

Crystal Structure of Orthorhombic $\text{LT-Na}_2\text{TiSiO}_5$ and Its Relation to the Tetragonal HT-Form

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$\text{Na}_2\text{TiSiO}_5$ is trimorphous. Single crystals of the low temperature modification have been obtained by a flux method ($\text{V}_2\text{O}_5/\text{MoO}_3$). The crystal structure of $\text{LT-Na}_2\text{TiSiO}_5$ represents a new structure type with a hitherto unknown three-dimensional net of TiO_5 square pyramids and SiO_4 tetrahedra. $\text{LT-Na}_2\text{TiSiO}_5$ crystallizes in the orthorhombic space group $Pmc2_1$ with unit cell parameters $a = 9.1814(3)$ Å, $b = 4.8075(2)$ Å, $c = 9.8604(4)$ Å, $Z = 4$. Chains of *trans*-connected TiO_6 octahedra are linked by corners of SiO_4 tetrahedra. The octahedra are distorted to square pyramids with five short (1×1.70 Å, 4×1.97 Å) and one long (3.11 Å resp. 3.48 Å) Ti–O distances. There are two different chains with parallel and antiparallel orientation of the short Ti–O bonds leading to a polar structure. Single crystals are frequently twinned because of a phase transition at 772°C . A structure model for the tetragonal HT-form is proposed and its relation to the LT-form discussed. Because of special structural features $\text{LT-Na}_2\text{TiSiO}_5$ is interesting as a new nonlinear optical material. © 1996 Academic Press, Inc.

I. INTRODUCTION

The tendency of Ti(IV) to prefer a fivefold coordination (square pyramids) and to build up chains of corner linked distorted octahedra is well known. KTiPO_5 (KTP) and related compounds show very similar crystal chemistry. They are important materials for nonlinear optics (NLO), so we are interested to characterize new compounds for which comparable structural features are expected. Furthermore, we want to understand the effects of the nature and size of the alkali metal, the transition metal, and the main group element on crystal chemistry, thermal stability, and physical properties (ferroelectricity, ionic conductivity) of these phases (1). In the course of our investigations on systems $A_2M\text{SiO}_5$ (A = alkali cation, M = tetravalent cation) recently we reported the crystal

structure of $\text{Li}_2\text{TiSiO}_5$ (2). Now we present the results of our studies on $\text{Na}_2\text{TiSiO}_5$.

Investigations in the system $\text{Na}_2\text{O-TiO}_2\text{-SiO}_2$ are also important for understanding glass and ceramic forming processes. One of the stable quarternary species is sodium titanosilicate $\text{Na}_2\text{TiSiO}_5$. This compound has been reported by Bayer and co-workers (3) and Glasser and Marr (4). They indexed the powder diagram at room temperature on orthorhombic unit cell ($a = 9.66$ Å, $b = 9.86$ Å, $c = 9.10$ Å). They were unable to determine the crystal structure because single crystals were always twinned. Furthermore, they found a phase transition at ca. 772°C and proposed a tetragonal HT-form ($a = 9.90$ Å, $c = 9.02$ Å). The third modification, natisite, can be synthesized under hydrothermal conditions (500°C , 650 bar) and is well characterized (5, 6)

II. EXPERIMENTAL

(a) Growth of Single Crystals

Single crystals were grown from a melt of $\frac{4}{5} \text{Na}_2\text{MoO}_4 + \frac{1}{5} \text{NaVO}_3$ with a ratio solute weight/flux weight = 1:10. The mixture of appropriate amounts of reagent grade starting materials Na_2CO_3 , TiO_2 , SiO_2 , V_2O_5 , and MoO_3 was ground, filled in a Pt crucible, and submitted to the following heat treatment:

- slow heating to 850°C ,
- melting at 850°C for 24 h, and
- slow cooling (5°C/h) to 530°C (solidification of the melt) before quenching to room temperature.

Colorless single crystals of $\text{Na}_2\text{TiSiO}_5$ and quartz as a by-product were extracted by dissolving the flux in distilled water. Tetragonal platelets up to 2 mm were obtained. Large crystals always showed fissures and cracked corners

TABLE 1
Crystal Data and Refinement of LT-Na₂TiSiO₅

Formula weight	201.97
Crystal system	orthorhombic
Space group	<i>Pmc</i> 2 ₁ , No. 26
<i>a</i> (Å)	9.1814(3)
<i>b</i> (Å)	4.8075(2)
<i>c</i> (Å)	9.8604(4)
<i>V</i> (Å ³)	435.23(3)
<i>Z</i>	4
<i>d</i> _{calc.} (g/cm ³)	3.082
Radiation	MoKα
μ (cm ⁻¹)	23.57
Crystal size (mm)	0.01 × 0.08 × 0.08
Temperature (°C)	20
Data coll. range	- <i>h</i> , <i>k</i> , <i>l</i>
θ range (°)	30.44
Scan method	ω/2θ
No. of refl. measured	809
No. of refl. observed	717
No. of refl. used	654 with <i>I</i> > 2σ(<i>I</i>)
No. of variables	90
Absorption corr.	empirical, ψ-scan
Transmission coeff.	0.952 > <i>t</i> > 0.789
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.090P)^2 + 2.370P]$ with $P = (F_o^2 + 2F_c^2)/3$
Δρ _{max.} /Δρ _{min.} (e/Å ³)	+4.71/-1.50
<i>R</i> (<i>F</i>)	0.0525, all: 0.0615
<i>wR</i> (<i>I</i>)	0.135, all: 0.148

which seemed to be caused by internal stress while some small crystals were of regular shape and totally transparent.

(b) X-Ray Crystallography

Preliminary cell constants and space group assignment were from Weissenberg photographs. Large single crystals (see above) were always twinned. The evaluation of these data led to an orthorhombic unit cell (*a* = 9.18 Å, *b* = 9.60 Å, *c* = 9.86 Å) with pseudotetragonal metric (*b* ≈ *c*), as proposed by Bayer *et al.* (3) and Glasser and Marr (4). Investigation of a small untwinned single crystal showed that the true cell is orthorhombic with *a* = 9.18 Å, *b* = 4.81 Å, and *c* = 9.86 Å. The twinning element is a 90° rotation around [100], doubling the *b* axis. The reflection condition *h*0*l*: *l* = 2*n* corresponds to the space groups *Pmcm* (No. 51), *P2cm* (No. 28), or *Pmc*2₁ (No. 26). This small untwinned single crystal (0.01 × 0.08 × 0.08 mm) was used for structure determination. Data collection was carried out with a CAD4 Enraf-Nonius diffractometer. Details of data collection, reduction, and refinement are summarized in Table 1. Unit cell dimensions were received by least square refinement of 25 high angle reflections (18° < θ < 22°). A total of 809 reflections was collected and after empirical absorption correction using Ψ-scan data, a set of 717 unique reflections was obtained. By direct meth-

ods using the program SHELXS 86 (7) a first structure model in the space group *Pmcm* was developed and refined to an *R* value of ca. 0.20. The positions of one Ti and one O atom could not be refined properly, resulting in this high *R* value. After a symmetry reduction to the noncentrosymmetric space group *Pmc*2₁ the correct positions of Ti2 and O2 could be located. The following refinement with anisotropic displacement parameters (program SHELXL92 (8)) led to an *R* value of *R*(*F*) = 0.0525. The structure was tested for the right polarity according to the method described by Flack (9). Table 2 gives positional parameters and Table 3 contains relevant bond distances and angles. Further details of the structure determination (structure factors, anisotropic displacement parameters, further distances, and angles) are available on request from Fachinformationszentrum Karlsruhe 76344 Eggenstein-Leopoldshafen 2 (FRG) on quoting the depository number CSD 380102, the names of the authors, and the journal citation.

III. DESCRIPTION OF THE STRUCTURE

The crystal structure of Na₂TiSiO₅ (Fig. 1) represents a new structure type and can be described as a packing of two kinds of layers parallel (100) which are built up by linear chains of distorted TiO₆ octahedra. The two different chains of TiO₆ octahedra are linked exclusively by corners of SiO₄ tetrahedra to a three-dimensional net. Both types of TiO₆ octahedra are distorted in the same way, 1 + 4 + 1. Five short Ti–O bonds (Ti1–O1, 1.705(7) Å; 2*x* Ti1–O11, 1.951(5) Å; 2*x* Ti1–O12, 1.974(5) Å; Ti2–O2, 1.703(8) Å; 2*x* Ti2–O21, 1.990(5) Å, 2*x* Ti2–O22, 1.964(5) Å) form a nearly regular square pyramid while the sixth distance is much longer (Ti1–O1, 3.110(7) Å; Ti2–O2, 3.481(8) Å). The TiO₆ octahedra are linked to linear chains by sharing opposite corners (Ti1–O1 resp. Ti2–O2) leading to alternating short and long Ti–O distances in this direction and

TABLE 2
Coordinates and Thermal Parameters of LT-Na₂TiSiO₅

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq.}
Ti1	0.5	0.4655(3)	−0.0021(3)	0.0056(4)
O1	0.5	0.8201(13)	−0.0020(10)	0.0113(12)
O11	0.3519(5)	0.3596(10)	0.1334(6)	0.0067(9)
O12	0.3543(5)	0.6452(11)	0.3643(6)	0.0095(10)
Ti2	0.0	0.0259(3)	0.7835(3)	0.0072(4)
O2	0.0	0.8504(156)	0.4454(8)	0.0127(14)
O21	0.1472(5)	0.7498(10)	0.1836(6)	0.0077(9)
O22	0.1491(5)	0.2598(10)	0.3152(6)	0.0088(10)
Si	0.2500(2)	0.5043(4)	0.25	0.0036(4)
Na1	0.5	0.0068(12)	0.2544(6)	0.0146(10)
Na2	0.2510(4)	0.0036(6)	0.0061(4)	0.0093(6)
Na3	0.0	0.4039(9)	0.5040(6)	0.0117(8)

TABLE 3
Selected Distances (in Å) and Angles (in °) of LT- $\text{Na}_2\text{TiSiO}_5$

Ti1-O1	1.705(7)	Ti2-O2	1.703(8)	Si-O11	1.637(5)
-O2	1.951(5) 2×	-O21	1.990(5) 2×	-O12	1.627(6)
-O11	1.974(5) 2×	-O22	1.964(5) 2×	-O21	1.647(6)
···O1	3.110(7)	···O2	3.481(8)	-O22	1.629(5)
O1-Ti1-O11	104.9(3)	O2-Ti2-O21	105.9(3)	O11-Si-O21	109.1(2)
-O12	105.8(3)	-O22	95.4(3)	-O21	110.6(2)
O11-Ti1-O11	85.1(2)	O21-Ti2-O21	85.5(3)	-O22	107.2(3)
-O21	87.1(3)	-O22	89.1(2)	O12-Si-O21	108.3(3)
-O21	149.2(2)	-O22	158.6(3)	-O22	111.2(3)
O12-Ti1-O12	86.6(3)	O22-Ti2-O22	88.2(3)	O21-Si-O22	110.3(3)
Na1-O1	2.541(11)	Na2-O1	2.452(4)	Na3-O2	2.233(8)
-O1	2.682(11)	-O2	2.482(5)	-O2	2.723(9)
-O11	2.480(7) 2×	-O11	2.316(6)	-O21	2.347(7) 2×
-O12	2.446(7) 2×	-O12	2.389(7)	-O22	2.412(7) 2×
		-O21	2.336(7)		
		-O22	2.454(6)		

a pronounced polarity of the chain. O1 and O2 are coordinated only to Ti, while O11, O12, O21, and O22 belong to the SiO_4 tetrahedra, too. The SiO_4 tetrahedra are almost regular with Si-O bond lengths of 1.64(1) Å and O-Si-O angles between $107.2(3)^\circ$ and $111.2(3)^\circ$. Na atoms are six-fold coordinated as less (Na1) or more (Na2, Na3) distorted octahedra with Na-O distances between 2.223(8) and 2.723(9) Å.

Although the two chains look very similar there are important differences with respect to their orientation

(Fig. 2b). The layer with Ti1 consists of exactly linear chains with antiparallel orientation running parallel [010]. In the second layer the slightly corrugated chains are all parallel [007]. In contrast to the chains of Ti1, the square pyramids of Ti2 are rotated in the opposite sense by about 20° around [100]. Within one chain the orientation is constant. Because of this rotation the bond Ti2-O2 is not perpendicular to the basal plane of the pyramid (O2-Ti2-O21 , $105.9(3)^\circ$; O2-Ti2-O22 , $95.4(3)^\circ$) and the shortest Na-O distance of 2.223(8) Å is observed between Na3 and O2.

IV. DISCUSSION

(a) The HT-Structure of $\text{Na}_2\text{TiSiO}_5$ as an Explanation of the Phase Transition and Twinning

Bayer *et al.* (3) and Glasser and Marr (4) described a phase transition of $\text{Na}_2\text{TiSiO}_5$ at 772°C with a small hysteresis. It was impossible to quench the HT-form. Single crystals of the LT-form were always twinned. Furthermore, Bayer *et al.* observed quite complex behavior of deglassing below the transition point. The powder diagram at 850°C was indexed with a tetragonal unit cell ($a = 9.90$ Å, $c = 9.02$ Å) and showed great similarities to the LT-form, so they suggested a close structural relation between the two modifications and a displacive phase transition. On the basis of the known orthorhombic LT-structure it is possible to develop a structure model for the HT-modification. As indicated by the twinning the phase transition leads to a differentiation between the two chains which must be equivalent by symmetry in the tetragonal HT-form. Assuming a rotation of the SiO_4 tetrahedra that leaves the strong Si-O and Ti-O bonds unchanged, we can develop

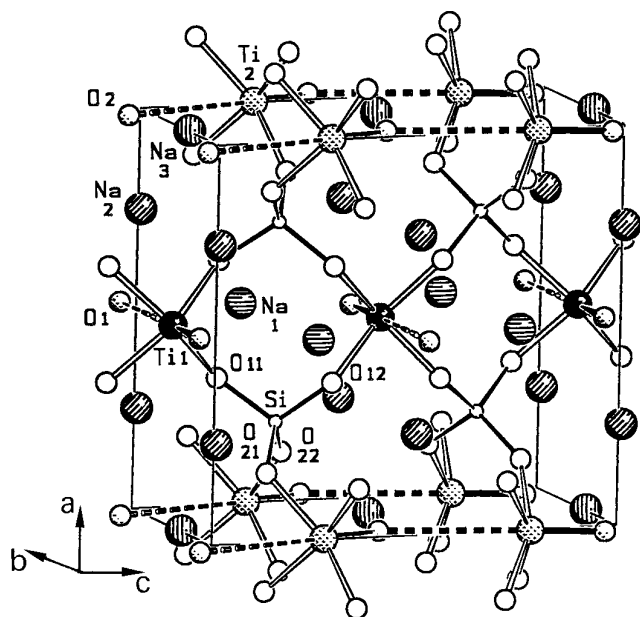


FIG. 1. Crystal structure of orthorhombic LT- $\text{Na}_2\text{TiSiO}_5$.

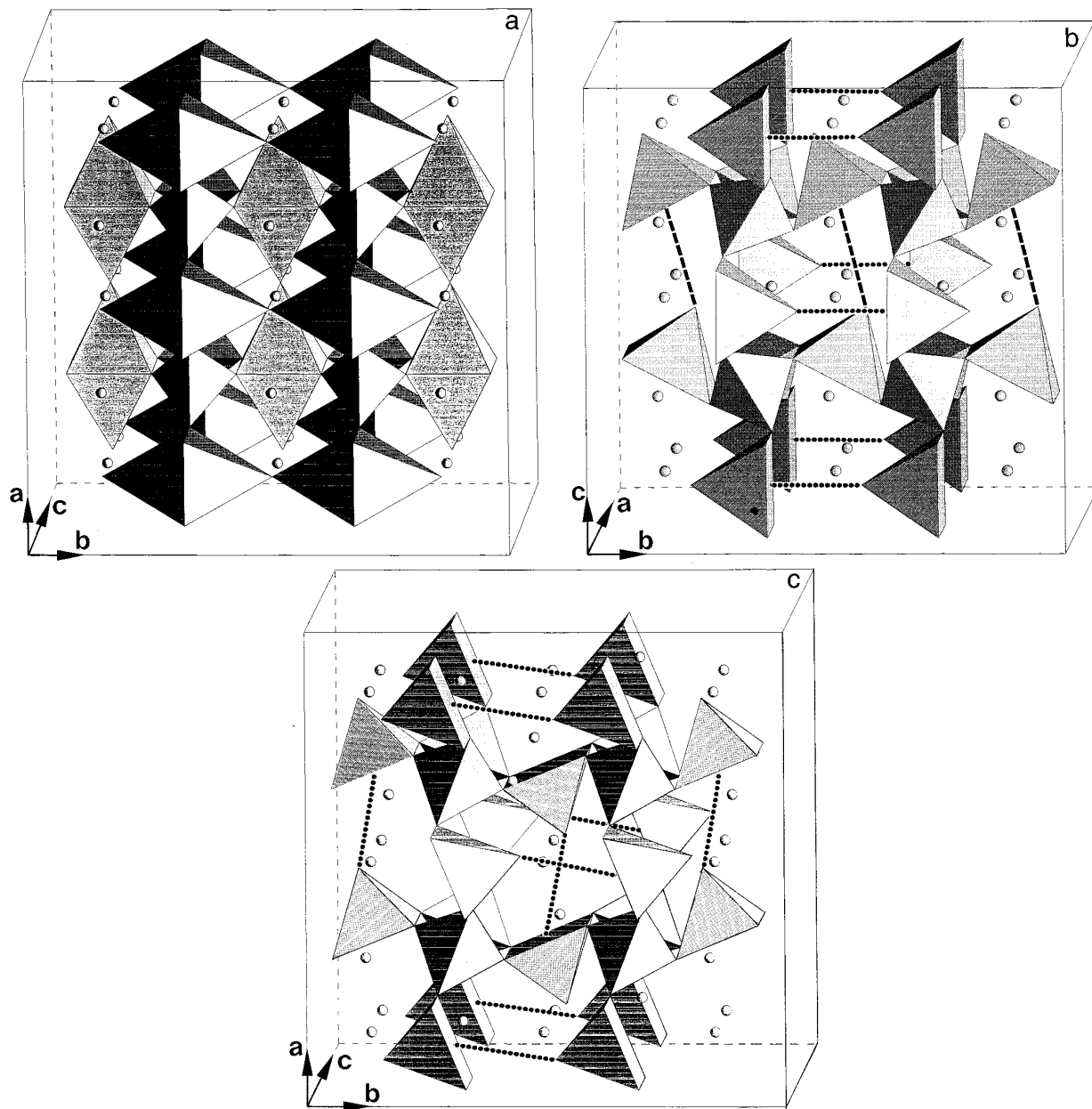


FIG. 2. Structure models for $\text{Na}_2\text{TiSiO}_5$, (a) idealized tetragonal structure ($P4_2/mmc$); (b) orthorhombic LT-form ($Pmc2_1$); (c) proposed model for the tetragonal HT-form ($P4_2/m$).

an idealized tetragonal structure in space group $P4_2/mmc$ ($a = 4.95 \text{ \AA}$, $c = 9.02 \text{ \AA}$) for which coordinates are listed in Table 4. Figure 2a shows a projection on the a - b plane. Theoretical powder data calculated with these parameters agree with the data published by Bayer *et al.* (Table 6). Reflections that demand doubling of a_0 have low intensity ($<10\%$) and can be explained as a consequence of small deviations from the idealized model (see below). If the mirror plane $m \perp a$ is retained very short distances Ti-O and Si-O result. Furthermore, Ti is coordinated 4 + 2,

so an equalizing of the distances by rotation of the SiO_4 tetrahedra or/and shifting the Ti atoms is quite probable. For the development of a real HT-model we made following assumptions:

- The principal structure elements (coordination polyhedra, connection of polyhedra) are closely related to the idealized tetragonal structure.
- Dimension and symmetry of the tetragonal unit cell demand that only one kind of Ti-O chains occurs.

TABLE 4

Coordinates of the Idealized Tetragonal HT-Form of $\text{Na}_2\text{TiSiO}_5$ with $a = 4.95 \text{ \AA}$, $c = 9.02 \text{ \AA}$, Space Group $P4_2/mmc$

Atom	Site	Symmetry	x	y	z
Ti	2d	mmm	0.5	0.0	0.0
Si	2f	$-4m2$	0.5	0.5	0.25
Na1	2c	mmm	0.5	0.0	0.5
Na2	2e	$-4m2$	0.0	0.0	0.25
O1	2a	mmm	0.0	0.0	0.5
O2	8p	$.m$	0.5	0.75	0.1475

—Ti is fivefold coordinated (tetragonal pyramids TiO_5) because octahedral coordination requires Ti–O distances of about 2.0 \AA (i.e., BaTiO_3) leading to $a \approx 8 \text{ \AA}$ ($4 \times \text{Ti–O}$).

For a first model we assumed the shift of Ti and O2 within the chain in opposite direction leading to the formation of square pyramids TiO_5 . This model can be described in the space group $P4_2/mbc$ with doubled a_0 . The comparison with the published powder diagram shows that the reflection conditions of $P4_2/mbc$ are not fulfilled.

A second model is obtained when all the SiO_4 tetrahedra are rotated in the same sense and O1 is shifted to one titanium atom to build a square pyramid. This model has the space group $P4_2/m$. The positions of the atoms listed in Table 5 can be derived if similar Ti–O and Si–O bond

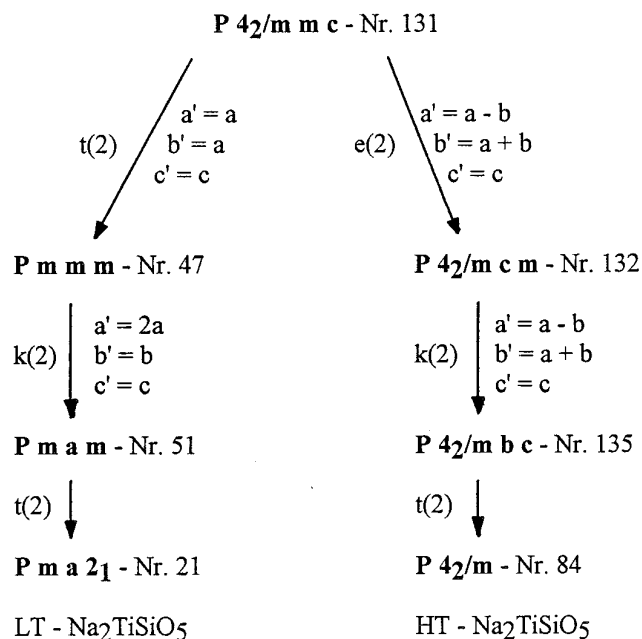


FIG. 3. Group-subgroup relations between LT-form of $\text{Na}_2\text{TiSiO}_5$ ($Pma2_1$), idealized tetragonal structure ($P4_2/mmc$), and proposed model for the HT-form ($P4_2/m$).

lengths are assumed as were observed for the orthorhombic polymorph. The positions of the Na atoms are more uncertain because they may be disordered in the HT-form. The theoretical powder diagram is in good agreement with the experimental data (Table 6). The group-subgroup relations between the proposed tetragonal HT-forms and the orthorhombic LT-polymorph are shown in Fig. 3. The main differences between the various structures are the patterns of rotations and the way Ti and O are shifted.

If only tetrahedra are rotated in the same direction a structure with space group $P4_2/m$ without enlarged unit cell results, similar to the relation between the natisite structure ($P4/nmm$) and the MoOPO_4 type ($P4/n$) (10). An orthorhombic structure with two different chains results, when the rotation of tetrahedra is the same in one direction (this will give the short b axis) and opposite in the other direction (leading to the doubling, see Fig. 2). Exchanging these two directions gives the relation between the twins and represents the twinning element.

(b) Comparison to Tetragonal Natisite $\text{Na}_2\text{TiSiO}_5$

Distances and angles are nearly the same in natisite as in LT- $\text{Na}_2\text{TiSiO}_5$. Only the angles between the short and the four longer Ti–O bonds are a little less in orthorhombic $\text{Na}_2\text{TiSiO}_5$, so differences occur in the way the polyhedra are joined into a three-dimensional net. The slightly lower density of the orthorhombic form (3.082 g/cm^3 compared to 3.12 g/cm^3) is caused by longer Na–O distances and might explain why natisite is formed under hydrothermal conditions at high pressure. Glasser and Marr reported (4) that a conversion of orthorhombic $\text{Na}_2\text{TiSiO}_5$ to natisite is possible under hydrothermal conditions (500°C , 650 bar) and reheating yields again orthorhombic $\text{Na}_2\text{TiSiO}_5$. Un-

TABLE 5

Coordinates of the Proposed HT Structure of $\text{Na}_2\text{TiSiO}_5$ ($a = 9.90 \text{ \AA}$, $c = 9.02 \text{ \AA}$, Space Group $P4_2/m$, See Text)

Atom	Site	Symmetry	x	y	z
Ti1	4j	m	0.24	0.03	0.0
Ti2	4j	m	0.24	0.53	0.0
Si1	2e	-4	0.0	0.0	0.25
Si2	2f	-4	0.5	0.5	0.25
Si3	4i	2	0.0	0.5	0.25
O1	4j	m	0.225	0.20	0.0
O2	4j	m	0.225	0.70	0.0
O3	8k	1	0.13	0.95	0.1475
O4	8k	1	0.37	0.05	0.1475
O5	8k	1	0.13	0.45	0.1475
O6	8k	1	0.37	0.55	0.1475
Na1	4j	m	0.75	0.0	0.5
Na2	4j	m	0.25	0.5	0.5
Na3	8k	1	0.25	0.25	0.25

TABLE 6
X-Ray Powder Data of the HT-form of Na₂TiSiO₅

Observed data			Idealized HT-structure			Proposed HT-structure		
d_{obs} in (Å)	I_{obs} in (%)	hkl	$d_{\text{calc.}}$ in (Å)	$I_{\text{calc.}}$ in (%)	hkl	$d_{\text{calc.}}$ in (Å)	$I_{\text{calc.}}$ in (%)	hkl
4.912	14	200	4.950	11	100	4.950	6	200
—	—	—	—	—	—	4.427	5	210
4.320	46	201	4.340	57	101	4.340	47	201
3.950	2	211	—	—	—	3.975	8	211
3.331	10	202	3.334	15	102	3.334	11	202
—	—	—	—	—	—	3.263	3	221
3.157	4	212	—	—	—	3.160	5	212
2.939	2	311	—	—	—	2.958	1	311
2.762	100	222	2.765	100	112	2.765	100	222
2.627	8	321	—	—	—	2.627	2	321
2.480	25	213/400	2.475	61	200	2.475	30	400
2.343	2	322	2.387	7	201	2.345	2	322
2.311	4	223	—	—	—	2.281	8	223
2.255	6	004	2.255	9	004	2.255	9	004
—	—	—	—	—	—	2.214	5	420
2.169	3	402	2.170	5	202	2.170	2	402
2.033	3	323	2.052	4	104	2.028	3	204/323
1.976	2	422	—	—	—	1.980	2	422/430
1.910	4	224	1.911	8	203	1.911	4	403
1.786	6	423	1.783	11	123	1.783	5	423
1.750	9	440	1.750	7	220	1.750	8	440
1.671	12	404	1.667	31	204	1.667	28	404
—	—	—	1.632	3	222	—	—	—
—	—	—	—	—	—	1.580	3	424
1.48	20	533	1.479	25	132	1.480	22	622

Note. Observed data are published by Bayer *et al.* ($a = 9.90$ Å, $c = 9.02$ Å) (3), calculated data are from the idealized tetragonal structure ($P4_2/mmc$, $a = 4.95$ Å, $c = 9.02$ Å) resp. the proposed model for the HT-structure ($P4_2/m$, $a = 9.90$ Å, $c = 9.02$ Å; see text). All values $I_{\text{calc.}} > 3\%$ are listed.

der normal conditions natisite is a metastable modification of Na₂TiSiO₅.

The long distance within the TiO₆ octahedra is obviously determined by the size of the alkali cation, because the values are nearly the same for both forms of Na₂TiSiO₅ (3.41 Å resp. 3.11 Å/3.48 Å) but much smaller in Li₂TiSiO₅ (2.70 Å) (2) or NbPO₅ (2.32 Å) (11). This indicates that the structure should better be described as a three-dimensional net of TiO₅ square pyramids and SiO₄ tetrahedra and the definition of chains or rods is more suitable for a topological characterization of the network.

(c) Description as Rod Packing

If the TiO₆ chains are seen as cylinders, the three modifications of Na₂TiSiO₅ can be described in terms of the rod packing concept introduced by O'Keeffe and Anderson (12). Natisite represents a tetragonal packing of rods. Each rod is surrounded by four other rods with antiparallel polarity if the distortion of the TiO₆ octahedra is regarded. The idealized structure of the HT-form is a simple tetrago-

nal layer packing, while the HT-structures in $P4_2/mbc$ and $P4_2/m$ can be classified as tetragonal layer packings with antiparallel polarity of the chains. The orthorhombic LT-form corresponds to a variant of the tetragonal layer packing with alternating layers of rods with parallel (Ti2 layers) and antiparallel polarity (Ti1 layers).

(d) Comparison of Other Compounds $A_2MM'O_5$ and Structures with MO_5 Square Pyramids and $M'O_4$ Tetrahedra

Na₂TiSiO₅ is a member of a large class of compounds. If the substitution of the tetravalent cations by five- and/or sixvalent is included, one can define a structural family of compositions $A_nMOM'O_4$ ($A = \text{Li, Na, K, Ca}$; $M = \text{Ti, Zr, V, Nb, Mo}$; $M' = \text{Si, P, As, S, Mo}$; $n = 0, 1, 2$) with (distorted) octahedral coordination of M and $M'O_4$ tetrahedra. These structures are usually characterized by a distortion of the octahedra to a less or more pronounced MO_5 square pyramid while the $M'O_4$ tetrahedra remain nearly unchanged. The differences between the structure

types result from the way octahedra and tetrahedra are connected. The structure of $\text{Na}_2\text{TiSiO}_5$ represents a new type of three-dimensional net composed of MO_6 octahedra and $M'O_4$ tetrahedra.

Until now only a few compounds of the composition $A_2M(\text{IV})\text{SiO}_5$ were known. Most of them adopt the tetragonal natisite structure ($\text{Na}_2\text{TiSiO}_5$ (5), $\text{Na}_2\text{TiGeO}_5$ (13), $\text{Li}_2\text{TiSiO}_5$ (2)). An exception is $\text{Na}_2\text{ZrSiO}_5$ (14) where two chains are built up by nearly undistorted *cis*-connected ZrO_6 octahedra.

Substitution of M by a pentavalent cation or of A by an earth alkali cation leads to the composition $AMM'O_5$. In the mineral titanite CaTiSiO_5 (15) slightly distorted TiO_6 octahedra are *trans*-connected. They build up two antiparallel chains which are coupled by inversion. The linkage between the chains is managed by two corners of the SiO_4 tetrahedra while one vertex is within the chain. The structure of $\alpha\text{-NaTiPO}_5$ (16) is very similar to titanite. In KTiPO_5 (KTP) (17) there is only one kind of chain containing *cis*- and *trans*-connected TiO_6 octahedra. These helical chains are linked by PO_4 tetrahedra. KTP, as well as a great number of related compounds, are excellent materials for nonlinear optics. They crystallize in the non-centrosymmetric space group $Pna2_1$. Many compounds show phase transitions ferroelectric \rightarrow paraelectric (space group $Pnan$) (18, 19).

Most of the compounds $MM'O_5$ belong to two structure types which can be regarded as defect variants of the structures described above. MoPO_5 ($P4/n$) (10) and some other species like NbPO_5 (11), VMoO_5 (20), $\alpha\text{-VPO}_5$ (21), and $\alpha\text{-VSO}_5$ (22) are related to natisite ($P4/nmm$). The other compounds ($\beta\text{-VSO}_5$ (10), $\beta\text{-NbPO}_5$ (23), TiSO_5 (24)) are similar to titanite.

(e) $\text{Na}_2\text{TiSiO}_5$ as a Possible NLO Material

As outlined in the structure description there are two different kinds of chains in $\text{Na}_2\text{TiSiO}_5$. Because of the pronounced distortion of the TiO_6 octahedra to square pyramids both chains are polar, but only $\text{Ti}2$ contributes to the macroscopic polarity. Unequal *trans*-metal–oxygen bond lengths are essential for good NLO properties (25). For $\text{Na}_2\text{TiSiO}_5$ the difference between the two distances $\text{Ti}2\text{--O}2$ is 1.78 Å, much more than in KTP and related materials (ca. 0.50 Å) (18). The deviations from centrosymmetry are also of interest. If the structure of the idealized tetragonal HT-form is taken as a reference for the deviation from a nonpolar arrangement remarkable shifts can be calculated ($\text{Ti}1$, 0.19 Å; $\text{Ti}2$, 0.34 Å; $\text{O}1$, 0.90 Å; $\text{O}2$, 0.95 Å; $\text{O}11$, $\text{O}12$, $\text{O}21$, and $\text{O}22$, 0.90 Å). The polarity of $\text{Na}_2\text{TiSiO}_5$ can also be referred to the structure in the centrosymmetric space group $Pmcm$ as it was received in the course of the refinement (see Experimental). Here the

differences amount to 0.33 Å for $\text{Ti}2$ and 0.90 Å for $\text{O}2$. These values are considerably greater than for the KTP family.

Another important aspect for possible applications as NLO material is that a phase transition occurs at 772°C. The nonlinear properties should be stable up to this temperature. Therefore, $\text{Na}_2\text{TiSiO}_5$ is a promising candidate for nonlinear optics and the corresponding measurements are in preparation.

In order to get a first overview we have done a SHG test (although the structure of $\text{LT-Na}_2\text{TiSiO}_5$ is surely noncentrosymmetric). The SHG test was positive up to ca. 800°C but above this temperature the signal vanished.

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