

Crystal Structure Refinement of Li_4TiO_4 Containing Tetrahedrally Coordinated Ti^{4+} and Tetragonally Packed Oxide Ions

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The crystal structure of Li_4TiO_4 has been determined by Rietveld refinement of powder X-ray diffraction data. It is isostructural with Li_4GeO_4 and contains tetrahedrally coordinated Ti^{4+} ions and an approximately tetragonally packed oxide ion array. © 1994

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INTRODUCTION

Synthesis, crystal data, and an x-ray powder pattern of Li_4TiO_4 have been reported previously (1, 2). Because of the similarity of the powder patterns of Li_4TiO_4 and Li_4GeO_4 , it was suggested (1) that Li_4GeO_4 and Li_4TiO_4 are isostructural. By analogy with the crystal structure of low Li_4GeO_4 (3) it was concluded that titanium in Li_4TiO_4 is tetrahedrally coordinated to oxygen. In general, Ti^{4+} prefers octahedral coordination, although the occurrence of Ti^{4+} in tetrahedral sites is not unknown since Ba_2TiO_4 (4) contains tetrahedrally coordinated titanium. The present study was undertaken in order to refine the crystal structure of Li_4TiO_4 and to confirm the presence of tetrahedral titanium. It was also of interest to investigate the packing arrangement of oxide ions since it had been speculated that Li_4GeO_4 may have an arrangement based on tetragonal packing (5, 6).

EXPERIMENTAL

Synthesis of Li_4TiO_4

Li_4TiO_4 is reported to be highly sensitive to atmospheric CO_2 , especially at temperatures of 400–800°C; it reacts to form Li_2CO_3 and Li_2TiO_3 (7). Li_4TiO_4 was therefore prepared by solid state reaction in an argon atmosphere. Starting materials were Analar grade Li_2CO_3 and TiO_2 (99.95% purity). Reagents were mixed in the stoichiometric ratio and heated in a gold foil boat in argon. The temperature was initially raised slowly from 500° to 700°C to expel CO_2 and then held at 900°C for 12 hr. The product

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was found by X-ray powder diffraction to be single phase Li_4TiO_4 . Although, over a period of weeks, Li_4TiO_4 reacts with CO_2 , freshly prepared samples could be analyzed under ambient conditions by X-ray diffraction.

Structure refinement

Powder X-ray diffraction data for Rietveld refinement were collected with a STOE STADI/P diffractometer in transmission mode using a small linear position sensitive detector, with $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54056 \text{ \AA}$) and a germanium monochromator. Scan ranges of $5^\circ \leq 2\theta \leq 110^\circ$ in steps 0.02° were used in the data collection.

Starting atomic parameters were taken from the crystal structure of low Li_4GeO_4 (3, 8), with which Li_4TiO_4 was believed to be isostructural. The pattern fitting structure refinement (PFSR)–Rietveld method was applied for the refinement, using a STOE software package, and the analysis was carried out using the Pearson VII function with exponent $m = 2$ to model peak shape. Peak full width at half maximum was described by the function

$$\text{FWHM} = A * T(0, x) + B * T(1, x) + C * T(2, x)$$

where A , B , and C are refinable parameters, the $T(n, x)$ are shifted Chebyshev polynomials of degree n , and

$$x = \frac{(2\theta - 2\theta_{\min})}{(2\theta_{\max} + 2\theta_{\min})}$$

RESULTS AND DISCUSSION

The structure was refined to $R(p) = 2.9\%$ and $R(wp) = 3.8\%$ for 126 powder reflections. The fitted X-ray diffraction profile for Li_4TiO_4 and a difference plot (observed – calculated) are shown in Fig. 1. Tables 1(a), 1(b), and 2 present crystal data, final atomic coordinates, and bond lengths and angles, respectively. A projection of the structure on the xy plane is shown in Fig. 2.

All cations are tetrahedrally coordinated and the structure is built up by linking $[\text{TiO}_4]$ and $[\text{LiO}_4]$ tetrahedra.

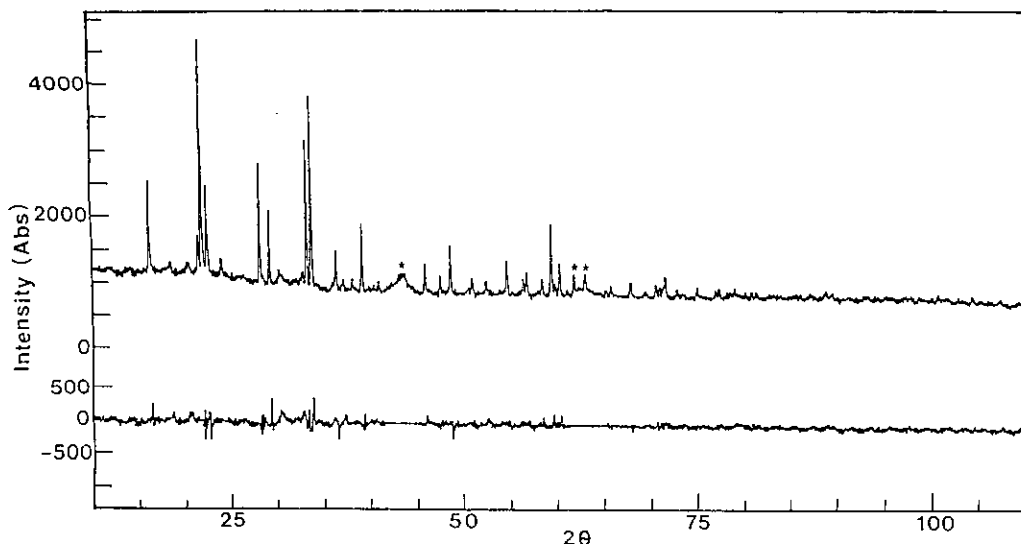


FIG. 1. Observed X-ray powder diffraction pattern for Li₄TiO₄ and difference plot after Rietveld refinement. Regions marked * are due to an impurity and have been eliminated from the refinement.

Li(1) tetrahedra are fairly regular with a mean Li(1)–O distance of 1.93 Å and a mean O–Li(1)–O angle of 110°. Li(2) tetrahedra are rather distorted with Li(2)–O distances ranging from 2.03 to 2.10 Å and angles from 96.1° to 140.9°. [TiO₄] tetrahedra appear regular with a mean Ti–O distance of 1.84 Å and a mean O–Ti–O angle of 109°. The Ti–O distance is within the range of values 1.79–1.84 Å, observed in the α' and β polymorphs of Ba₂TiO₄ (9) which contain TiO₄ tetrahedra.

The oxide ion packing arrangement is a distorted version of tetragonal packing, characterised by an anion–anion coordination number of 11 nearest neighbors + 2 next nearest neighbors (5, 6). This can be seen from the oxygen–oxygen distances for atoms O(1) and O(2) listed in Table 2b; eleven distances are in the range

TABLE 1

(a) Crystal data for Li ₄ TiO ₄						
<i>a</i> = 7.9116(8) Å, <i>b</i> = 7.4328(8) Å, <i>c</i> = 6.1368(6) Å, <i>V</i> = 360.9 Å ³ , <i>D_x</i> = 2.561, <i>Z</i> = 4, Space group <i>Cmcm</i> (No. 63)						
(b) Fractional coordinates from Rietveld refinement						
Atom	Multiplicity and Wyckoff notation	Occupancy	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>u₁₁</i>
Li(1)	8e	1.0	0.165(7)	0.0	0.0	0.010
Li(2)	8g	1.0	0.333(6)	0.243(6)	0.25	0.010
Ti	4c	1.0	0.0	0.342(1)	0.25	0.019
O(1)	8f	1.0	0.0	0.192(3)	0.005(2)	0.022
O(2)	8g	1.0	0.192(2)	0.471(2)	0.25	0.020

2.85–3.32 Å with an additional 2 at either 4.05 or 3.83 Å, respectively.

Ideal tetragonal packing is characterized by fourfold symmetry with two sets of mutually perpendicular buckled anion layers. These buckled oxide layers are clearly present in Fig. 2, perpendicular to [110] and [1 $\bar{1}$ 0], although structural distortions remove the fourfold symmetry axis which would have been parallel to *c*.

TABLE 2

(a) Selected bond lengths (Å) and angles (°) for Li ₄ TiO ₄			
Li(1)–O(1) × 2	1.93(4)	O(1)–Li(1)–O(2) × 2	117.9(2)
O(2) × 2	1.92(3)	O(2)–Li(1)–O(1) × 2	109.1(2)
mean Li(1)–O	1.93	O(1)–Li(1)–O(1)	95.1(2)
		O(2)–Li(1)–O(2)	107.9(2)
		mean O–Li(1)–O	110
Li(2)–O(1) × 2	2.10(3)	O(1)–Li(2)–O(2) × 2	107.1(2)
–O(2) × 2	2.03(4)	O(2)–Li(2)–O(1) × 2	98.7(2)
mean Li(2)–O	2.07	O(1)–Li(2)–O(1)	96.1(1)
		O(2)–Li(2)–O(2)	140.9(2)
		mean O–Li(2)–O	108
Ti–O(1) × 2	1.87(2)	O(1)–Ti–O(2) × 4	108.5(1)
–O(2) × 2	1.80(2)	O(1)–Ti–O(1)	106.7(1)
mean Ti–O	1.84	O(2)–Ti–O(2)	115.7(1)
		mean O–Ti–O	109

(b) Oxygen–oxygen distances/Å

Distances about O(1): Eleven nearest oxygen neighbors, 2.85, 2.98 (×2), 3.01, 3.13, 3.14 (×2), 3.30 (×2), 3.32 (×2). Two next-nearest oxygen neighbors, 4.05 (×2).
Distances about O(2): Eleven nearest oxygen neighbors, 2.98 (×2), 3.04, 3.10 (×2), 3.14 (×2), 3.30 (×2), 3.32 (×2). Two next-nearest oxygen neighbors, 3.83 (×2).

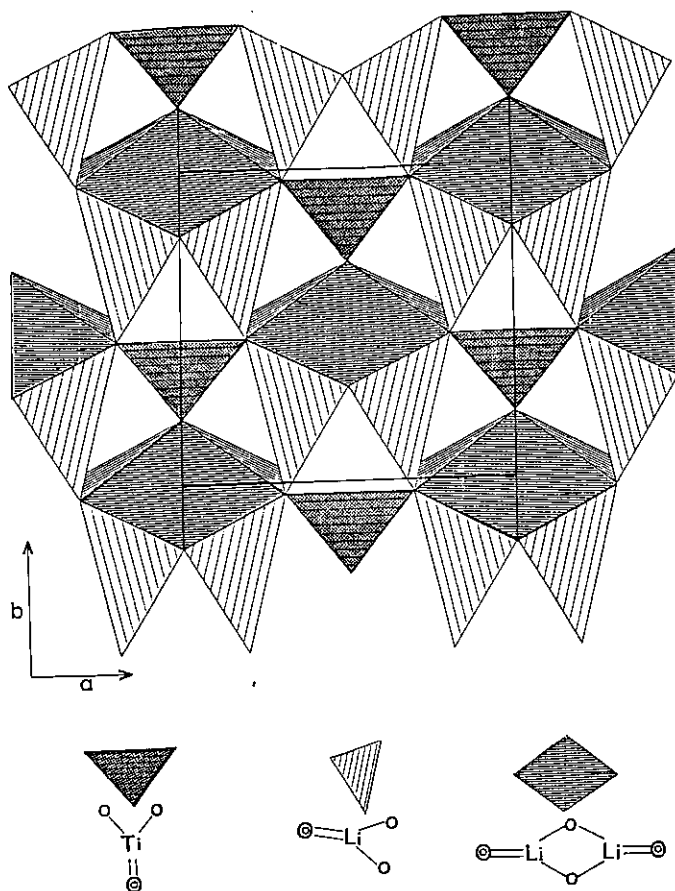


FIG. 2. Projection of the structure of Li_4TiO_4 on the ab plane showing the three types of tetrahedral units and their linking via edge and corner sharing.

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