3O_7F$ primarily results in an increase of the orthorhombic unit cell volume, in contrast to previous results concerning $NbO_2F$ (*1*). In the $NbO_2F$ framework the only kind of atomic sites available for Li is the large, 12-coordinated interstices (the so called perovskite holes). In order to host Li atoms in small amounts, a shrinkage of these holes and consequently a decrease of the unit cell volume seems necessary. In $Nb_3O_7F$ the Li atoms can enter two different interstices: the 12-coordinated perovskite holes in the slabs of corner-sharing octahedra and the 6-coordinated holes in the shear planes, both shown in the ideal structure model of $Nb_3O_7F$ in Fig. 6. The increase of the cell volume could perhaps be explained by the introduction of some Li into the interstices in the shear planes (a possibility discussed by Gatehouse *et al.* in Ref. (*12*)).

On the other hand, the triclinic $Li_{3x}Nb_3O_7F$, coexisting with the orthorhombic polytype, showed a considerably smaller unit cell volume per formula unit (see Table I). The appearance of this phase may be explained by the introduction of some Li into the perovskite interstices, giving a shift of the shear planes with respect to each other so that the 12-coordinated holes become distorted in order to host the Li atoms. Figure 7 shows an ideal structure model where both the orthorhombic and the smaller, triclinic unit cells can be seen.

For high values of $x$ in $Li_{3x}Nb_3O_7F$, the samples consisted mostly of the $LiNbO_3$ structure type, which is consistent with the results for $Li_xNbO_2F$ (1). The Li entering $Nb_3O_7F$ can be presumed to adopt 6-coordi-

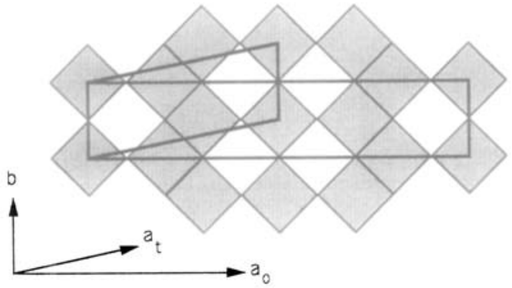

FIG. 7. An ideal model of the $Nb_3O_7F$ structure type, viewed in the [001] direction. Both the orthorhombic and the triclinic unit cells are depicted.

nated sites, and the structure seems to be reorganized so that the shear planes are disrupted and the $LiNbO_3$ structure is finally obtained. The large number of amorphous fragments observed in the EM investigations may indicate that the transformation of $Nb_3O_7F$ proceeds via an amorphous transition state.

The delithiation was performed by reacting the inserted samples with a solution of DDQ in acetonitrile. It is customary to use an iodine solution, but it has been experimentally shown that DDQ is more efficient (which is also consistent with the electrode potential values given in (*13*)). However, all Li could not be extracted, i.e., the samples did not turn white. It is interesting to note that if the powder diffractogram of a specimen to be delithiated showed traces of orthorhombic or triclinic $Li_{3x}Nb_3O_7F$, the delithiation product contained almost only the relatively pure orthorhombic phase. If, on the other hand, the powder film showed the disordered $LiNbO_3$ to be the only phase present (as for $x = 1.4$), the product became amorphous. From these results it can be concluded that a relatively well-ordered nucleus in the particles is needed to restore the original structure with a delithiation reaction. The HREM studies of the orthorhombic $Li_{3x}Nb_3O_7F$ obtained in one of the delithiated samples revealed some stacking faults. The same type of fault is also found in pure $Nb_3O_7F$, but much less frequently. This shows that the structure can not be perfectly rebuilt by delithiation.

The results of the thermal decomposition of $Li_{3x}Nb_3O_7F$ are very much the same as those obtained for $Li_xNbO_2F$ (*2*). In both cases the decomposition starts at a lower temperature for the Li-inserted samples than for the pure starting materials, which indicates that introduction of Li into the host structures causes some degree of instability. The stability of $Li_{3x}Nb_3O_7F$ depends markedly on the relative amounts of the phases obtained during the insertion reaction, since the starting temperature of the decomposition decreases stepwise with increasing Li content of the bulk material. Both materials yielded approximately close-packed anion arrangements in most of the decomposition products, and even the phases obtained are almost the same. Since the high-pressure form of $Nb_3O_7F$ is intergrown in small amounts in the low-pressure form (the polytype studied here), and is formed as one of the products in the decomposition of $Li_x NbO_2F$, it would have been expected at the decomposition of $Li_{3x}Nb_3O_7F$, too. However, no such phase could be detected.

The phase content of the decomposition products (Table III) depended on the overall Li content in the starting materials, as in the earlier experiments (*2*). Common to all the products was the presence of LiF and "$NbO_2$". The amount of LiF formed was presumably limited by the lithium content for small values of $x$ and by the fluorine content for large $x$ values. The "$NbO_2$" formed could be presumed to contain some lithium since the cell volume changes with the overall Li content (see Table I). The appearance of some extra reflections in the ED patterns was initially also taken as a sign of Li incorporation, but this evidence seems to be spurious, since identical ED patterns have been recorded from pure $NbO_2$. The fact that these extra spots became weaker as the crystal was tilted (Fig. 4b) maybe indicates that their appearance is caused by double diffraction. The extra spots in the diffractogram shown in Ref. (*2*) may perhaps also be explained by this phenomenon.

For low Li contents $LiNb_3O_8$ is formed. The amount of this phase is perhaps limited by the Li to anion ratio so that when the amount of Li increases, the related structure type of "$LiNbO_3$" is formed. $LiNb_3O_8$ shows no signs like those of $NbO_2$ of extra Li incorporation.

In conclusion, it is obvious from this study that the introduction of a set of shear planes into the $NbO_2F$ structure influences neither the Li-insertion reactions nor the thermal decomposition significantly. The resulting product for high Li contents is the same for the two different host materials, i.e., the $LiNbO_3$ structure type. A small difference is seen for low Li contents: for the $NbO_2F$ the cubic cell volume decreases with increasing amounts of Li, whereas the orthorhombic cell volume of $Nb_3O_7F$ increases. In both cases the thermal decomposition of the Li-containing samples mainly results in the formation of products with a more close-packed anion arrangement than the starting material.

This investigation has been extended to include an examination of the possible influence of a second set of shear planes on the behavior of a host of the $NbO_2F$ structure type. The results will soon be published.

## Acknowledgments

I express my warm gratitude to Dr. Monica Lundberg for her encouraging interest and for many valuable discussions. Professors Lars Kihlborg and Mats Nygren are cordially acknowledged for enlightening comments on the manuscript. I also thank Anna Linderbrandt for experimental assistance. This work has been supported by the Swedish Natural Science Research Council.

## References

*1.* L. PERMÉR AND M. LUNDBERG, *J. Solid State Chem.* **81,** 21 (1989).
*2.* L. PERMÉR AND M. LUNDBERG, *J. Less-Common Met.* **156,** 145 (1989).
*3.* R. J. CAVA, D. W. MURPHY, AND S. M. ZAHURAK, *J. Electrochem. Soc.* **130.** 3245 (1983).
*4.* S. ANDERSSON AND A. ÅSTRÖM, *Acta Chem. Scand.* **19,** 2136 (1965).
*5.* P.-E. WERNER, *Ark. Kemi* **31,** 513 (1969).
*6.* A. J. SKARNULIS, G. LILJESTRAND, AND L. KIHLBORG, *Chem. Commun., Univ. Stockholm* **1** (1979).
*7.* M. A. O'KEEFE, *in* "Electron Optical Systems for Microscopy, Microanalysis and Microlithography" (J. J. Hren, F. A. Lenz, E. Munro, and P. B. Sewer, Eds.), pp. 209–220, Proc. 3rd Pfefferkorn Conf., SEM Inc., AMF O'Hare, IL (1986).
*8.* S. ANDERSSON, *Acta Chem. Scand.* **18,** 2339 (1964).
*9.* L. PERMÉR AND M. LUNDBERG, *Mater. Res. Soc. Symp. Proc.* **183,** 305 (1990).
*10.* B.-O. MARINDER, *Ark. Kemi* **19,** 435 (1962).
*11.* M. LUNDBERG, *Acta Chem. Scand.* **25,** 3337 (1971).
*12.* B. M. GATEHOUSE, P. GOODMAN, AND A. OLSEN, *J. Solid State Chem.* **72,** 193 (1988).
*13.* D. W. MURPHY AND P. A. CHRISTIAN, *Science* **205,** 651 (1979).