

Crystal Structure of the Li⁺ Ion Conductor Dilithium Trititanate, Li₂Ti₃O₇*

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Abstract

Li₂Ti₃O₇, *Pbnm*, $a = 5.016(3)$, $b = 9.543(5)$, $c = 2.945(2)$ Å, $V = 140.97$ Å³, $\mu = 4.90$ mm⁻¹, $D_c = 3.629$ Mg m⁻³. The structure has been refined using 733 Mo $K\alpha$ *hkl* intensities to $R = 0.058$. The Li⁺ ion positions are disordered.

In assessing the possibility of high ionic conductivity needed for battery applications, various Li-containing materials, particularly those with structural arrangements containing tunnels or diffusion paths, have been examined. In the Li₂O–TiO₂ system (Jonker, 1957), stoichiometries very close to a Li₂O:TiO₂ ratio of 1:3, *i.e.* Li₂Ti₃O₇, are found to crystallize in space group *Pbnm* (Lundberg & Andersson, 1964) with a structural arrangement similar to that found in the mineral ramsdellite, MnO₂ (Byström, 1949). Several other minerals with similar structural arrangements in *Pbnm* are known and show rather large differences in the atomic coordinates for one of the two crystallographically different O atoms (Wyckoff, 1965). There is no detailed structure determination previously reported on Li₂Ti₃O₇.

In ramsdellite, the metal and the two crystallographically different O atoms occupy fourfold special positions on mirror sites, $\pm(x, y, \frac{1}{4}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{4})$. For the stoichiometry Li₂Ti₃O₇, vacancies on the metal-atom sites would possibly be necessary, suggesting (Li_{2.29}□_{1.71})(Ti_{3.43}□_{0.57})O₈, where □ are vacancies, as one of the possible 'structural' formulae. Furthermore Roth, Parker & Brower (1973) suggested that part of the Li⁺ ions might substitutionally occupy Ti sites and, hence, formulated the compound as (Li_{1.72}□_{2.28})(Li_{0.57}Ti_{3.43})O₈. Part of the present refinement was an attempt to clarify the positions occupied by these Li⁺ ions.

The present crystals were a deep-yellow color rather than colorless (Lundberg & Andersson, 1964) because

of the Rh-contaminated Pt used in the ampoule to contain the melt. The crystals, hence, contained approximately 100 p.p.m. Rh. (Subsequent crystals grown with pure Pt growth ampoules were colorless.) Our lattice constants are $a = 5.016(3)$, $b = 9.543(5)$, and $c = 2.945(2)$ Å which are in good agreement with previously published values. The crystal used for data collection was cleaved to an irregular shape with dimensions less than 0.3 mm from a larger specimen which was also used for microwave conductivity measurements (Richards, 1978). The θ – 2θ scan technique and a scintillation detector employing pulse-height discrimination were used to measure the Mo $K\alpha$ Zr-filtered intensity data to 95° (2θ) on four octants. The higher than normal 2θ value was initially considered necessary in order to distinguish between models containing substitutional Li⁺ in Ti sites and those without Li⁺ in such sites. Of the 733 averaged, unique intensities measured, 624 were greater than 3σ where $\sigma = (N_{sc} + K^2 N_B)^{1/2}$ and N_{sc} , N_B , and K are the total scan count, background counts and the time ratio of the scan to background, respectively. No absorption corrections ($\mu = 4.90$ mm⁻¹) were made. Because of the differences in the atomic coordinates observed in minerals with similar structural arrangements, initial parameters for Ti and O were obtained from a Patterson function, rather than from ramsdellite, and the intensity data were subjected to least-squares refinement. The function $w(F_o - F_c)^2$ was minimized with $w = 1/\sigma^2$ and with structure factors calculated using scattering factors for Ti⁴⁺, O⁻ and Li⁺ computed from Hartree–Fock wave functions (Cromer & Mann, 1968). Based on only Ti and O contributions and including an extinction parameter, the values of R ($= \sum |F_o| - |F_c| / \sum |F_o|$) are 0.077 and 0.061 for isotropic and anisotropic thermal parameters, respectively. This difference Fourier synthesis showed positive electron density near -0.059 , 0.458 , 0.25 (peak 1) of 1.5 e Å⁻³, near 0.540 , 0.053 , 0.25 (peak 2) of 1.5 e Å⁻³, as well as a few 1.2 e Å⁻³ peaks at locations close to Ti atoms. In addition, a broad positive background value ranging from 0.2 – 0.6 e Å⁻³ is noted in other

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parts of the channel (Fig. 1) at $z = \frac{1}{4}$. This suggests Li^+ ion disorder even though the photographs taken of our specimen did not exhibit any unusually large amount of thermal diffuse scattering.

Models based on Li^+ ions located at sites for peaks 1 and 2 are suggested for both 'structural' formulae, *i.e.* formula (I), $(\text{Li}_{2.29}\square_{1.71})(\text{Ti}_{3.43}\square_{0.57})\text{O}_8$, or formula (II), $(\text{Li}_{1.72}\square_{2.28})(\text{Ti}_{3.43}\text{Li}_{0.57})\text{O}_8$. For formula (II), the Li positional and thermal parameters are constrained to be identical to those for the Ti atom. Introduction of Li at either peak 1 or peak 2 always resulted in a difference synthesis which retained the $\sim 1.5 \text{ e } \text{\AA}^{-3}$ peak at the remaining site. This suggests that the Li^+ ions are disordered in this structure, occupying two different special-position sites. Hence, formula (I) would be expanded to $(\text{Li}_{2.29}\square_{1.71})_{1-x}(\text{Li}_{2.29}\square_{1.71})_x(\text{Ti}_{3.43}\square_{0.57})\text{O}_8$ and formula (II) would require a corresponding expansion. If one assumes equal occupancy

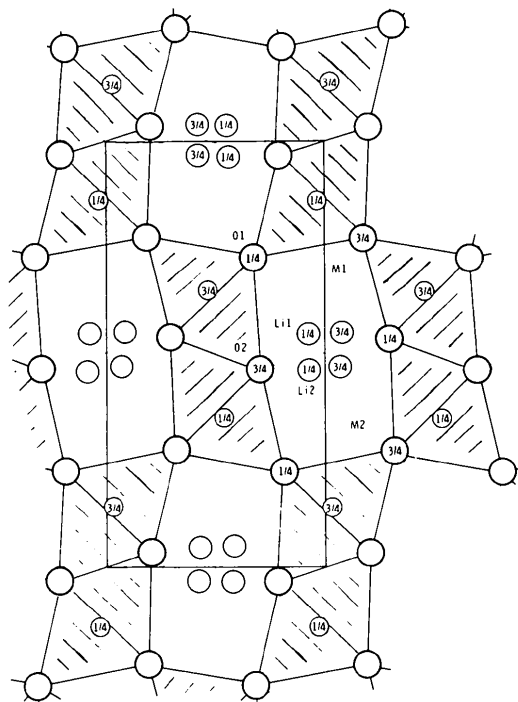


Fig. 1. A representation of the structure of $\text{Li}_2\text{Ti}_3\text{O}_7$ along (001). The rectangle defines the a (horizontal) and b (vertical) axes. Edge-shared TiO_6 octahedra form ribbons perpendicular to view with Ti separations along c of 2.945 \AA and, in the view, of $3.058(1) \text{ \AA}$. Corner sharing of such ribbons results in open channels in this structure. There are eight possible tetrahedral sites (four sets of two symmetry-related sites) in each channel. Li^+ ions occupy two sets of such sites indicated with medium-sized circles; $M1$ and $M2$ (indicated in only one channel for only $z = \frac{1}{4}$ positions) are the other two sets of sites and these may also be involved in the Li^+ ion conductivity observed in this material. The z coordinates of O atoms surrounding this channel are indicated so that the reader may construct tetrahedra to ascertain positions of tetrahedral sites and their faces relative to the faces of the octahedra.

factors ($x = 0.5$) for peaks 1 and 2, the model based on formula (I) yields $R = 0.060$ [U values for Li(1) and Li(2) are $0.024(3)$ and $0.045(8) \text{ \AA}^2$, respectively] while that on formula (II) yields $R = 0.058$ (parameter values given in Table 1). The slightly lower value for R suggests that the 'structural' formula for $\text{Li}_2\text{Ti}_3\text{O}_7$ corresponds to formula (II) and this is taken to be the most probable, final structure.* Attempts to employ occupancy factors other than equal values for Li (I) and Li (II), *i.e.* $x \neq \frac{1}{2}$, as well as values less than 0.57 for Li (III) gave intermediate results and such models were discarded as too complex. The Ti and O parameters in all models considered, including that without Li contribution, are within 2σ from those given in Table 1. Note that for the final structure, the thermal parameters for Li(1) and Li(2) are reasonable and approximately equal to those for the other atoms in the structure. The positive background value for electron density in the Fourier synthesis remains and may also be involved in the Li^+ ion disorder in this structure as indicated below.

The structure (Fig. 1) consists of TiO_6 octahedra (strictly speaking, $\text{Ti}_{0.86}\text{Li}_{0.14}\text{O}_6$ octahedra) which are edge-shared in two different ways, directly above and below forming a string along c , and to an adjacent string displaced $\frac{1}{2}$ along c ; two such connected strings form a ribbon. Corner sharing of these ribbons results in open channels along c for this structure. In any one channel, there are eight possible tetrahedral sites (four sets of two symmetry-related sites). Two of these sets closest to the center of the channel are occupied by Li(1) and Li(2) while the remaining two, more distant sets are at locations associated with the broad, positive value for the electron density (indicated as $M1$ and $M2$ in Fig. 1). The Ti atoms are displaced away from the shared edge resulting in slightly different Ti—O distances (1.95 – 2.03 \AA) and, together with the stretching of the octahedra along the ribbon, O—Ti—O angles which depart from 90° (Table 2). The Li^+ ions are displaced slightly from the ideal tetrahedral position and involve one longer (2.15 and 2.26 \AA) and one

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34094 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters for $\text{Li}_2\text{Ti}_3\text{O}_7$ ($x, y, \frac{1}{4}$ sites)

	p	x	y
Li(1)	0.215	$-0.060(4)$	$0.451(2)$
Li(2)	0.215	$0.532(7)$	$0.050(4)$
Li(3)	0.14	$-0.03244(8)$	$0.13938(4)$
Ti	0.86		
O(1)	1.0	$0.6742(3)$	$0.2744(1)$
O(2)	1.0	$0.2030(2)$	$-0.0331(1)$

shorter (1.80 and 1.83 Å) bond length. In both cases, this displacement is in the direction of the center of the channel. The sites *M1* and *M2*, if idealized, would be situated ~1.90 Å from the O atoms, a distance ~0.11 Å shorter than the average Li–O bond distance found in this structure. This would then be a more unfavorable location for the Li⁺ ion.

Single-crystal d.c. conductivity (Boyce, 1978) and microwave dielectric-constant measurements (Richards, 1978) show no strong anisotropy in this material, suggesting Li⁺ ion paths perpendicular to the channel directions. The Ti site accommodates an ion of radius ~0.69 Å and is sufficiently large for the Li⁺ ion.

In fact, the present structure study obtained the best fit to the experimental data with the model in which Li⁺ ions fill the vacant Ti sites. For Li⁺ ion diffusion perpendicular to the channel directions, the Li⁺ ion would need to hop through the octahedral face shared with the tetrahedron containing the empty *M1* or *M2* sites and then on to the center of the channel to the Li(1) and Li(2) sites. The time spent on *M1* and *M2* is very small as indicated by the very low value of electron density at these sites. Hops from the octahedral site to *M1* are along the *b* direction while those to *M2* are along the *a* direction. Thus, the Li⁺ ion disorder in the channels, the small positive value for the electron density at the *M1* and *M2* sites and the structural arrangement of shared faces between the octahedra and *M1* or *M2* tetrahedra are consistent with the lack of anisotropy in the ionic conductivity of this material.

Table 2. Bond lengths (Å) and angles (°) in Li₂Ti₃O₇

Ti–O(1)	1.956 (1)	O(1)–Ti–O(1')	96.90 (5)
Ti–O(1')	1.980 (1) × 2	O(1)–Ti–O(2)	90.70 (5)
Ti–O(2)	1.982 (1) × 2	O(1)–Ti–O(2')	80.56 (4)
Ti–O(2')	2.026 (1)	O(1')–Ti–O(1')	96.10 (4)
		O(1')–Ti–O(2)	91.87 (5)
		O(2)–Ti–O(2')	80.56 (4)
		O(2')–Ti–O(2')	95.95 (4)
Li(1)–O(2)	1.80 (2)	O(2)–Li(1)–O(2')	123 (1)
Li(1)–O(2')	2.05 (2) × 2	O(2')–Li(1)–O(2')	92 (1)
Li(1)–O(1)	2.15 (2)	O(2)–Li(1)–O(1)	133 (1)
		O(2')–Li(1)–O(1)	87 (1)
Li(2)–O(2)	1.83 (3)	O(2)–Li(2)–O(2')	125 (1)
Li(2)–O(2')	1.99 (2) × 2	O(2')–Li(2)–O(2')	95 (1)
Li(2)–O(1)	2.26 (4)	O(2)–Li(2)–O(1)	134 (2)
		O(2')–Li(2)–O(1)	82 (1)

References

- BOYCE, D. (1978). Private communication.
 BYSTRÖM, A. M. (1949). *Acta Chem. Scand.* **3**, 163–173.
 CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321–324.
 JONKER, G. H. (1957). *Trab. Reun. Int. Reactiv. Solidos 3 Madr.* 1956, **1**, 413–421.
 LUNDBERG, M. & ANDERSSON, S. (1964). *Acta Chem. Scand.* **18**, 817.
 RICHARDS, P. M. (1978). Private communication.
 ROTH, R. S., PARKER, H. S. & BROWER, W. S. (1973). *Mater. Res. Bull.* **8**, 327–332.
 WYCKOFF, R. W. G. (1965). *Crystal Structures*, Vol. 1, pp. 290–293. New York: John Wiley.

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The Crystal Structure of β-Si₃N₄; Structural and Stability Considerations Between α- and β-Si₃N₄

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Abstract

β-Si₃N₄, grown from a silicon melt, has space group *P6₃* with *a* = 7.595 (1), *c* = 2.9023 (6) Å, *Z* = 2. *R* = 0.037 for 345 independent reflections. The close relation to the α-Si₃N₄ structure is shown. Madelung energy calculations suggest that β-Si₃N₄ is the more stable form at about 293 K.

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Introduction

The high-temperature ceramic Si₃N₄ is of technological interest because of its good refractory properties. However, the relationship between the two forms α and β is not completely understood. It was supposed that α- and β-Si₃N₄ are low- and high-temperature forms, respectively, but only a transformation from α to β has been observed, never the reverse.

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