

# Synthesis and Crystal Structure of $\text{Li}_x\text{Ti}_3\text{O}_6$ ( $x = 0.74$ ): An Intergrowth Phase of Rutile and Ramsdellite Structure

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A new lithium titanate bronze,  $\text{Li}_x\text{Ti}_3\text{O}_6$  ( $x = 0.74$ ), is black in color and crystallizes in monoclinic symmetry, space group  $C2/m$  with  $a = 14.1198(11)$  Å,  $b = 2.9486(11)$  Å,  $c = 4.9373(13)$  Å,  $\beta = 92.693(14)^\circ$ , and  $Z = 2$ . The structure was determined from a single-crystal X-ray study and refined to the conventional values  $R = 0.043$  and  $wR = 0.036$  for 1022 observed reflections. The basic units of the structure are built up from rutile-type and double-rutile-type edge-shared  $\text{TiO}_6$  chains along the  $b$  axis. Lithium atoms are located in the ramsdellite-type tunnel sites with an occupancy factor of 0.37(2). This compound can be described as an intergrowth phase between ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  and rutile-type  $\text{TiO}_2$ . © 1997 Academic Press

## INTRODUCTION

During investigations of the system  $\text{Li}_2\text{O}-\text{Ti}_2\text{O}_3-\text{TiO}_2$  using sealed iron vessels at 1373–1473 K, we recently synthesized single crystals of spinel-type  $\text{LiTi}_2\text{O}_4$  (1) and new ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  (2) compounds and determined their crystal structures. The framework of the ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  consists of edge-shared rutile-type  $\text{TiO}_6$  chains (double-rutile chains) with repeat distances of about 3.0 Å, which form a one-dimensional tunnel structure. This is quite different from those of the other reduced Li–Ti–O compounds, whereas similar tunnel compounds with rutile-type chain structure were recently observed in some mixed-valence sodium titanates, e.g.,  $\text{NaTi}_2\text{O}_4$  (3) and  $\text{Na}_{1.7}\text{Ti}_6\text{O}_{11}$  (4).

We have examined the system  $\text{Li}_2\text{O}-\text{Ti}_2\text{O}_3-\text{TiO}_2$  by the reactions of metallic lithium and titanium oxides at high temperatures between 1173 and 1273 K so as to isolate some new crystals with  $\text{Ti}^{3+}/\text{Ti}^{4+}$  mixed-valence states for determining the crystal structures and their physical properties. In this paper, we describe the synthesis and crystal structure of a new one-dimensional monoclinic phase having the chemical formula  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$ .

## EXPERIMENTAL AND RESULTS

### Sample Preparation

Starting materials were  $\text{TiO}_2$  powder (99.9%), which was composed of rutile and anatase and was dried at 673 K, and lithium metal blocks with 99% purity. They were placed in a sealed iron vessel with an atomic ratio of  $\text{Li}/\text{Ti} = 1/2$ , heated in a resistance furnace at 1373 K under an argon gas flow for 10 hr, and slowly cooled to room temperature. No apparent leakage of lithium vapor from the vessel was observed.

As previously reported (1), the main product of this synthesis method was blue-black powder, which could not be identified as the reported compounds in the Li–Ti–O system. In the central part of the vessel, single crystals of NaCl-type  $\text{LiTiO}_2$  (JCPDS No. 16-223) and spinel-type  $\text{LiTi}_2\text{O}_4$  (1) were precipitated as a droplet-like crystal form. Then, we carefully checked the unknown blue-black powder, and successfully picked up the corresponding single crystals with the average size of  $100 \times 100 \times 20$  μm.

EDX analysis showed that the crystals were free from iron contamination from the vessel. The chemical composition, analyzed by ICP using powder sample, indicated that the measured metal ratio was Li (2.05 wt %) and Ti (58.54 wt %), respectively. The corresponding chemical formula, assuming O = 6, was  $\text{Li}_{0.72}\text{Ti}_{2.98}\text{O}_6$ . The chemical composition of this compound derived from the present structure analysis is  $\text{Li}_{0.74(4)}\text{Ti}_3\text{O}_6$ , which is well consistent with the chemical analysis result. The single crystals of  $\text{Li}_x\text{Ti}_3\text{O}_6$  were almost uniform in chemical composition,  $x = 0.74$ , and neither more nor less lithium-deficient samples could be prepared.

Precession photographs indicate that the crystal belongs to the monoclinic system with the possible space group  $Cm$ ,  $C2$ , or  $C2/m$ . The lattice parameters, determined by a least-squares refinement using  $2\theta$  values of 25 strong reflections in the range  $20^\circ$ – $30^\circ$  and  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073$  Å) on an automated Rigaku AFC-5S four-circle diffractometer, are  $a = 14.1198(11)$  Å,  $b = 2.9486(11)$  Å,  $c = 4.9373(13)$  Å, and  $\beta = 92.693(14)^\circ$ .

$\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  crystals are stable in air at room temperature. This fact shows a sharp contrast to the ramsdellite-type  $\text{Li}_x\text{TiO}_2$  compounds (2, 5), where the oxidation reaction together with increasing lithium defects occurred vigorously in air.

### Structure Analysis

A small block crystal,  $100 \times 100 \times 20 \mu\text{m}$  in size, was used for the intensity data collection. The intensity data were collected by the  $2\theta-\omega$  scan mode with a scan rate of  $2^\circ/\text{min}$  at room temperature on a four-circle diffractometer (operating conditions: 40 kV, 30 mA) using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The fluctuation of the intensities, monitored by examining a set of three standard reflections ((020),  $(60\bar{2})$ , (312)) taken after every 50 observations, was within 0.7%. A total of 2485 reflections were obtained within the limit of  $2\theta \leq 110^\circ$ . Averaging the structure factors ( $R_{\text{int}} = 4.0\%$ ) resulted in a total of 1022 independent reflections which have a criteria of  $|F_o| > 3\sigma(|F_o|)$ . No absorption and extinction corrections were performed.

In the structure analysis that followed, the space group of highest symmetry  $C2/m$ , confirmed by successful refinement, was adopted. Initial positions for two titanium atoms and three oxygen atoms were determined by heavy-atom Patterson methods PATTY (6) using the teXsan program package (7). The  $R$  value using isotropic displacement parameters was 6.3%, showing that the structure model adopted was reasonable. Then, the atomic parameters, scale, and aniso-

**TABLE 1**  
Experimental and Crystallographic Data for  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$

Structural formula	$\text{Li}_{0.74(4)}\text{Ti}_3\text{O}_6$
Crystal system	monoclinic
Space group	$C2/m$
$a$ ( $\text{\AA}$ )	14.1198(11)
$b$ ( $\text{\AA}$ )	2.9486(11)
$c$ ( $\text{\AA}$ )	4.9373(13)
$\beta$ ( $^\circ$ )	92.693(14)
$V$ ( $\text{\AA}^3$ )	205.33(10)
$Z$	2
$D_x$ ( $\text{g/cm}^3$ )	3.96
Crystal size ( $\mu\text{m}$ )	$100 \times 100 \times 20$
Scan type	$2\theta-\omega$
Scan speed ( $^\circ/\text{min}$ )	2
Maximum $2\theta$	110
Measured reflections	2485
$R_{\text{int}}$ of 1134 replicates	0.040
Independent reflections	1351
Observed reflections ( $> 3\sigma$ )	1022
Number of variables	36
$R$	0.043
$wR$ [ $w = 1/\sigma^2 F$ ]	0.036
$S$	2.15(5)

**TABLE 2**  
Atomic Coordinates, Equivalent Displacement Parameters, and Site Occupancy Factors

Atom	$x$	$y$	$z$	$U_{\text{eq}}$	s.o.f.
Li	0.212(2)	0	0.060(3)	0.022(6)	0.37(2)
Ti(1)	0	0	0	0.0070(1)	1
Ti(2)	-0.15280(4)	1/2	-0.5261(1)	0.0081(1)	1
O(1)	-0.2296(1)	0	-0.7021(4)	0.0073(4)	1
O(2)	-0.0972(1)	0	-0.3098(4)	0.0087(4)	1
O(3)	-0.0696(2)	1/2	0.1802(4)	0.0101(4)	1

tropic displacement parameters were refined by the full-matrix least-squares method using the Xtal 3.2 program (8). The converged  $R$  value was 4.8%. At this stage, difference-Fourier synthesis revealed the position of lithium atoms in the ramsdellite-type tunnel space, such as in the case of the ramsdellitetype  $\text{Li}_x\text{TiO}_2$  compounds (2, 5). The refined lithium content was 0.37(2), which corresponded to the chemical formula  $\text{Li}_{0.74(4)}\text{Ti}_3\text{O}_6$ . This chemical composition was consistent with the chemical analysis result. As a result, this fact indicates that the lithium atoms are located only in the ramsdellite tunnel sites, and there is no necessity for introducing additional lithium atoms in the octahedral titanium sites as a solid solution model. In addition, no other lithium positions could be observed in the final difference Fourier map. Finally, the structure was refined to  $R = 4.3\%$  and  $wR = 3.6\%$  for 1022 reflections, with a shift/error for all 36 parameters less than 0.001. The crystallographic and experimental data are summarized in Table 1. The final atomic coordinates and displacement parameters are given in Tables 2 and 3.

## STRUCTURE DESCRIPTION AND DISCUSSION

### General Features

The crystal structure of  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  projected down the  $b$ -axis direction is drawn with DIAMOND program (9) (Fig. 1). The basic units of the structure are built up from single-rutile-type  $\text{Ti}(1)\text{O}_6$  chains and double-rutile-type edge-shared  $\text{Ti}(2)\text{O}_6$  chains along the  $b$  axis (Fig. 2). The  $\text{Ti}(1)\text{O}_6$  rutile chain connects the four corners to the four

**TABLE 3**  
Anisotropic Displacement Parameters

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Li	0.04(1)	0.021(9)	0.001(6)	0	0.003(6)	0
Ti(1)	0.0067(2)	0.0068(2)	0.0075(2)	0	0.0003(2)	0
Ti(2)	0.0061(2)	0.0066(2)	0.0115(2)	0	0.0007(1)	0
O(1)	0.0072(7)	0.0061(6)	0.0085(6)	0	0.0009(5)	0
O(2)	0.0103(7)	0.0062(6)	0.0092(7)	0	-0.0029(6)	0
O(3)	0.0120(8)	0.0074(7)	0.0111(7)	0	0.0044(6)	0

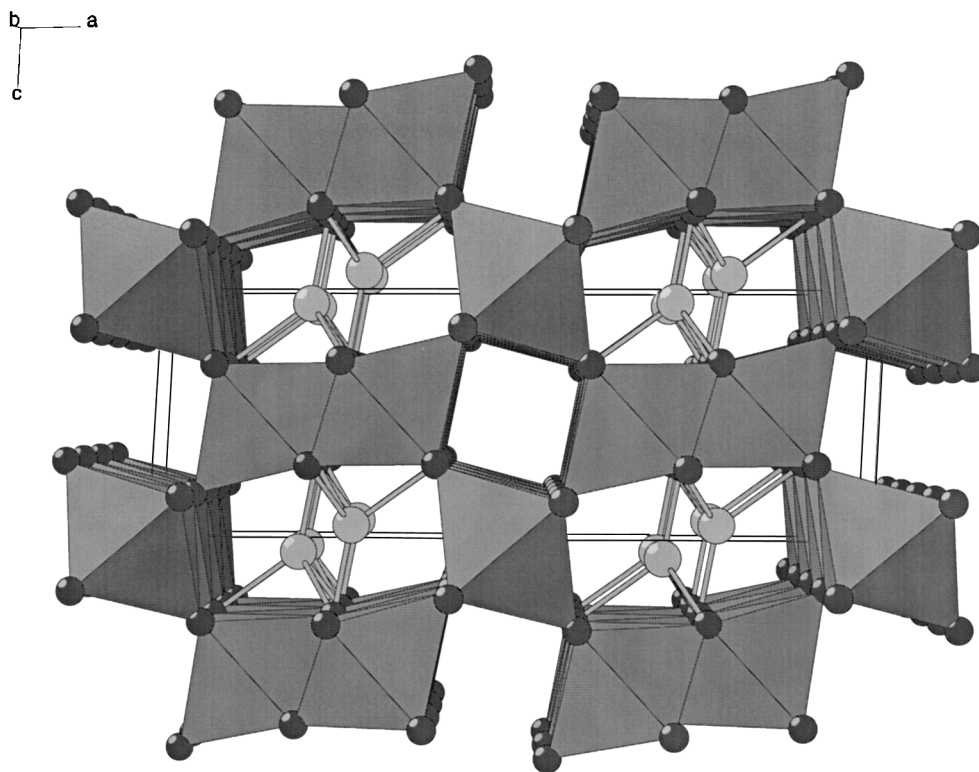


FIG. 1. Crystal structure of  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  viewed along  $[010]$ . The  $\text{TiO}_6$  unit is illustrated as an octahedron.

$\text{Ti}(2)\text{O}_6$  double-rutile chains, and forms two types of tunnels along the  $b$  axis. One is the pseudo-rectangular  $[2 \times 1]$  type, and the other is the pseudo-square  $[1 \times 1]$  type. The former unit can be seen in the ramsdellite-type structure, such as in  $\text{Li}_{0.5}\text{TiO}_2$  (2) (Fig. 3a), and the latter unit is the same as that in the rutile structure (Fig. 3b). From this point of view, this compound can be described as an intergrowth phase between ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  and rutile-type  $\text{TiO}_2$ . Lithium atoms are located only in the former ramsdellite-type  $[2 \times 1]$  tunnel spaces with an occupancy factor of 0.37(2), as shown in Fig. 1.

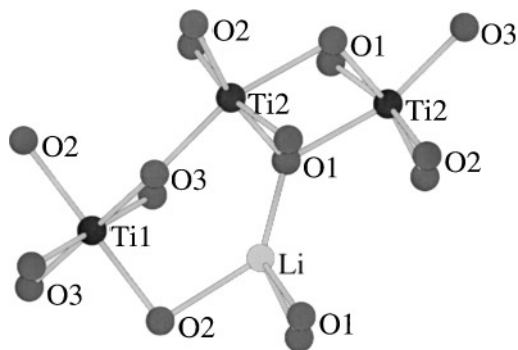


FIG. 2. The basic unit of  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  viewed along  $[010]$ .

The  $\text{Ti}(1)\text{O}_6$  octahedron has little distortion ( $\text{Ti}(1)\text{--O}$  distance 2.003–2.006 Å, average 2.004 Å), and the  $\text{O}\text{--O}$  edge distance ranges little between 2.712 and 2.949 Å (Table 4). In contrast, the  $\text{Ti}(2)$  atoms in the double-rutile-type chains are displaced away from the shared edge, resulting in slightly different  $\text{Ti}(2)\text{--O}$  distances (1.909–2.050 Å), and the mean  $\text{Ti}(2)\text{--O}$  distance is 1.982 Å. The shared  $\text{O}(1)\text{--O}(1')$  edge distance is 2.568 Å, which is very short as an oxygen–oxygen contact distance. Such a distortion of the octahedron is always observed in the double-rutile-type titanates, e.g.,  $\text{Li}_{0.5}\text{TiO}_2$  (2),  $\text{NaTi}_2\text{O}_4$  (3), and  $\text{CaTi}_2\text{O}_4$  (10). This may be due to the nature of  $\text{TiO}_6$  octahedra forming a double-rutile chain, and may serve to minimize repulsive forces between neighboring titanium cations with their large charges of +3 or +4.

The lithium ions occupy a tetrahedral site in the ramsdellite-type tunnel space with the 37% occupation, as in the case of ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  (2). The  $\text{LiO}_4$  tetrahedron is distorted because Li ions are displaced slightly from the ideal tetrahedral position in the direction of the center of the tunnel. Therefore, one longer (2.09(1) Å) and one shorter (1.80(2) Å) bond distances are given, and the average tetrahedral  $\text{Li}\text{--O}$  distance is 1.99 Å. This situation of  $\text{LiO}_4$  tetrahedral coordination is similar to that in the ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  (2).

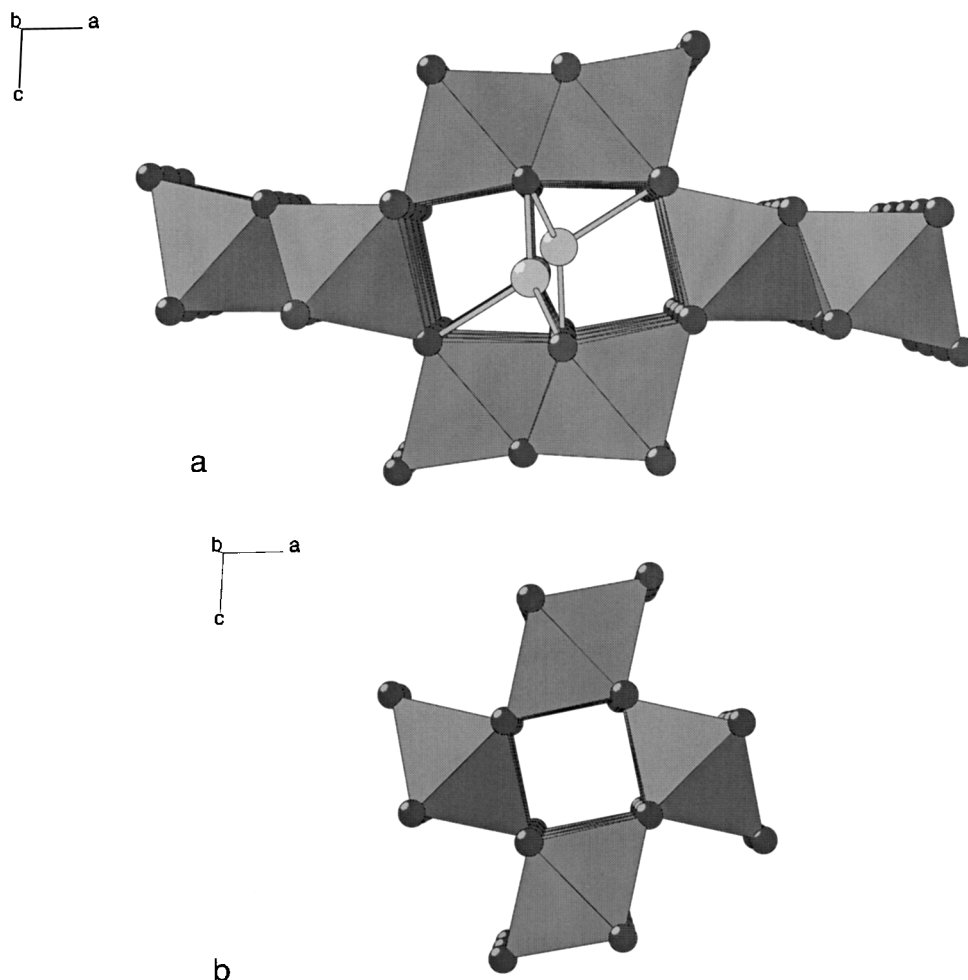


FIG. 3. Crystal structures of ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  (a) and rutile-type  $\text{TiO}_2$  (b).

TABLE 4  
Selected Bond Distances

LiO <sub>4</sub> tetrahedron			
Li–O(1)	2.03(1) × 2	O(1)–O(1)	2.949(1)
Li–O(1')	1.80(2)	O(1)–O(1')	3.316(2)
Li–O(2)	2.09(2)	O(1)–O(2)	2.859(2)
mean	1.99	O(2)–O(1')	3.609(3)
Ti(1)O <sub>6</sub> octahedron			
Ti(1)–O(2)	2.006(2) × 2	O(2)–O(3)	2.844(2)
Ti(1)–O(3)	2.003(2) × 4	O(2)–O(3)	2.826(3)
mean	2.004	O(3)–O(3)	2.949(1)
		O(3)–O(3)	2.712(3)
Ti(2)O <sub>6</sub> octahedron			
Ti(2)–O(1)	2.004(1) × 2	O(1)–O(1)	2.949(1)
Ti(2)–O(1')	2.050(2)	O(1)–O(1')	2.568(2)
Ti(2)–O(2)	1.963(1) × 2	O(1)–O(2)	2.628(3)
Ti(2)–O(3)	1.909(2)	O(1)–O(3)	2.782(2)
mean	1.982	O(2)–O(1')	2.859(2)
		O(2)–O(2)	2.949(1)
		O(2)–O(3)	2.959(3)

#### Structural Comparison with Manganese Oxides

As described earlier, the framework of both the ramsdellite-type  $\text{Li}_{0.5}\text{TiO}_2$  (2) and the present  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  consists of edge-shared rutile-type  $\text{TiO}_6$  chains with repeat distances of about 3.0 Å, which form one-dimensional tunnel structures. Similar rutile-related-type linkages of octahedra are often observed in some mixed-valence sodium titanates, e.g., calcium-ferrite-type  $\text{NaTi}_2\text{O}_4$  (3), and in some manganese oxide minerals. Table 5 shows structures of some synthetic and natural manganese oxides in comparison with the rutile-related-type synthetic titanate compounds. For example, pyrolusite ( $\beta\text{-MnO}_2$ ), which is isostructural to rutile, with single chains of the  $\text{MnO}_6$  octahedra, and ramsdellite of double chains have small vacant  $[1 \times 1]$ -type and  $[2 \times 1]$ -type tunnels, respectively. Interestingly, compared with the present  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$ , natural nsutite (14, 15) and the corresponding synthetic  $\gamma\text{-MnO}_2$  compounds have similar intergrowth structure consisting of randomly alternating layers of two kinds, derived from the structures of ramsdellite

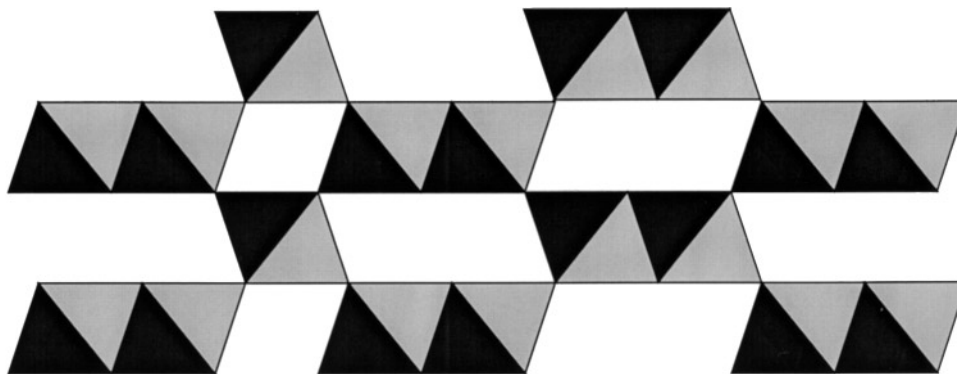


FIG. 4. Schematic drawing of part of the proposed random layer model for  $\gamma\text{-MnO}_2$ , after de Wolff (14).

and pyrolusite, respectively. Nsutite is a major manganese oxide that occurs in minable quantities in several terrestrial localities and has also been reported to occur in manganese nodules. It has industrial importance since the intergrowth mineral and its synthetic analog ( $\gamma\text{-MnO}_2$  (15) and so-called " $\gamma\text{-}\beta\text{-MnO}_2$ " (16)) are used as the cathodic material in rechargeable batteries.

The nsutite structure was envisioned to consist mainly of double chains with randomly interspersed single chains of pyrolusite (14, 15) (Fig. 4). However, no superstructures were found in X-ray diffraction patterns of nsutite, and so regular alternation of single and double chains was not predicted. In contrast, the present  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  has the monoclinically distorted regular alternation of single and double chains, and the structure has been successfully determined using the single-crystal X-ray diffraction data. From this point of view, the present structure determination of  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$  serves as a model for the intergrowth structures of nsutite and synthetic  $\gamma\text{-MnO}_2$ .

In  $\text{Li}/\gamma\text{-MnO}_2$  battery cells it is generally known that discharge occurs predominantly by lithium insertion into the ramsdellite-type  $[2 \times 1]$  tunnels, and the  $\beta\text{-MnO}_2$  domains can only accommodate 0.2  $\text{Li}^+$  ions in the  $[1 \times 1]$  tunnels (16). This fact is well consistent with the present lithium occupation model of  $\text{Li}_{0.74}\text{Ti}_3\text{O}_6$ , where the lithium ions occupy only a tetrahedral site in the ramsdellite-type tunnel space with the 37% occupation.

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TABLE 5

### Some Rutile-Related-Type Titanium Oxide Compounds in Comparison with the Corresponding Manganese Oxides

Rutile-related titanium oxides	Tunnel size <sup>a</sup>	Isostructural manganese dioxides	References
$\text{K}_x\text{TiO}_2$	$[2 \times 2]$	Hollandite ( $\alpha\text{-MnO}_2$ )	(11)
$\text{TiO}_2$ (Rutile)	$[1 \times 1]$	Pyrolusite ( $\beta\text{-MnO}_2$ )	(12)
$\text{Li}_x\text{TiO}_2$	$[2 \times 1]$	Ramsdellite	(2, 5)
$\text{Li}_x\text{Ti}_3\text{O}_6$	$[2 \times 1] + [1 \times 1]$	Nsutite ( $\gamma\text{-MnO}_2$ )	This study

<sup>a</sup>The expression  $[m \times n]$  is after Turner and Buseck (13).