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# The Crystal Structure of $Li_2TiSiO_5$

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**The crystal structure of $Li_2TiSiO_5$ was solved at 20°C in the tetragonal space group $P4/nmm$ with unit cell parameters $a$ = 6.444(3)Å, $c$ = 4.399(2)Å, $V$ = 182.67 Å$^3$, $D_c$ = 3.09 g cm$^{-3}$ and $Z$ = 2. The structure parameters were refined to a final $R$ value of 1.95% for 339 independent reflections with $I > 3\sigma(I)$. The crystal structure can be regarded as a layered one with infinite sheets of $SiO_4$ tetrahedra and $TiO_5$ square pyramids linked by common corners, connected by layers of Li cations.**

## I. INTRODUCTION

Lithium titanosilicate, $Li_2TiSiO_5$, has been reported by Kim and Hummel as a distinct compound within the ternary system $Li_2O$–$SiO_2$–$TiO_2$ (1). Although the structures of equivalent compositions, $Na_2M^{IV}XO_5$ ($M^{IV}$ = Ti, $X$ = Si, Ge; $M^{IV}$ = Zr, $X$ = Si), were solved two decades ago, no sound structural data concerning the title compound were available in the literature at the beginning of the present study (2–4). Only lattice parameters are known (1, 5). Furthermore, no member of the chemical families $A^I_2M^{IV}XO_5$ ($A^I$ = monovalent cation, $M^{IV}$ = tetravalent cation) other than $Li_2TiSiO_5$, $Na_2TiSiO_5$, $Na_2TiGeO_5$, and $Na_2ZrSiO_5$, is so far identified. The purpose of the present work is to investigate the crystal structure of the title compound, in order to get a better insight into the crystal chemistry of these compounds. The ultimate goal is to determine the effect of the nature and size of the cations $A^I$ and $M^{IV}$ on the thermochemical stability, structure type, and physical properties of these phases (6).

## II. EXPERIMENTAL

### (a) Growth of Crystals

Single crystals suitable for X-ray structure analysis were grown from a melt of $Li_2MoO_4$ and $LiVO_3$ (molar ratio 4 : 1), with a fixed ratio (solute weight/flux weight) = 0.10. The mixture of appropriate amounts of reagent grade starting materials $Li_2CO_3$, $TiO_2$, $SiO_2$, $V_2O_5$, and $MoO_3$ is ground before being submitted to the following heat treatment:

—slow heating to 870°C,
—melting at 870°C over a 48-hr period,
—slow cooling (5°C/hr) to 300°C before quenching to room temperature.

Single crystals of quartz and $Li_2TiSiO_5$ are extracted by dissolving the flux in distilled water.

### (b) X-Ray Crystallography

Preliminary cell constants and the space group were determined from precession and Weissenberg photographs. The space group was uniquely assigned as $P4/nmm$ (No. 129) on the basis of the tetragonal Laue symmetry $P4/mmm$ and the reflection conditions $hk0: h + k = 2n$. Accurately determined angles of 25 centered reflections with $2\theta > 26°$ and with values of $\chi$ between 10 and 60° were used for the refinement of the lattice parameters. In accord with the parameters in Table 1, intensity data were collected on an Enraf–Nonius diffractometer CAD4 with graphite monochromatized Mo$K_\alpha$ radiation. The program SHELXTLPC was used for solution and refinement of the crystal structure (7). After a correction for absorption by a face method (8) and data reduction to a set of 339 independent reflections, a Patterson map showed the positions of Ti and Si; following isotropic refinement a

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**TABLE 1**
**Crystal Data for $Li_2TiSiO_5$**

| | |
|---|---|
| Formula weight | 169.845 |
| Space group | $P/4nmm$ (No. 129) |
| Crystal system | Tetragonal |
| $a$(Å) | 6.444(3) |
| $c$(Å) | 4.399(2) |
| $V$(Å$^3$) | 182.6 |
| $Z$ | 2 |
| $D_{calc}$ (g/cm$^3$) | 3.09 |
| Radiation | Mo$K_\alpha$, $\lambda = 0.71069$ Å |
| $\mu$(cm$^{-1}$) | 23.92 |
| Crystal size (mm) | $0.39 \times 0.39 \times 0.05$ |
| Temperature (°C) | 20 |
| Collection range | $+h, \pm k, \pm l$ |
| 2 $\theta$ range (°) | $2 < \theta < 38$ |
| Scan method | $\omega - 2\theta$ |
| Scan width | $0.8 \pm 0.35 \tan\theta$ |
| No. of reflections measured | 2270 |
| No. of reflections unique | 339 |
| No. of variables | 20 |
| Transmission coefficient, max/min | 0.89/0.52 |
| Absorb cor | Face method |
| Weighting scheme | $w = .838/(\sigma^2(F) + 10^{-5}F^2)$ |
| Largest difference peak/hole (eÅ$^{-3}$) | 0.45/0.58 |
| Extinction cor | $F_{corr} = F_c[1 + 10^{-5}F_c^2/\sin\theta]$ |
| $R(F)$[a] | 0.0195 |
| $R_W(F)$[b] | 0.0210 |

[a] $R = \Sigma\Delta/\Sigma F_o$.

[b] $R_W = (\Sigma[\Delta\sqrt{w}])/\Sigma[F_o\sqrt{w}]$, with $\Delta = \|F_o| - |F_c\|$.

difference Fourier map gave the positions of remaining O and Li atoms. Full anisotropic refinement yielded the final structure shown in Fig. 1, while Table 2 gives positional parameters, and Table 3 contains relevant bond distances and angles.

Further details of the structure determination (e.g., structure factors) have been deposited and can be ordered from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, F.R.G., as Collection No. CSD-57905.

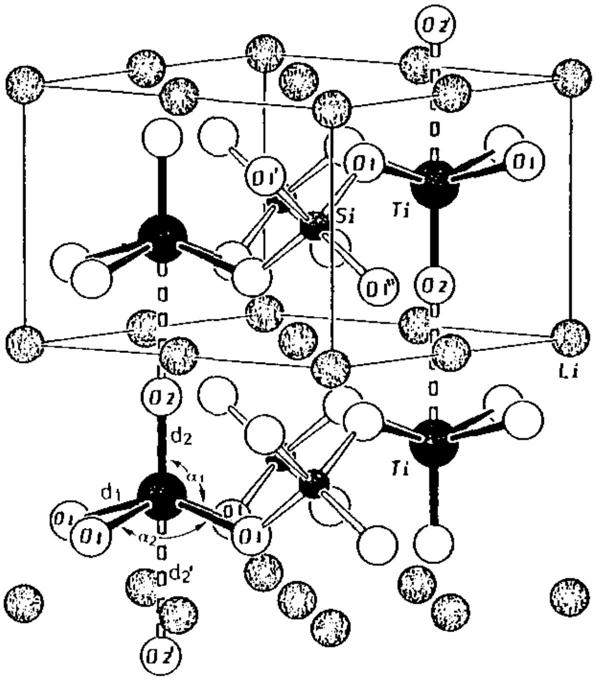

FIG. 1. Three-dimensional view of $Li_2TiSiO_5$ structure (see Table 4 for numerical data of octahedral bonds and angles).

## III. DESCRIPTION OF THE STRUCTURE

Figure 1 represents a three-dimensional view of the lattice, providing evidence for a layer structure. $SiO_4$ tetrahedra share all their apices with the four adjacent $TiO_5$ square pyramids so as to develop infinite sheets (Fig. 2) parallel to (001). The layered $[TiSiO_5]^{2-}$ anions are bound by planes of $Li^+$ cations. The structure can also be viewed as chains consisting of linear O-bridged $TiO_6$ octahedra of $ReO_3$ type as shown in Fig. 1. The chains of strongly (5 + 1)-distorded $TiO_6$ octahedra running parallel to [001] are linked together in a three-dimensional network by $SiO_4$ tetrahedra. The silicon is located in an almost regular tetrahedron with identical Si–O bond lengths of 1.633(1)Å

**TABLE 2**
**Atomic Coordinates and Thermal Parameters for $Li_2TiSiO_5$**

| Atom | $X$ | $Y$ | $Z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ | $U_{eq}$[a] |
|---|---|---|---|---|---|---|---|---|---|---|
| Ti | 0.25 | 0.25 | 0.5966(1) | 0.0054(1) | $U_{11}$ | 0.0066(2) | 0 | 0 | 0 | 0.0058(1) |
| Si | 0.75 | 0.25 | 0.5 | 0.0040(2) | $U_{11}$ | 0.0062(3) | 0 | 0 | 0 | 0.0047(2) |
| O1 | 0.5441(2) | 0.25 | 0.7165(2) | 0.0057(3) | 0.0102(4) | 0.0089(3) | 0 | 0 | −0.004(2) | 0.0083(3) |
| O2 | 0.25 | 0.25 | 0.2107(5) | 0.0170(6) | $U_{11}$ | 0.0083(7) | 0 | 0 | 0 | 0.0141(6) |
| Li | 0 | 0 | 0 | 0.022(2) | $U_{11}$ | 0.021(2) | 0.008(2) | 0.010(1) | U13 | 0.022(2) |

[a] $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

TABLE 3
Selected Bond Distances (Å) and Angles (°) for $Li_2TiSiO_5$

| | | |
|---|---|---|
| Ti–O1 | 1.968(2) 4x | O1–Ti–O1 85.88(1) |
| Ti–O2 | 1.698(2) | O1–Ti–O2 105.55(3) |
| Ti–O2′ | 2.701(3) | O1–Ti–O2′ 74.45(3) |
| O1–O1 | 2.681(2) 4x | |
| O1–O2 | 2.923(2) 4x | |
| O1–O2′ | 2.885(2) 4x | |
| Si–O1 | 1.633(1) 4x | |
| O1–O1′ | 2.653(2) | O1–Si–O1′ 108.64(7) |
| O1–O1″ | 2.673(2) | O1–Si–O1″ 109.89(3) |
| Li–O1 | 2.057(1) 4x | O1–Li–O1 81.34(5) |
| Li–O2 | 2.460(1) 2x | O1–Li–O2 78.82(6) |

and O–Si–O angles of 109.9 and 108.6° (Table 3). The octahedral sites of lithiums are relatively distorted, with two short bonds Li–O = 2.057(1)Å and four longer bonds Li–O = 2.460(1) Å. Titanium sites are the most distorted ones in the lattice: four oxygens are located at 1.968(2)Å, one at 1.698(3)Å, and a sixth at 2.701(3)Å.

## IV. DISCUSSION

The crystal structure of $Li_2TiSiO_5$ has been found to be common to various chemical families: silicates or germanates ($Na_2MOXO_4$ with $X$ = Si, Ge; $M$ = Ti), phosphates ($MOPO_4$ with $M$ = V, Nb, Mo), molybdates ($VOMoO_4$), and sulfates ($VOSO_4$) (2, 4, 9–15). The chemical analogy between all these compounds becomes evident when the former formulae are written in their most general form: $A_2^{\mathrm{I}}M^{\mathrm{IV}}OXO_4$ ($A^{\mathrm{I}}$ = monovalent cation; $M^{\mathrm{IV}}$ = tetravalent cation; $X$ = Si, Ge). The structural data collected in Table 4 allow the following conclusions: (1) the lattice parameter $a_0$, compared to $c_0$, appears to be nearly independent of the stoichiometry with an average value of ca. 6.43 Å. However, its value for $MoOPO_4$ seems to be too small although Mo–O(1) distances are identical to $M'$–O(1) lengths ($M'$ = Nb, V, Ti). The highest value recorded for $Na_2TiOGeO_4$ is probably due to the size of Ge. Larger than Si, the latter is expected to induce larger $XO_4$ tetrahedra and $TiO_6$ octahedra, which results in an expansion of the unit cell parameters. (2) the lattice parameter $c_0$ is closely related to the distorsion of the octahedra $M^{\mathrm{IV}}O_6$ and $M'O_6$ since $c_0 = M^{\mathrm{IV}}\text{–O(2)} + M^{\mathrm{IV}}\text{–O(2')}$ or $c_0 = M'\text{–O(2)} + M'\text{–O(2')}$. It is also sensitive to the size of the cations intercalated between the sheets made of tetrahedra $XO_4$ and square pyramids $M^{\mathrm{IV}}O_5$ (or $M'O_5$) as shown in Fig. 1. The distance between these layers and the cationic planes increases significantly with increasing size of the cations inserted: Ti–O(2) is much higher for $Na_2TiOSiO_4$ than for $Li_2TiOSiO_4$. Nonetheless, Ti–O(2) and M′–O(2) lengths do not vary in the same proportions. This could be attributed to the fact that the oxygens O(2) are also linked to $XO_4$ tetrahedra which cannot expand as much as $M^{\mathrm{IV}}O_6$ and $M'O_6$ octahedra owing to the high covalent $X$–O bond.

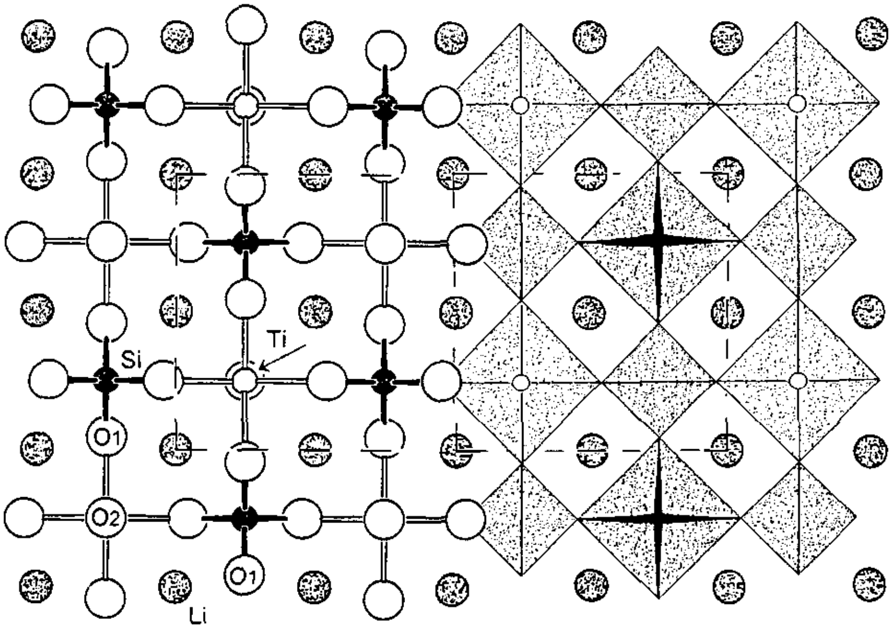

FIG. 2. Structure of $Li_2TiSiO_5$ projected on (001).

TABLE 4

Structural Data of Some Oxometalates $A_2TiOXO_4$ ($A$ = Li, Na; $X$ = Si, Ge) and $MOXO_4$ ($M$ = V, Nb, Mo; $X$ = P, S, Mo)

| | | Lattice parameters | | | Octahedral bond distances and angles[a] | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | Space group | $a_0$(Å) | $c_0$(Å) | $V$(Å$^3$) | $d_1$(Å) | $d_2$(Å) | $d_{2'}$(Å) | $\alpha_1$(°) | $\alpha_2$(°) | X–O(Å)[b] | References |
| $Li_2TiOSiO_4$ | *P4/nmm* | 6.44 | 4.40 | 182.7 | 1.97 | 1.70 | 2.70 | 105.6 | 85.9 | 1.63 | This work |
| $Na_2TiOSiO_4$ | *P4/nmm* | 6.48 | 5.11 | 214.4 | 1.99 | 1.70 | 3.41 | 107.5 | 84.9 | 1.64 | (4) |
| $Na_2TiOGeO_4$ | *P4/nmm* | 6.67 | 5.16 | 229.6 | 2.0 | 1.72 | 3.44 | 109.4 | 84.9 | 1.74 | (2) |
| $NbOPO_4$ | *P4/n* | 6.39 | 4.10 | 167.4 | 1.97 | 1.78 | 2.32 | 98.7 | 88.7 | 1.73 | (10) |
| $VOMoO_4$ | *P4/n* | 6.61 | 4.26 | 186.2 | 1.97 | 1.68 | 2.59 | 102.4 | 87.3 | 1.76 | (11) |
| $MoOPO_4$ | *P4/n* | 6.18 | 4.29 | 163.8 | 1.97 | 1.66 | 2.63 | 103 | 87 | 1.53 | (10, 12) |
| $\alpha$-$VOPO_4$ | *P4/n* | 6.01 | 4.45 | 160.9 | 1.86 | 1.58 | 2.85 | 101.6 | 87.7 | 1.54 | (13) |
| $\alpha$-$VOSO_4$ | *P4/n* | 6.26 | 4.10 | 160.8 | 2.04 | 1.63 | 2.47 | 101 | 88 | 1.46 | (14) |

[a] See Fig. 1 for bond length and angles.

[b] $XO_4$ tetrahedra are almost regular (see corresponding reference).

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