

Transformation of LiTi_2O_4 from Spinel to Ramsdellite on Heating

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Time of flight powder neutron diffraction has been used to study the structural changes on heating LiTi_2O_4 from 25 to 1000°C. A phase transition from the spinel to the ramsdellite form occurred between 875 and 925°C; the two structure types coexisted, apparently in equilibrium over much of this range. About 300°C below the transition, an anomalous change in the spinel structure was seen to occur. This anomaly was only observed in the parameters associated with Li and is thought to reflect migration of about 10% of the Li atoms from the 8a site. Above 925°C, the ramsdellite form is stable and the structure was retained after rapid cooling. The structure of the high temperature ramsdellite form was refined by Rietveld analysis using the $Pbnm$ space group. The refinement gave final R_{wp} and R_p values of 2.91 and 3.74%, respectively. © 1997 Academic Press

INTRODUCTION

The $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ spinel system was initially reported by Deschanvres *et al.* (1) and was found to form a solid solution over the compositional range $0 \leq x \leq 0.33$. The $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ spinel system has been the subject of considerable investigation since the discovery by Johnston *et al.* of superconductivity at 13 K in samples with compositions near $x = 0$ (2–4). Samples at the $x = 0$ end of the solid solution have semiconducting properties, with the $x = 0.33$ end member being found to be electronically insulating. The transition temperature for LiTi_2O_4 was considered to be high for an oxide material at the time, and thus the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ solid solution became the focus of much study (5–7). Research on titanates received a new lease on life with the discovery of the high T_c cuprate materials (8). Cuprates and titanates are related electronically by the d^{n-1} rule and have been reported to show some similarities in properties, notably the absence of an isotope effect and the proximity to the metal insulator transition (9–11).

In the spinel structure, the oxide ions occupy a 32e site of the $Fd3m$ space group (227) with positional parameter u , which allows slight distortion from cubic close packing. This is accommodated by a cooperative expansion of the Li–O bonds. The Li ions occupy tetrahedral 8a sites within

the structure and the titanium ions occupy octahedral 16d sites. The structure of the end member, LiTi_2O_4 , is reported to be normal (12), and as Li content in the solid solution series $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ increases, the spinel becomes less normal with some Li occupying 16d sites within the structure.

Johnston (1) indicated that on heating spinel samples with the composition LiTi_2O_4 , a conversion to a ramsdellite-like structure with a slight difference in the unit cell from that seen for $\text{Li}_2\text{Ti}_4\text{O}_7$ (13) was observed. Johnston was unable to unambiguously confirm the stoichiometry of the “ramsdellite” phase. Akimoto *et al.* (14) recently succeeded in preparing single crystals of this material and confirmed that the stoichiometry of this phase with the ramsdellite structure type is close to LiTi_2O_4 .

The ramsdellite structure type was first described by Bystrom *et al.* (15) for $\gamma\text{-MnO}_2$. The structure consists of distorted MO_6 octahedra which link up with adjacent octahedra, by sharing opposite edges, thus forming columns. Adjacent pairs of columns share edges to form double columns, giving rise to an open framework type structure. In between these columns there are tetrahedral channel sites into which smaller ions such as H (16) and Li can be placed. The ramsdellite structure of LiTi_2O_4 as described by Akimoto (17) is presented in Fig. 1.

Thackeray and co-workers (17) have proposed a mechanism for the ramsdellite-spinel transformation in ramsdellite MnO_2 and various lithiated forms. They suggested that the R- MnO_2 structure initially shears in the (100) direction; this is followed by a cooperative displacement of the manganese and then by a second shear in the (111) direction to give the spinel framework. They also indicated that the transformation was reversible. In this communication we report structural changes observed in high-temperature neutron diffraction experiments before and during the spinel to ramsdellite transformation and also confirm the structure of LiTi_2O_4 ramsdellite by neutron diffraction.

EXPERIMENTAL

A two stage synthesis route was chosen involving $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2 , and Ti metal, using the Eqs. [1] and [2].

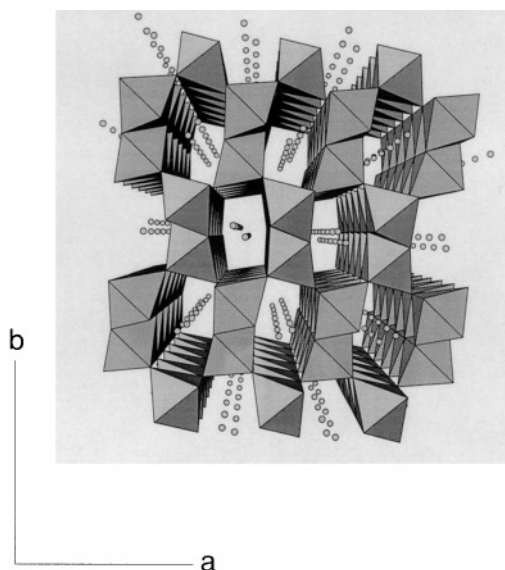
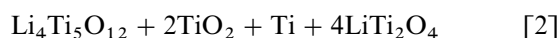
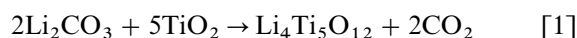


FIG. 1. Representation of the ramsdellite LiTi_2O_4 structure showing a framework of edge-sharing TiO_6 with Li atoms occupying channel sites (50% occupation) (14).



The following high-purity reagents were used: ^7Li enriched Li_2CO_3 (ISIS isotope bank), Ti metal (Johnson Matthey), and Rutile TiO_2 (Tioxide Specialities).

For the preparation of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the Li_2CO_3 and TiO_2 were predried at 500°C for at least 6 h. On drying, they were immediately weighed out in the appropriate ratios according to [1] and ground under acetone for approximately 30 min in an agate mortar and pestle. The mixture was then transferred to an alumina crucible and fired in the temperature range $680\text{--}705^\circ\text{C}$ overnight to remove CO_2 . The resultant mixture was then pelleted in a 13-mm die at 2–3 tonnes and refired for 4 days in a muffle furnace at 915°C to form the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel. LiTi_2O_4 was prepared in the spinel form using $\text{Li}_4\text{Ti}_5\text{O}_{12}$, TiO_2 , and Ti metal in the correct ratios as described in [2]; the constituents were again mixed under acetone and then pelleted as described previously. The pellets were then wrapped in gold foil and fired at 840°C under an argon/5% hydrogen atmosphere. On removal from the furnace the samples were a royal blue color.

Powder neutron diffraction was performed on the high-intensity Polaris diffractometer situated at the ISIS neutron facility, Rutherford Appleton Laboratories, Didcot, Oxon, UK. A pattern of LiTi_2O_4 was collected at room temperature in a standard vanadium sample can collecting for 4 h (700 μAh). This data was used to provide a starting point in the refinements.

The sample of spinel was heated *in situ* under vacuum in a vanadium furnace, increasing temperature in a stepwise fashion up to 1000°C . Data was collected at a number of temperatures in the range $200\text{--}800^\circ\text{C}$ and then in 25°C steps up to 1000°C . From 800°C , data were collected in three segments at each temperature, so that the transformation could be investigated as a function of time as well as of temperature. The sample was exposed to the neutron beam at each temperature/time for approximately 45 min (300 μAh after equilibrating at that temperature for 15 min). The sample was then rapidly cooled from 1000°C and the neutron powder pattern was collected for 4 h at room temperature in a standard sample holder. Rietveld refinement was performed using the CCL software packages running on the ISIS HUB computer (18,19). Refinement of the neutron patterns was performed on data collected from the backscattering detectors only ($135^\circ < 2\theta < 160^\circ$).

X-ray investigations were performed using a Stoe Stadi P diffractometer for data collection and the GSAS Rietveld method (20) for structure refinement.

RESULTS

Structure of Spinel at Room Temperature

The initial structure of the spinel was investigated by both neutron and X-ray powder diffraction performing standard Rietveld refinements. The space group used was $Fd3m$. From the combined X-ray and neutron refinement the unit cell was found to be $8.4046(2)$ Å in close agreement with the values of 8.404 Å reported by Lambert *et al.* (21) and 8.405 by Johnson for LiTi_2O_4 , although a slightly higher value has recently been reported by Dalton (3). Initial Ti occupancy for neutron refinement was obtained from X-ray refinement. Refinement of the neutron powder diffraction data confirmed the spinel composition as LiTi_2O_4 (Table 1). Although models with Li on the $16d$ site were tested, no evidence was obtained to support such cross-substitution. The final R values obtained for the neutron refinement of the spinel starting material were $R_{\text{wp}} = 5.83\%$ and $R_{\text{p}} = 4.81\%$; this indicated that the refined pattern was a relatively good fit to the experimental model.

TABLE 1
Crystallographic Data for LiTi_2O_4 Spinel

Crystal system	Cubic
Space group	$Fd3m$
a (Å)	$8.4046(2)$
R_{wp} (%)	5.83
R_{p} (%)	4.81

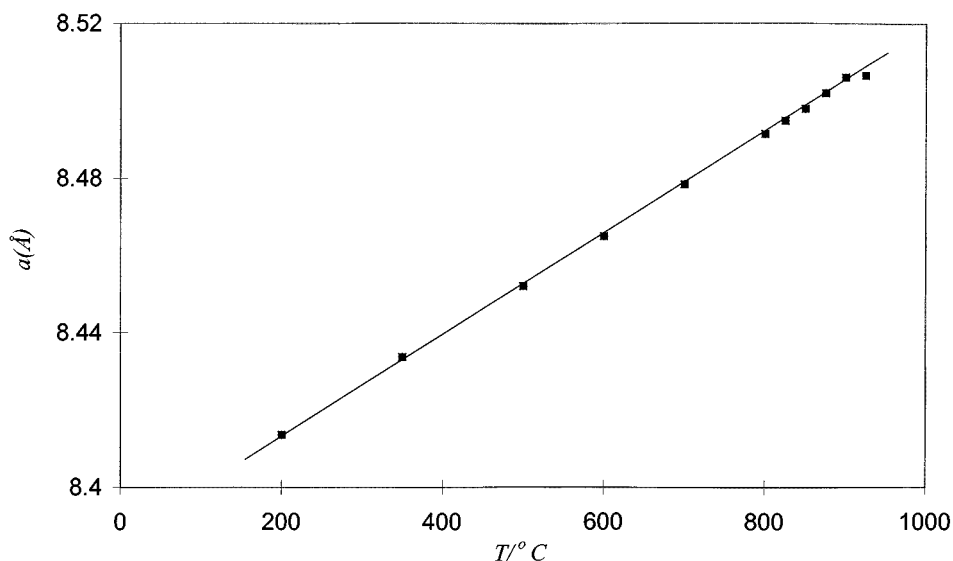


FIG. 2. Expansion of cubic unit cell edge a of LiTi_2O_4 spinel versus temperature.

Changes in Structure of Spinel on Heating

The most obvious change in the structure of the spinel on heating to 900°C was a linear expansion of the unit cell, as shown in Fig. 2. The coefficient of thermal expansion was found to be $1.58(1) \times 10^{-5} \text{ K}^{-1}$ up to 900°C . At 925°C , the unit cell edge was observed to deviate from linear behavior (Fig. 2), perhaps indicating a change in the spinel phase composition. Above 925°C , there was no evidence of spinel in the sample.

The change in unit cell edge was not the only change observed in the spinel structure. Clear anomalies were observed in both the isotropic temperature factor (ITF) and the site occupancy of Li at temperatures below the spinel to ramsdellite transition. As these two parameters are interdependent, two different models were utilized to examine the anomalies in more detail. In the first model, the occupancies of all sites were assumed constant from 25 to 900°C , and the isotropic temperature factors (ITF) were refined for O, Ti, and Li (Fig. 3). The ITFs for oxygen and titanium were observed to increase linearly with temperature; however, the ITF for lithium deviated sharply from linearity at about 500°C and showed a maximum at 700°C . In the second model, the occupancy of Li and Ti on the $8a$ and $16d$ sites, respectively, were refined assuming that all the ITFs vary linearly with temperature, as has previously been predicted (22) and observed in other oxides (23). A linear fit of the data, presented in Fig. 3, was used to obtain estimated values of ITF, ignoring the anomalous intermediate temperature range for Li. The resulting variation in Li and Ti occupancies are presented in Fig. 4. Although Ti occupancies remain constant throughout the experiment, the Li

occupancy of the $8a$ site clearly drops by 8% above 500°C . Fourier difference maps indicated that the missing Li had probably moved to the $16c$ site; however, it was not possible to refine the Li occupancy of this site.

Spinel to Ramsdellite Transformation

On heating from 875 to 950°C , the neutron powder pattern changes from that of the spinel to that of the ramsdellite form (Fig. 5). The changes in the ratio of the ramsdellite (140) peak to the spinel (400) peak with temperature and

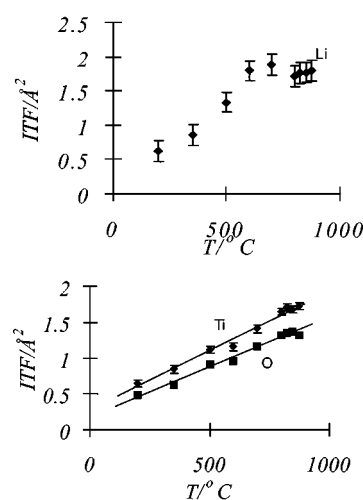


FIG. 3. Refined isotropic temperature factors as a function of temperature for Li, Ti, and O in LiTi_2O_4 spinel, assuming constant occupation of sites over all temperatures. Best fit lines shown for Ti and O ITFs.

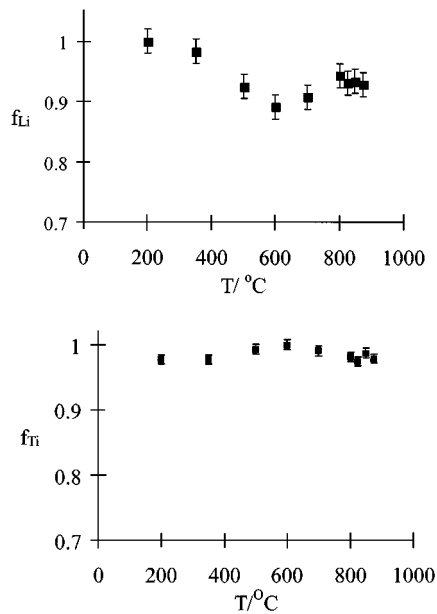


FIG. 4. Refined Li and Ti site occupancies in LiTi_2O_4 spinel as a function of temperature, assuming a linear increase in ITF values with temperature.

time are presented in Fig. 6. The transformation commences between 875 and 900°C, with some peaks from the ramsdellite phase becoming apparent in the diffraction patterns at 900°C. After 3 h at 900°C, the rate of conversion of the spinel to ramsdellite was seen to slow down, indicating that the system was approaching an equilibrium state, without going to completion. When the temperature was increased from 900 to 925°C, the rate of conversion was seen to increase drastically, but again the extent of conversion was seen to come to equilibrium without attaining completion at this temperature. At 950°C there was no evidence for any remaining spinel.

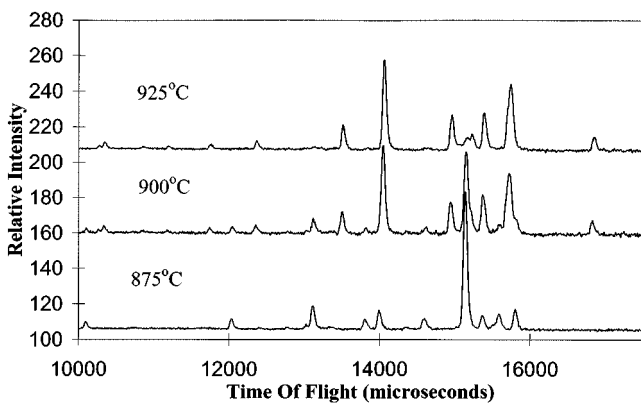


FIG. 5. Changes in neutron powder pattern of LiTi_2O_4 with temperature from 875 (spinel) to 925°C (ramsdelite dominant).

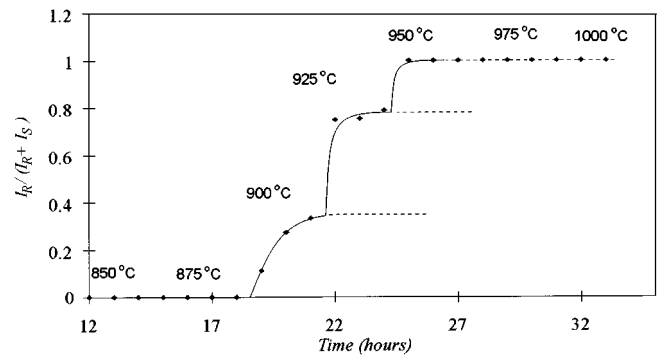


FIG. 6. Changes in ratio of ramsdellite (140) peak (I_R) to the spinel (400) peak (I_S) as a function of temperature.

Structure of Ramsdellite after Cooling to Room Temperature

The structure of the ramsdellite form was refined in the $Pbnm$ space group (62) using an initial model based on Akimoto *et al.*'s single crystal X-ray study (14). Initially the structure was refined holding the lithium parameters constant. The background, lattice, atomic positional coordinates, and isotropic temperature factors were refined and gave R_{wp} and R_p of 5.40 and 5.26, respectively. With the TiO_6 octahedra stable, the lithium position and isotropic temperature factors were refined and values of R_{wp} and R_p of 3.28 and 4.15, respectively, were obtained. The temperature factors of the lithium were then refined anisotropically and final R_{wp} and R_p values of 2.91 and 3.74 obtained. The Li occupancy of the tetrahedral channel site had a final value of 0.475 lying between 0.45, reported by Akimoto from X rays (14), and 0.5, predicted from the chemical formula. The value of 0.475 for Li occupancy is only slightly less than the ideal value of 0.5 for LiTi_2O_4 and the discrepancy should not be viewed as significant.

Grins *et al.* (24) proposed other possible Li sites within the channels of the ramsdellite structure for the $\text{Li}_{2+x}(\text{Li}_x\text{Mg}_{1-x}\text{Sn}_3)\text{O}_8$ ($0 \leq x \leq 0.5$) and $\text{Li}_2\text{Mg}_{1-x}\text{Fe}_{2x}\text{Sn}_{3-x}\text{O}_8$ ($0 \leq x \leq 1$) analogues. Difference Fourier analysis was performed to determine if there was any residual scattering

TABLE 2
Crystallographic Data Obtained for LiTi_2O_4 Ramsdellite

Crystal system	Orthorhombic
Space group	$Pbnm$
a (Å)	5.03426(3)
b (Å)	9.62019(6)
c (Å)	2.94816(2)
R_{wp} (%)	2.91
R_p (%)	3.74

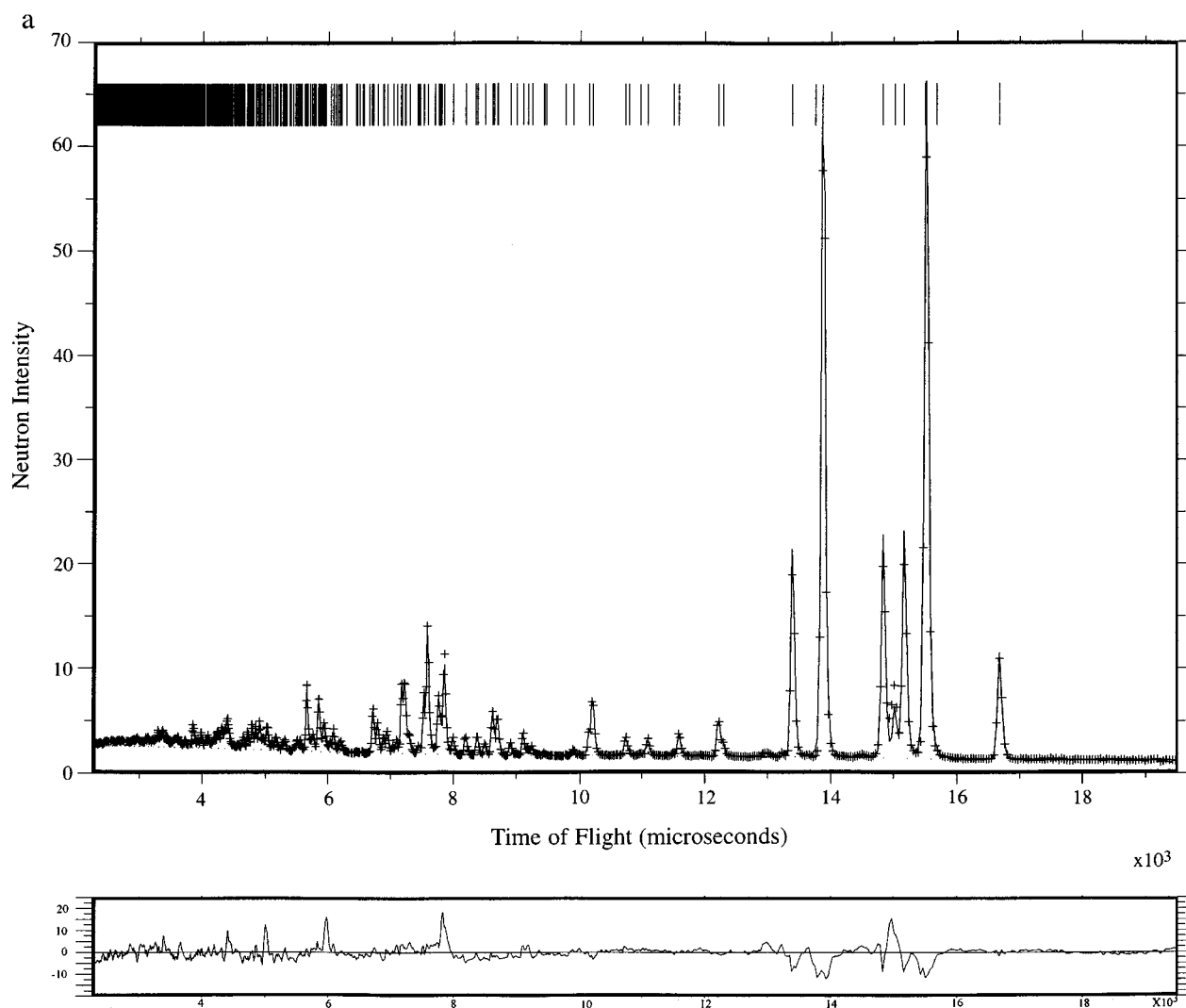


FIG. 7. Time of flight neutron powder diffraction pattern and weighted difference profile of LiTi_2O_4 ramsdellite after rapid cooling to room temperature (a) for the time of flight region 3–19.5 ms and (b) for the time of flight region 2.25–5 ms.

after the initial stages of the refinement; however, no significant scattering density was found and therefore it could be concluded that only one lithium channel site was present in this ramsdellite. No evidence was found to

support partial Li occupancy of the titanium framework sites.

The observed and calculated neutron powder patterns for the ramsdellite phase are presented in Fig. 7. The four

TABLE 3

Atomic Position Parameters and Anisotropic Temperature Factors Obtained for LiTi_2O_4 Ramsdellite at Room Temperature

	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>b</i> ₁₁ (±)	<i>b</i> ₂₂ (±)	<i>b</i> ₃₃ (±)	<i>b</i> ₁₂ (±)	<i>b</i> ₁₃	<i>b</i> ₂₃	S.O.F.
Li	−0.058(2)	0.467(1)	0.25000	1.3(2)	8.5(6)	1.79(3)	−0.61(4)	0	0	0.47(5)
Ti	−0.0182(3)	0.1420(2)	0.25000	0.45(5)	0.49(4)	0.17(3)	0.11(4)	0	0	1
O1	0.7000(3)	0.2801(1)	0.25000	0.87(3)	0.89(3)	0.47(3)	0.43(3)	0	0	1
O2	0.2020(2)	−0.0355(1)	0.25000	0.37(2)	0.41(3)	0.54(3)	−0.02(3)	0	0	1

Note. S.O.F. is the site occupancy factor.

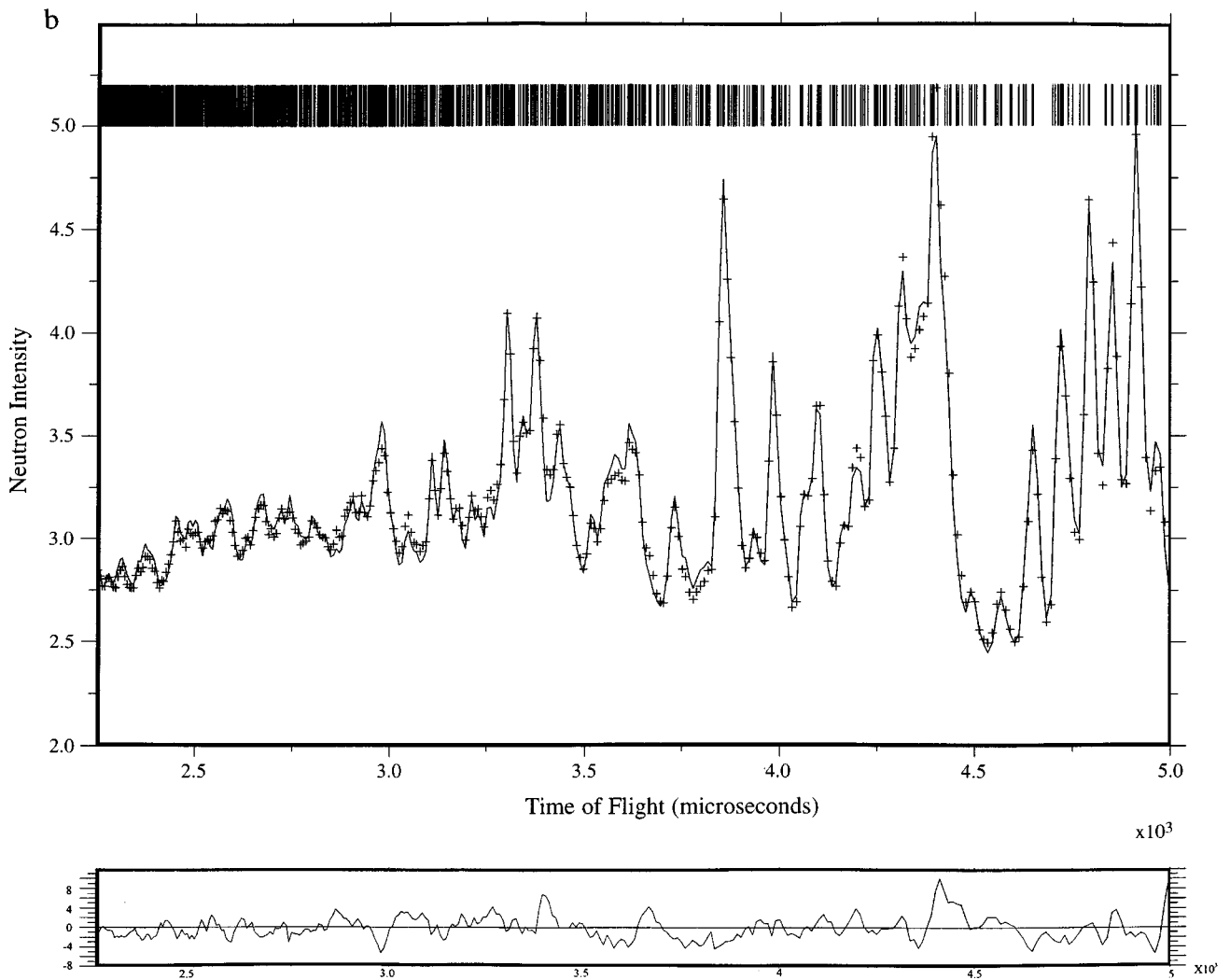


FIG. 7—Continued

largest peaks in the difference curve are attributable to the vanadium sample can, as the peak positions correlate with those expected for vanadium. These peaks were only observed in experiments performed *in situ* in the furnace. No absorbance correction was performed during these refinements. All unit cell data, bond angles, and bond lengths are presented in Tables 2–4.

The structural parameters obtained from neutron powder diffraction for this *in situ* prepared sample are in good agreement with previous single crystal results. Bond angle and bond length calculations show that the Ti atoms are slightly displaced away from the shared edge, distorting the TiO_6 octahedral units. The Li–O(1) and Li–O(2) bond lengths are quite different, indicating a significant distortion of the LiO_4 tetrahedra, moving the Li away from the ideal $(0, 1/2, Z)$ position of the channel site. This is related to the Li–Li intersite which is approximately 1.69 \AA , which is

much too short for both sites to be occupied by Li ions (25). The maximum occupation of this site can only be 50%.

The temperature factors for Li are higher than for Ti, O1, and O2; this suggests that the Li atoms may be mobile, as in $\text{Li}_2\text{Ti}_3\text{O}_7$ (26). The largest anisotropic temperature factor is that seen for $b22$, which is in the b direction and this could indicate that some intersite hopping is occurring within the channels.

DISCUSSION

These results indicate that the transformation of LiTi_2O_4 from spinel to ramsdellite polymorph is not a simple single step transformation, which is not surprising from symmetry considerations. At temperatures well below the transition temperature some Li is observed to migrate from its $8a$ site, probably moving to the $16c$ site. This initially affects the Li

TABLE 4
Selected Bond Lengths and Angles from Neutron Diffraction,
and Comparison with Single Crystal Data (14)

Bond lengths	Neutrons (Å)	X rays (14) (Å)	Angles	Neutrons (°)	X rays (°)
Li-O(1)	2.19(2)	2.22(2)	O(2)-Li-O(2')	127.4(4)	128.5(5)
Li-O(2)	1.80(6)	1.80(2)	O(2')-Li-O(2')	94.6(3)	94.4(7)
Li-O(2') × 2	2.01(1)	2.01(1)	O(2)-Li-O(2)	114.0(7)	120.4(9)
Mean	2.00	2.01	O(2)-Li-O(1)	86.06(1)	85.5(5)
Ti-O(1)	1.943(2)	1.947(2)	O(1)-Ti-O(1')	98.4(1)	98.02(3)
Ti-O(1') × 2	1.985(2)	1.993(2)	O(1)-Ti-O(2)	90.70(2)	90.77(7)
Ti-O(2) × 2	2.019(2)	2.010(1)	O(1)-Ti-O(2')	166.1(2)	166.21(9)
Ti-O(2')	2.036(2)	2.031(2)	O(1')-Ti-O(1')	95.89(3)	95.42(10)
Mean	1.997	1.997	O(1')-Ti-O(2')	90.80(3)	91.23(7)
			O(1')-Ti-O(2)	84.44(2)	84.44(6)
			O(2)-Ti-O(2)	93.73(2)	94.34(9)
			O(2)-Ti-O(2')	79.90(1)	79.91(7)

ITF values, which become anomalously large as Li ions start to move from their $8a$ site. At higher temperatures the ITF values stabilize and the Li occupation of the $8a$ site has been seen to drop by 8–10%. This change in spinel structure with temperature has important implications for studies of its superconducting properties. Samples of LiTi_2O_4 prepared by rapid cooling are likely to have significantly different Li distributions in their structures from those prepared by slow cooling and this will affect their properties.

The transformation of the spinel to ramsdellite form clearly involves a two-phase intermediate region between 900 and 925°C. The apparent decrease in the unit cell parameter of the spinel at 925°C seems to indicate that there is a change in composition of the spinel phase as the two-phase region is crossed. This decrease would tend to indicate an increase in oxidation state of Ti in the spinel. This may well reflect the higher temperature limit of stability for the spinel form of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (27), 1015°C, than for LiTi_2O_4 , although a more careful study of the transition region would be required to ascertain the exact chemical changes occurring in the transition region. There was no evidence for any intermediate phase, between the spinel and ramsdellite, in the neutron powder diffraction patterns.

CONCLUSIONS

In this study, we have shown that the spinel form of LiTi_2O_4 is apparently stable to at least 875°C, although there is a significant change in the structure of the spinel at about 600°C. The conversion from spinel to ramsdellite appears to be indirect with a two-phase equilibrium region extending at least from 900 to 925°C. The high-temperature form of LiTi_2O_4 has been confirmed to have the ramsdellite structure type and that it is closely related to the Ti^{IV} ramsdellite $\text{Li}_2\text{Ti}_3\text{O}_7$ (28). Time of flight neutron diffraction

has again been shown to be an excellent technique for the study of time-dependent phase transitions.

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