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Synthesis and Crystal Structure of Ramsdellite-Type $Li_{0.5}TiO_2$

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Black single crystals of $Li_{0.5}TiO_2$ were synthesized by the reaction of lithium metal and titanium dioxide at 1473 K. It crystallizes in the orthorhombic ramsdellite-type structure, space group *Pbnm* with $a = 5.0356(6)$, $b = 9.6377(8)$, $c = 2.9484(7)$ Å, $V = 143.09(4)$ Å^3, and $Z = 4$. The structure was determined from a single-crystal X-ray study and refined to the conventional values $R = 0.038$ and $wR = 0.046$ for 744 independent reflections. The distorted octahedral sites are occupied only by Ti atoms, and a Li atom is located at one tetrahedral tunnel site with the occupancy factor of 0.45(2).

INTRODUCTION

Ramsdellite-type $Li_2Ti_3O_7$ is a compound famous as a one-dimensional ionic conductor (1–4). The structural formula of this compound was originally determined by a single-crystal X-ray study (1) as $Li_{0.43}(Ti_{0.86}Li_{0.14})O_2$ ($Z = 4$), in which the octahedral sites were occupied by both Ti and Li atoms. The remaining lithium atoms partly occupied two kinds of distorted tetrahedral sites in the tunnel space. Recent refinements of the lithium distribution using the powder neutron diffraction data confirm the two kinds of Li sites in $Li_2Ti_3O_7$ (2).

In the $Li_{4/3}Ti_{5/3}O_4$–$LiTi_2O_4$ solid solution system (5), the spinel-type structure is maintained by the lower valency titanium cations from $Li(Ti^{4+}_{1.67}Li_{0.33})_2O_4$ ($Z = 8$) to $Li(Ti^{4+}Ti^{3+})_2O_4$ ($Z = 8$). From this fact, similar mixed-valence compounds having the ramsdellite-type structure can be predicted. Johnston (6) originally reported that the spinel-type $LiTi_2O_4$ was not stable above 1223 K and that an orthorhombic ramsdellite-type phase existed for the same composition at higher temperatures. He reported the lattice parameters of the ramsdellite phase. However, the precise chemical and structural information has not been confirmed yet.

Recently, we have succeeded in preparing spinel-type $LiTi_2O_4$ single crystals by the reaction of lithium metal and TiO_2 at 1373 K in a sealed iron vessel (7). The high lithium vapor pressure in this preparation method may play an important role in the preparation of the spinel-type $LiTi_2O_4$ crystals at high temperatures above 1223 K (6). In a similar preparation method at a higher temperature of 1473 K, we have synthesized black single crystals of the orthorhombic ramsdellite-type compounds. In this paper, the chemical formula, magnetic property, and the precise crystal structure of this compound are reported.

EXPERIMENTAL AND RESULTS

Sample Preparation

Starting materials were 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 Li/Ti = 1/2, heated at 1473 K in an argon gas flow for 20 hr, and slowly cooled to room temperature. No apparent leakage of lithium vapor from the vessel was observed. Black crystals, $0.3 \times 0.2 \times 0.2$ mm^3 maximum in size, were prepared together with the NaCl-type $LiTiO_2$ (JCPDS No. 16-223) and the spinel-type $LiTi_2O_4$ crystals (7). Figure 1 shows a typical as-grown black crystal. EDX analysis showed that the black crystals were free from iron contamination from the vessel. Chemical analysis by ICP showed the Li/Ti ratio was 0.52. The corresponding chemical formula assumed O = 2 is $Li_{0.51}Ti_{0.99}O_2$ and was simplified to $Li_{0.5}TiO_2$.

Precession photographs indicated that the crystals belong to the orthorhombic system with the possible space group *Pbnm* or $Pbn2_1$. Table 1 shows the X-ray powder diffraction data of crushed $Li_{0.5}TiO_2$ crystals obtained at a

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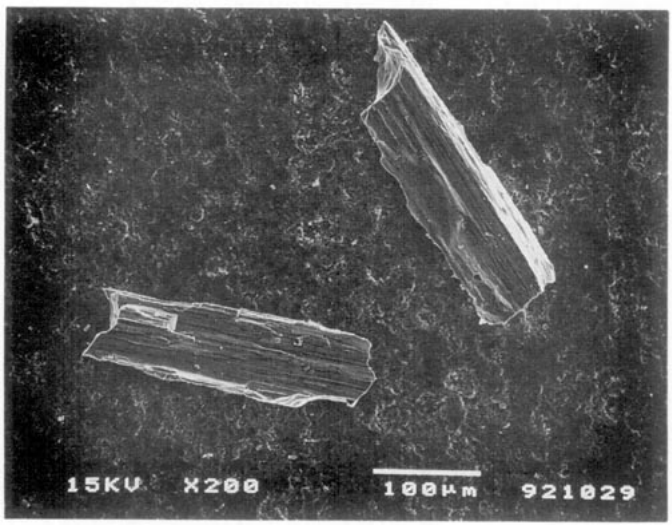

FIG. 1. SEM photograph of as-grown $Li_{0.5}TiO_2$ crystal.

scan rate of 2°/min in 2θ using graphite-monochromatized Cu$K\alpha_1$ radiation (λ = 1.5406 Å) and a Si internal standard. The lattice parameters, determined by a least-squares refinement using powder data, are a = 5.033(3), b = 9.628(5), c = 2.946(1) Å, and V = 142.77(8) Å^3. These values are consistent with the values reported by Johnston (6), a = 5.033, b = 9.626, c = 2.944 Å, and V = 142.6 Å^3. The compound having the chemical formula $Li_{0.5}TiO_2$ was prepared previously by a topotactic lithium insertion into anatase-type TiO_2 (8). The structure has the anatase-type framework (9) and is quite different from that of the present ramsdellite-type.

TABLE 1
X-Ray Powder Diffraction Data for $Li_{0.5}TiO_2$

h	k	l	d_{calc}[a] (Å)	d_{obs} (Å)	I/I_0
1	1	0	4.460	4.471	18
1	3	0	2.706	2.703	67
2	0	0	2.516	2.520	2
1	1	1	2.458	2.455	100
0	4	0	2.407	2.408	11
1	2	1	2.248	2.247	50
2	2	0	2.230	2.229	3
1	4	0	2.172	2.170	3
1	3	1	1.993	1.992	16
2	2	1	1.778	1.777	31
2	4	0	1.739	1.739	15
1	5	1	1.535	1.536	8
3	3	0	1.487	1.486	5
0	2	2	1.409	1.409	11
2	6	0	1.353	1.353	7
3	5	0	1.265	1.266	1
2	4	2	1.124	1.124	5

[a] Refined cell parameters using powder data are a = 5.033(3), b = 9.628(5), c = 2.946(1) Å, and V = 142.77(8) Å^3.

Under air atmosphere, $Li_{0.5}TiO_2$ crystals were very reactive, and a remarkable change in the lattice parameters was observed on the four-circle diffractometer, together with a decrease in the Li content. The lattice parameters we reported previously (7) are a = 4.979(1), b = 9.561(1), c = 2.955(1) Å, and V = 140.69(7) Å^3, which are quite different from the present values. This was caused by the exposure to air atmosphere for about one month for the purpose of single-crystal X-ray camera work. For this reason, special care was required for the sampling conditions. The lattice parameters, Li content, and crystal structures of Li_xTiO_2 crystals with $x \leq 0.5$ are reported elsewhere (10).

Johnston (6) reported that none of the samples with the ramsdellite-type structure was found to be superconducting above 1.5 K, although magnetic susceptibility data as a function of temperature was not shown. Magnetic susceptibility of the present $Li_{0.5}TiO_2$ crystals was measured between 4.3 and 300 K using a SQUID magnetometer. As shown in Fig. 2, the molar susceptibility χ of $Li_{0.5}TiO_2$ was nearly temperature independent in the range of 100 to 300 K. A sharp upturn in χ was, however, observed below 100 K, which might be due to a localized electron paramagnetic center or a paramagnetic impurity. These behaviors are quite different from those of other compounds having the $Li_{0.5}TiO_2$ composition; the spinel-type $LiTi_2O_4$ shows a superconductivity below 12 K (7), and the anatase-type $Li_{0.5}TiO_2$ gives a good fit to the Curie–Weiss law over the temperature range 10 to 200 K (8).

Structure Determination

A small block crystal, 0.15 × 0.15 × 0.05 mm in size, which was held in an evacuated glass capillary of 0.3 mm diameter with 0.01 mm thickness, was used for the

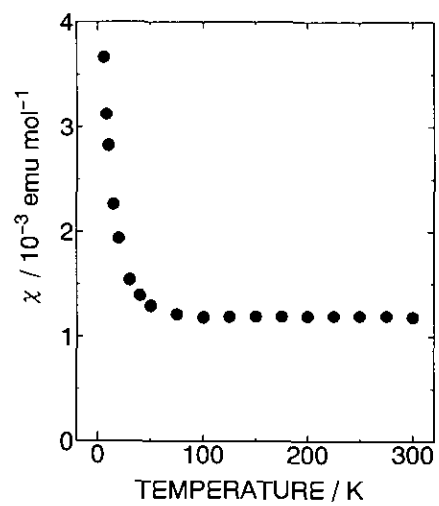

FIG. 2. Magnetic susceptibility of $Li_{0.5}TiO_2$ below room temperature.

structural analysis. The lattice parameters, determined by a least-squares refinement using 2θ values of 25 strong reflections in the range 20–30° and Mo$K\alpha$ radiation (λ = 0.71069 Å) on an automated Rigaku AFC-5 four-circle diffractometer, are a = 5.0356(6), b = 9.6377(8), c = 2.9484(7) Å, and V = 143.09(4) Å^3. These values are consistent with the results from the X-ray powder diffraction. The intensity data were obtained on the four-circle diffractometer (operating conditions: 40 kV, 40 mA) using a graphite-monochromatized Mo$K\alpha$ radiation (λ = 0.71069 Å) in the $2\theta - \omega$ scan mode with a scan rate of 4°/min at room temperature and reduced to structure factors after due correction for Lorentz and polarization effects. Fluctuations of the intensities, monitored by examining a set of the three standard reflections ((240), (002), (221)) taken after every 50 observations, were within 0.95%. A total of 845 independent reflections was obtained within the limit of $2\theta \leq 100°$, of which 744 reflections have a criteria of $|F_{obs}| > 3\sigma(|F_{obs}|)$, and were used for the subsequent crystal structure determination. No absorption or extinction corrections were made.

The structure refinement was initiated with the TiO_2 framework using the atomic coordinates in $Li_2Ti_3O_7$ (1). At first, the space group of highest symmetry *Pbnm*, confirmed by successful refinement, was adopted. A full-matrix least-squares refinement using the computer program RFINE-II (11) with isotropic and anisotropic temperature factors converged to R = 6.6% and R = 5.3%, respectively. At this stage, difference-Fourier synthesis using the GSFFR program (12) revealed the positions of lithium atoms. Figure 3 shows the $z = \frac{1}{4}$ section of the difference-Fourier map in the tunnel space. The electron density peak at $(-0.06, 0.47, \frac{1}{4})$ is clearly observable, and other significant peaks could not be confirmed. Then the lithium atom with the occupancy parameter of 0.5 was introduced. A subsequent lithium site occupancy refinement with anisotropic temperature parameters converged finally to R = 3.8% and wR = 4.6% [$w = 1/\sigma^2(F_{obs})$] for 744 reflections, with a shift/error for all parameters less than 0.01. The final lithium site occupancy is converged to 0.45(2), which is consistent with the analytical value. A difference-Fourier synthesis using the final atomic parameters showed no significant residual peak. A substitutional model using a small amount of lithium atoms was also applied to the octahedral site at the final stage. However, such a treatment did not significantly improve either the R value or the difference-Fourier map. The scattering factors for the neutral Li, Ti, and O atoms tabulated by Cromer and Mann (13) were used in the calculations. The anomalous dispersion correction factors were taken from the "International Tables for X-Ray Crystallography" (14). The crystallographic and experimental data are summarized in Table 2. The final atomic coordinates and temperature factors are given in Table 3.

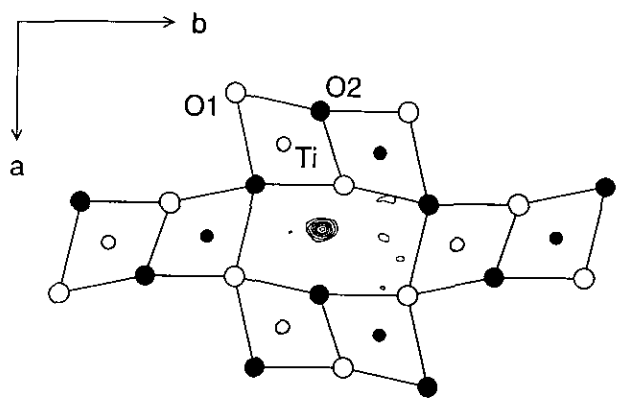

FIG. 3. A difference-Fourier map at $z = \frac{1}{4}$, superimposed onto projections of the ramsdellite-type TiO_2 framework viewed down [001]. The filled circles represent atoms at $z = \frac{1}{4}$, and the open circles, those at $z = \frac{3}{4}$. The large circles indicate O, and the small circles, Ti atoms. The contour lines are drawn with the interval of 0.6 e/Å^3.

TABLE 2
Crystallographic and Experimental Data for $Li_{0.5}TiO_2$

Crystal system	Orthorhombic
Space group	*Pbnm*
a (Å)	5.0356(6)
b (Å)	9.6377(8)
c (Å)	2.9484(7)
V (Å^3)	143.09(4)
Z	4
D_x (g/cm^3)	3.85
Maximum 2θ (°)	100
Scan width of 2θ (°)	1.0 + 0.5 tan θ
Scan speed (°/min)	4.00
Number of observed reflections	845
Number of used (>3σ) reflections	744
Final R	0.038
Final wR	0.046

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The crystal structure of ramsdellite-type $Li_{0.5}TiO_2$ projected down the c-axis direction is drawn with STRUPLO90 (15) (Fig. 4). The basic unit of the structure is the "double-rutile" chain (16), in which a pair of edge-shared TiO_6 octahedra pile up along the c-axis with sharing edges. By connecting four corners, the double rutile chains form pseudorectangular tunnels along the c-axis. The lithium ions occupy the tetrahedral site in the tunnels. The selected interatomic distances and bond angles calculated using UMBADTEA (17) are listed in Table 4.

Ti atoms are displaced away from the shared edge, resulting in slightly different Ti–O distances (1.947–2.031 Å), and the mean Ti–O distance is 1.997 Å. The O(1)–Ti–O(2′) angle, the value of which is 166.21°, is considerably smaller than 180°, as in a regular octahedron (Table 4). Therefore, the TiO_6 octahedron is apparently distorted. The coordination environment, i.e., bond

TABLE 3
Atomic Positional Parameters[a] and Anisotropic Temperature Factors[b]

Atom	x	y	β_{11}	β_{22}	β_{33}	β_{12}	B_{eq}	s.o.f.
Li	−0.057(3)	0.473(2)	0.006(5)	0.007(2)	0.08(3)	0.002(3)	1.95	0.45(2)
Ti	−0.01778(10)	0.14103(5)	0.0051(1)	0.00119(3)	0.0201(4)	0.00016(6)	0.55	1.0
O(1)	0.7015(4)	0.2800(2)	0.0072(6)	0.0019(2)	0.018(2)	0.0020(3)	0.68	1.0
O(2)	0.2005(4)	−0.0362(2)	0.0031(5)	0.0013(1)	0.014(2)	0.0003(2)	0.42	1.0

[a] All atoms in point position $4c$, $\pm(x, y, \frac{1}{4})$, $\pm(\frac{1}{2} - x, \frac{1}{2} + y, \frac{3}{4})$.
[b] $\beta_{13} = \beta_{23} = 0$.

lengths and bond angles in the present TiO_6 octahedron, is very similar to that in the (Ti, Li)O_6 octahedron of $Li_2Ti_3O_7$ (1, 2). This fact can be explained by the similarity in both of the average ionic sizes and the formal valence states in the octahedral sites. Using Shannon's ionic radii (18), the average octahedral ionic radii of the central ions are 0.64 Å (50% Ti^{3+} and 50% Ti^{4+}) and 0.63 Å (86% Ti^{4+} 14% Li^+) in $Li_{0.5}TiO_2$ and in $Li_2Ti_3O_7$ (1), respectively, and the average formal valence states are 3.50 (50% Ti^{3+} and 50% Ti^{4+}) and 3.58 (86% Ti^{4+} and 14% Li^+) in $Li_{0.5}TiO_2$ and $Li_2Ti_3O_7$ (1), respectively. Among the reduced titanate compounds, the average Ti–O distance in the present $Li_{0.5}TiO_2$ (1.997 Å) is consistent with the average Ti–O distances in the compounds which have the formal titanium valence of +3.5 : 2.014 Å in $NaTi_2O_4$ (19), 2.009 Å in Ti_4O_7 (20), 2.006 Å in anatase-type $Li_{0.5}TiO_2$ (9), and 2.005 Å in spinel-type $LiTi_2O_4$ (7).

Figure 5 shows the lithium ion distribution in a tunnel space of (a) $Li_{0.5}TiO_2$ and (b) $Li_2Ti_3O_7$ (1). In $Li_2Ti_3O_7$ (1), two kinds of Li sites are piled up to the c-axis direction in a double file with occupancy factors of 0.215 (Fig. 6). As indicated by Abrahams *et al.* (2), Li(1) in $Li_2Ti_3O_7$ is the most energetically favorable site because there are no face sharing contacts to the framework octahedra. The Li(2)–O tetrahedron shares one triangle face with the framework octahedron with a cation–cation distance of 2.33 Å. The shared triangle face is indicated by an arrow in Fig. 5b. The result of neutron refinement (2) indicates that the site occupancies reflect the relative stabilities of the tunnel sites with over 60% of the tunnel lithium located in the Li(1) site.

In the case of the $Li_{0.5}TiO_2$ compound, only one tetrahedral site, the same one as the Li(1) site in $Li_2Ti_3O_7$ (1, 2) is occupied by lithium ions with about 50% occupation (Fig. 5a). The 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 (2.22 Å) and one shorter (1.80 Å) bond distance are given, and the average tetrahedral Li–O distance is 2.01 Å. Compared with the Li(1) site in $Li_2Ti_3O_7$, the Li site position in $Li_{0.5}TiO_2$ is shifted in the direction of the center of the tunnel space $(0, \frac{1}{2}, z)$ from $y = 0.445$ in $Li_2Ti_3O_7$ (2) to $y = 0.473$ in $Li_{0.5}TiO_2$. From these structural points of view, it is possible to say that the one-dimensionality of the lithium arrangement in $Li_{0.5}TiO_2$ is superior to that in $Li_2Ti_3O_7$, and that the lithium ions in $Li_{0.5}TiO_2$ have a more ordered arrangement than those in $Li_2Ti_3O_7$.

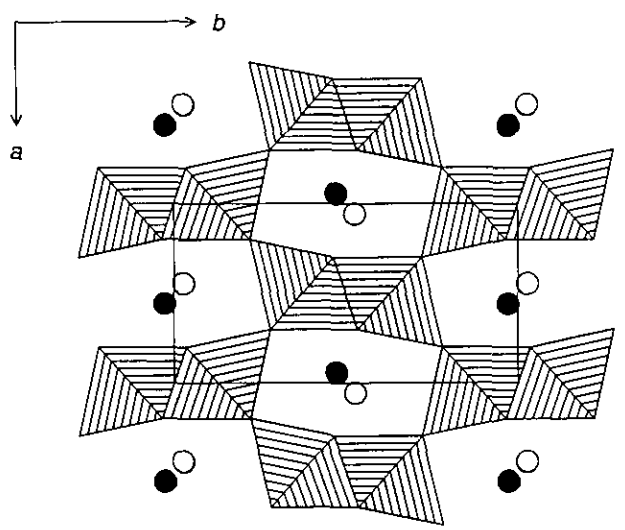

FIG. 4. Crystal structure of $Li_{0.5}TiO_2$ viewed along [001]. The TiO_6 unit is illustrated as a hatched octahedron. The filled circles represent Li atoms at $z = \frac{1}{4}$ and the open circles, those at $z = \frac{3}{4}$.

TABLE 4
Selected Interatomic Distances (Å) and Bond Angles (°) with Estimated Standard Deviations in Parentheses

Li–O(1)	2.22(2)	O(2)–Li–O(2′)	128.5(5)
O(2)	1.80(2)	O(2′)–Li–O(2′)	94.4(7)
O(2′)	2.01(1) × 2	O(2)–Li–O(1)	120.4(9)
		O(2′)–Li–O(1)	85.5(5)
Mean	2.01		
Ti–O(1)	1.947(2)	O(1)–Ti–O(1′)	98.02(3)
O(1′)	1.993(2) × 2	O(1)–Ti–O(2)	90.77(7)
O(2)	2.010(1) × 2	O(1)–Ti–O(2′)	166.21(9)
O(2′)	2.031(2)	O(1′)–Ti–O(1′)	95.42(10)
		O(1′)–Ti–O(2′)	91.23(7)
Mean	1.997	O(1′)–Ti–O(2)	84.44(6)
		O(2)–Ti–O(2)	94.34(9)
		O(2)–Ti–O(2′)	79.91(7)

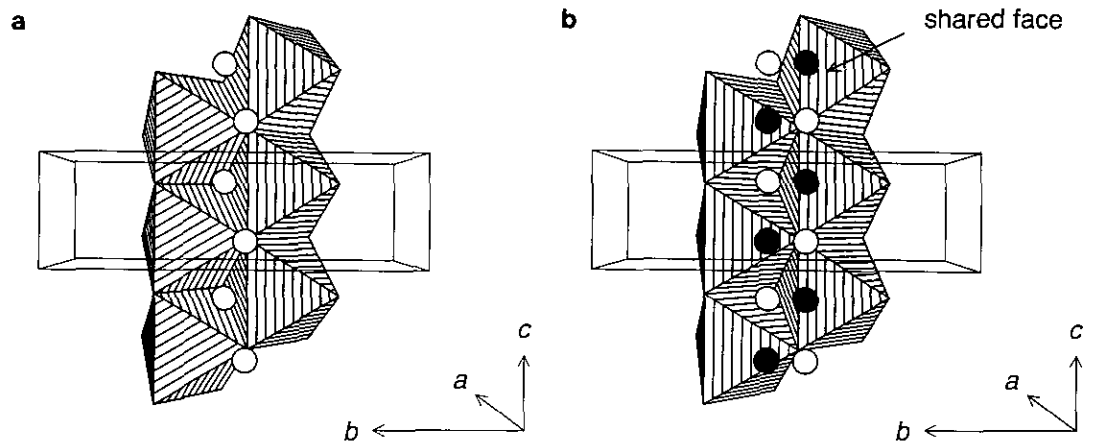

FIG. 5. Lithium ion arrangements in a single tunnel of (a) $Li_{0.5}TiO_2$ and (b) $Li_2Ti_3O_7$ (1), viewed down [100]. A double rutile chain constructing the tunnel framework is also drawn. In $Li_2Ti_3O_7$, the open circles represent Li(1) atoms and the filled circles represent Li(2) atoms. A shared triangle face between the $Li(2)O_4$ tetrahedron and the (Ti, $Li)O_6$ octahedron is indicated by an arrow.

The lithium occupancy of about 50% in $Li_{0.5}TiO_2$ enables the very short Li–Li distance of 1.666(15) Å. Under the present experimental conditions, the lithium contents of the as-grown crystals were almost uniform, and more lithiated samples could not be prepared. However, the Li_xTiO_2 ($x > 0.5$) samples may be prepared using some insertion methods. For example, lithium insertion studies on $Li_2Ti_3O_7$ (21) have shown that $Li_{2.5}Ti_3O_7$ is formed at room temperature, while at 50–60°C more lithium is taken up to form $Li_3Ti_3O_7$. The partial reduction of Ti^{4+} ions to Ti^{3+} in $Li_3Ti_3O_7$ is confirmed by ESR and electrical conductivity measurements. A further lithium insertion study of the $Li_{0.5}TiO_2$ host is presently being carried out so as to isolate more lithiated ramsdellite-type Li_xTiO_2 compounds.

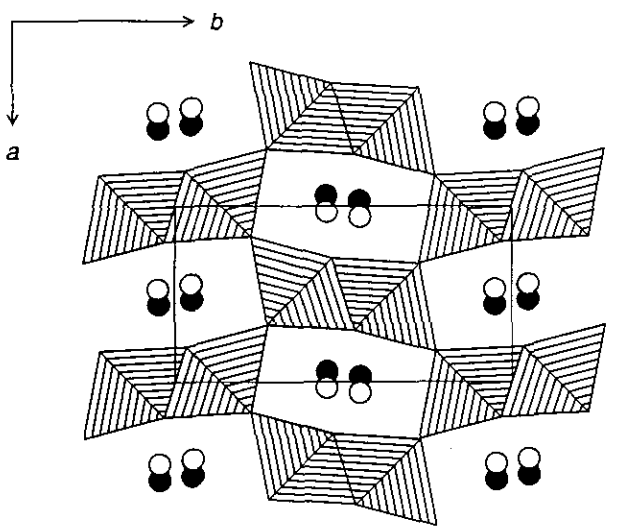

FIG. 6. Crystal structure of $Li_2Ti_3O_7$ (1) viewed along [001]. The filled circles represent Li atoms at $z = \frac{1}{4}$ and the open circles, those at $z = \frac{3}{4}$.

On the other hand, more lithium-deficient Li_xTiO_2 samples can be easily produced by air oxidation of as-grown $Li_{0.5}TiO_2$, as mentioned above. From the results of further topotactic oxidation experiments of the present $Li_{0.5}TiO_2$, the tunnel ions can be completely removed, and single crystals of ramsdellite-type TiO_2 have been prepared as final products. The precise crystal structures of Li_xTiO_2 with $0 \leq x \leq 0.5$ phases are reported in Ref. (10).

CONCLUSION

We have succeeded in the synthesis of ramsdellite-type $Li_{0.5}TiO_2$ single crystals by the reaction of lithium metal and titanium dioxide at 1473 K. The lattice parameters of $Li_{0.5}TiO_2$ were consistent with the original values reported by Johnston (6) as the high-temperature phase of the spinel-type $LiTi_2O_4$. The as-grown $Li_{0.5}TiO_2$ crystals were very reactive, and easily oxidized to more lithium-deficient Li_xTiO_2 crystals under air atmosphere at room temperature. From the result of single-crystal X-ray structure analysis, the lithium ions in $Li_{0.5}TiO_2$ are occupied at one tetrahedral site with an occupancy factor of about 50%. This is apparently different from the lithium occupation model in $Li_2Ti_3O_7$, in which two kinds of Li sites in the tunnel space are occupied by lithium ions, from the results of both the single-crystal X-ray (1) and the powder neutron diffraction structure analyses (2).

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