

NaTi₂(PS₄)₃: A New Thiophosphate with an Interlocked Structure

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The crystal structure of NaTi₂P₃S₁₂ was determined from single-crystal X-ray diffraction data. This compound was obtained as dark needles by heating the elements in stoichiometric amounts in an evacuated silica tube at 600°C. It crystallizes in the hexagonal symmetry, space group *P6cc* (no. 184), *a* = 19.906(4) Å and *c* = 11.552(2) Å, *V* = 3965(4) Å³, *Z* = 8. Reliability factors are *R* = 0.0665 and *R_w* = 0.0512 for 1234 reflections and 122 variables. The structure of NaTi₂(PS₄)₃ is built up from TiS₆ octahedra and PS₄ tetrahedra linked to each other only by edges. One TiS₆ group is bonded to three PS₄ units and one PS₄ unit to two TiS₆ groups. It exhibits very wide tunnels along the *c* axis. © 1996 Academic Press, Inc.

INTRODUCTION

Super ionic conductors exhibit generally specific crystal structures in that there are layers or open tunnels (2D or 3D structure) through which the mobile ions move.

Nasicon-type compounds AM₂(PO₄)₃ are such materials (1, 2) with a 3D skeleton built up of corner-sharing MO₆ octahedra and PO₄ tetrahedra. Besides, many compounds in the *M*-S or *M*-P-S family with a 2D or 3D structure were reported in the literature (3). These compounds present good qualities as intercalation or insertion materials.

In order to obtain new materials with ionic properties, we have synthesized new phosphosulfide compounds, chemically homologous to Nasicon phosphates like NaTi₂(PS₄)₃.

EXPERIMENTAL AND RESULTS

Synthesis

Sodium and mixed powders of titanium, red phosphorus, and sulfur in stoichiometric amounts were put in a dry evacuated sealed silica tube. After a slow heating to 600°C (2°C · hr⁻¹), 3 days at 600°C, and a slow cooling (5°C ·

hr⁻¹), we obtained small dark entangled needles with metallic lustre. These air sensitive single crystals were kept and handled in a dry glove box.

X-Ray Data

A needle crystal with a hexagonal section was selected; due to its air instability, it was necessary to put it in a sealed-off Lindemann glass capillary. The Laue pattern showed a hexagonal symmetry and systematic absences (*0kl*, *h0l*, and *hhl*: *l* = 2*n*) on precession and Weissenberg films indicated the space groups *P6cc* (no. 184) and *P6/mcc* (no. 192). The measured cell parameters were confirmed later by diffractometer techniques with a least-square refinement of 24 reflections with 2θ ranging from 28° to 30°: *a* = 19.906(4) Å, *c* = 11.552(2) Å, *V* = 3965(4) Å³. Based on statistical analysis of intensity distribution, the structure was solved and refined in the acentric space group *P6cc*. Single crystal data were collected from a four-circle Enraf-Nonius CAD 4 diffractometer. The analytical and crystallographic data of the study are gathered in Table 1. After the Lorentz and polarization effects correction, an absorption correction was made by an analytical method. The crystal is here described as a hexagonal needle with identical opposite sides. The structure was determined by direct methods with the SHELXS86 program (4).

Refinement of the Structure

The refinement with isotropic atomic displacement parameter (ADP) for Na atoms and anisotropic ADP for Ti, P, and S atoms led to *R* and *R_w* factors of 0.0665 and 0.0512, respectively, for 122 variables. All the Na atoms are described with a partial occupancy factor and can be divided into two groups. Two sets of position parameters (Na(1) and Na(2)) are used to describe the electronic density in small cages. Four sets of position parameters (Na(3) to Na(6)) take into account the electronic density in the

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TABLE 1
Crystal Data, Intensity Measurement, and Structure Refinement Parameters

Crystal data	
Formula, molecular weight	NaTi ₂ (PS ₄) ₃ , 596.48 g · mol ⁻¹
Crystal sizes	0.08 × 0.18 × 0.80 mm ³
Crystal system, space group	Hexagonal, <i>P6cc</i> (no. 184)
Cell parameters	<i>a</i> = 19.906(4) Å, <i>c</i> = 11.552(2) Å <i>V</i> = 3965(4) Å ³ , <i>Z</i> = 8
<i>D</i> _{calc.} (g · cm ⁻³)	1.998
<i>μ</i> (MoKα)	22.54 cm ⁻¹
Data collection	
MoKα radiation (graphite monochromated)	<i>λ</i> = 0.71069 Å
Scan mode	<i>ω</i> - 2 <i>θ</i>
Scan rate	1.7° to 20.1° · min ⁻¹
Recording angular range (2 <i>θ</i>), scan width	2°-50°, 0.8 + 0.345 tan <i>θ</i>
Standard reflections	2 measured every 3600 sec
Number of data	1234
Number of reflections used for refinement	1234
Structure solution and refinements	
Extreme values of transmission factor	0.557 and 1.065
Refined parameters	122
Reliability factors	<i>R</i> = 0.0665 <i>R</i> _w = 0.0512 (<i>w</i> = 1/ <i>σ</i>)
Extreme values of difference Fourier map	-0.45 and 0.43 e · Å ⁻³

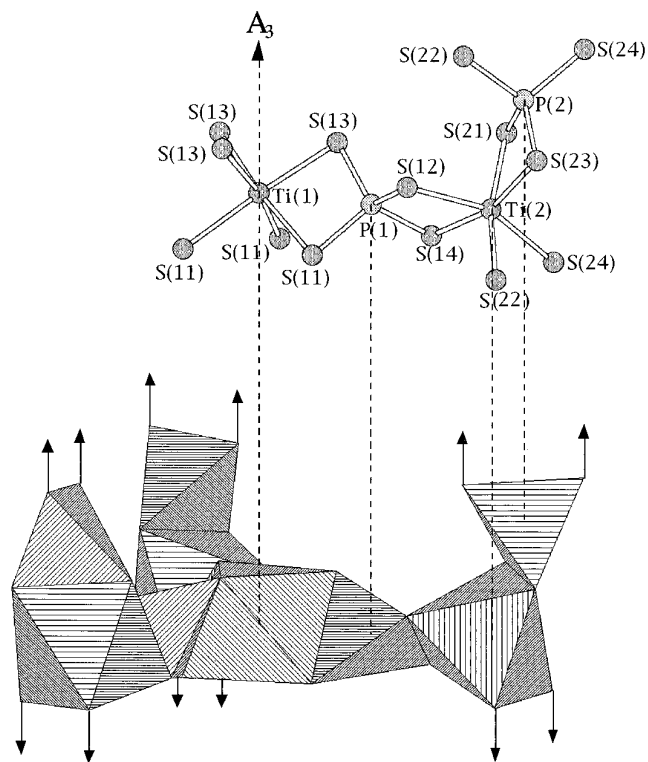

FIG. 1. Ti₄P₆S₃₀ structural unit. Arrows indicate the bond directions with neighboring units.

TABLE 2
Atomic Coordinates and Thermal Parameters

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²) ^a	<i>β</i> ₁₁ ^b	<i>β</i> ₂₂	<i>β</i> ₃₃	<i>β</i> ₁₂	<i>β</i> ₁₃	<i>β</i> ₂₃
Ti(1)	1/3	2/3	0	2.8(1)	26(1)	= <i>β</i> ₁₁	39(3)	= <i>β</i> ₁₁ /2	0	0
Ti(2)	0.6993(2)	0.0453(1)	0.0094(5)	2.91(7)	35(1)	26(1)	25(2)	14(1)	4(2)	2(2)
P(1)	0.6704(2)	0.1835(2)	0.0098(6)	2.82(9)	30(2)	24(2)	36(3)	13(2)	-30(2)	1(2)
P(2)	0.7094(2)	0.0112(3)	-0.2438(5)	3.14(9)	34(2)	27(2)	28(2)	12(2)	1(2)	-3(2)
S(11)	0.6185(3)	0.2201(2)	0.1237(5)	3.47(8)	40(2)	29(2)	43(3)	18(2)	12(2)	4(2)
S(12)	0.5977(3)	0.0752(2)	-0.0502(6)	3.85(5)	35(2)	24(2)	73(4)	12(2)	-18(3)	-10(2)
S(13)	0.7100(2)	0.2634(2)	-0.1203(5)	3.36(8)	39(2)	33(2)	35(3)	20(2)	9(2)	7(2)
S(14)	0.7560(2)	0.1727(2)	0.0898(5)	3.26(8)	33(2)	28(2)	41(3)	14(2)	-10(2)	-5(2)
S(21)	0.7892(2)	0.1004(2)	-0.1501(5)	4.34(9)	35(2)	35(2)	36(3)	0(2)	2(2)	-3(2)
S(22)	0.6051(3)	-0.0423(2)	0.1514(5)	3.97(8)	38(2)	37(2)	28(3)	9(2)	4(2)	6(2)
S(23)	0.6400(3)	-0.0659(2)	-0.1213(5)	3.40(8)	44(2)	21(2)	36(3)	12(2)	8(2)	0(2)
S(24)	0.7877(3)	0.0336(3)	0.1395(6)	4.15(7)	43(2)	55(3)	33(3)	31(2)	10(2)	10(3)
Na(1)	0.550(2)	0.060(2)	0.244(3)	5.1(7)	×0.25(2)	} Na occupancy factors				
Na(2)	0.513(5)	0.021(3)	0.205(4)	7(2)	×0.13(2)					
Na(3)	0.083(4)	0.019(5)	-0.084(6)	6(2)	×0.10(2)					
Na(4)	0.088(4)	0.038(6)	0.314(6)	6(2)	×0.09(2)					
Na(5)	0	0	0.410(9)	5(2)	×0.23(3)					
Na(6)	0	0	-0.043(5)	5(2)	×0.35(3)					

^a *B*_{eq} = 4/3 (Σ_{*i*}β_{*ij*}*a_ia_j*).

^b × 10³. The form of the anisotropic thermal parameter is exp[(β₁₁*h*² + β₂₂*k*² + β₃₃*l*² + 2β₁₂*hk* + 2β₁₃*hl* + 2β₂₃*kl*].

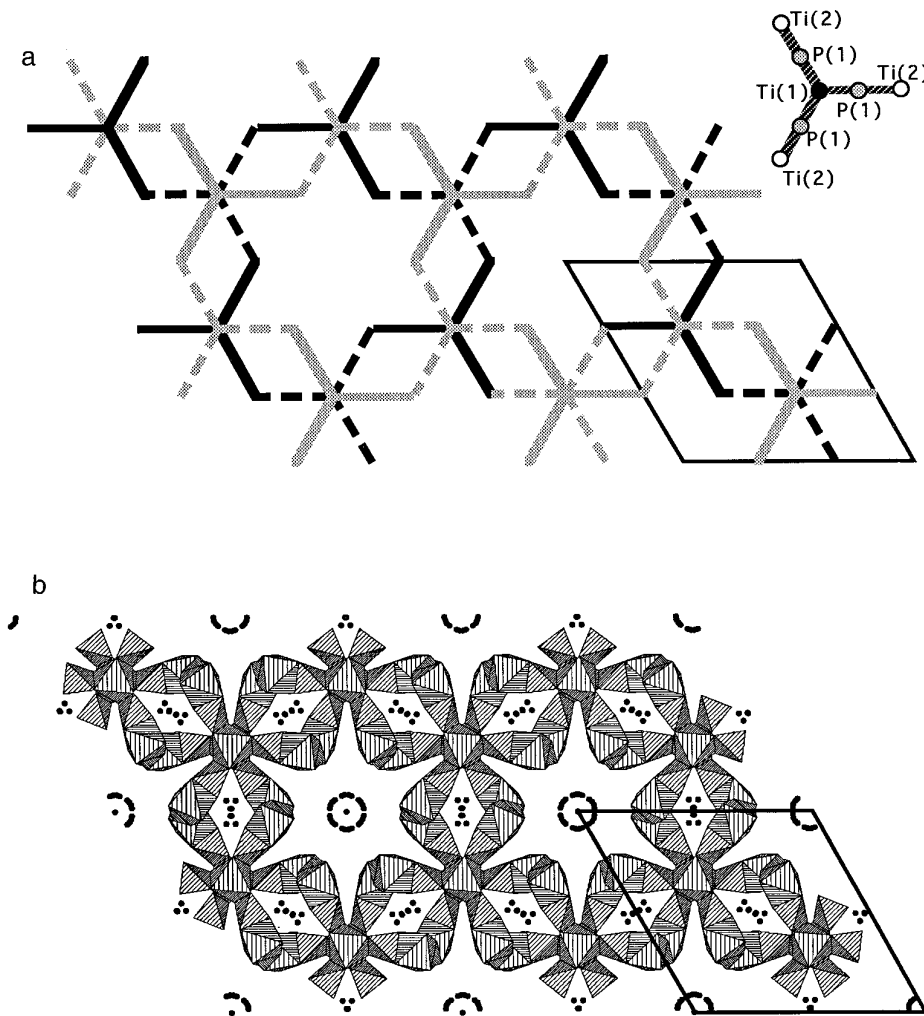


FIG. 2. (a) The two imbricated skeletons (black and gray) projected on (001). Dashed lines for $z = 0$ and full lines for $z = \pm 1/2$. (b) Projection of the structure on (001). Na atoms are black dots (Same scale as Fig. 2a).

infinite tunnels along the c axis. The atomic coordinates and ADPs are gathered in Table 2.

DESCRIPTION OF THE STRUCTURE

The crystal structure of $\text{NaTi}_2(\text{PS}_4)_3$ is a new type of $M_2(\text{PX}_4)_3$ framework built up from MX_6 (TiS_6) octahedra sharing all their edges with PX_4 (PS_4) tetrahedra and vice versa. This arrangement is fully different from the known compounds in the Ti–P–S family (5, 6). The connections in $\text{NaTi}_2(\text{PS}_4)_3$ expand around a $\text{Ti}(1)\text{S}_6$ octahedron; this one, located on a threefold axis, is linked by three $\text{P}(1)\text{S}_4$ tetrahedra to three $[\text{Ti}(2)\text{S}_6\text{-P}(2)\text{S}_4]$ groups in order to constitute a $\text{Ti}_4\text{P}_6\text{S}_{30}$ unit (Fig. 1). One structural unit (centered on $\text{Ti}(1)$ at $z = 0$) is linked to six other analogous units (three centered on $\text{Ti}(1)$ at $z = -1/2$ and three centered on

$\text{Ti}(1)$ at $z = 1/2$), making up a 3D skeleton. By c -glide plane symmetry, this skeleton generates another imbricated and equivalent one without a direct bond between them (Fig. 2a). Cohesion between the two interlocked networks is assumed only by Na atoms, principally $\text{Na}(1)$ and $\text{Na}(2)$ with shorter Na–S bonds (Table 3); this fact can explain the high value of ADPs.

$\text{NaTi}_2(\text{PS}_4)_3$ can be also described as a layer compound with $\text{Ti}_4\text{P}_6\text{S}_{30}$ planes, parallel to (001), bonded by all the $\text{P}(2)$ atoms in tetrahedral sites. The main feature of this new structural type is the presence of very wide tunnels along the c axis and of cages which contain the Na^+ cations (Fig. 2b and Fig. 3). The electronic density corresponding to an occupation of structural cavities by Na atoms has been optimized by an atomic distribution on different positions with an isotropic ADP model. $\text{Na}(1)$ and $\text{Na}(2)$ atoms partially occupy cages with strong Na–S bonds (Table 3);

TABLE 3
Main Angles(°), Distances (Å) in [PS₄] and [TiS₆] Units and Na–S Distances (Å)

		TiS ₆ octahedra	
Distances	Ti(1)–S(13) 2.411(5) × 3	Ti(2)–S(12) 2.476(5)	⟨Ti–S⟩ = 2.424 Å
	Ti(1)–S(11) 2.426(5) × 3	Ti(2)–S(21) 2.416(5)	
Angles	S(11)–Ti(1)–S(11) 88.8(2) × 3	Ti(2)–S(23) 2.440(5)	
	S(13)–Ti(1)–S(13) 90.1(2) × 3	Ti(2)–S(14) 2.390(5)	
	S(13)–Ti(1)–S(11) 83.8(2) × 3	Ti(2)–S(22) 2.446(5)	
	S(13)–Ti(1)–S(11) 98.2(2) × 3	Ti(2)–S(24) 2.412(5)	
	S(13)–Ti(1)–S(11) 169.7(2) × 3	S(23)–Ti(2)–S(12) 87.9(2)	
		S(22)–Ti(2)–S(12) 86.0(2)	
		S(14)–Ti(2)–S(24) 83.1(2)	
		S(14)–Ti(2)–S(21) 88.0(2)	
		S(14)–Ti(2)–S(23) 163.9(2)	
		S(14)–Ti(2)–S(22) 106.4(2)	
	S(14)–Ti(2)–S(12) 82.0(2)		
	S(24)–Ti(2)–S(21) 96.2(2)		
	S(24)–Ti(2)–S(23) 110.1(2)		
	S(24)–Ti(2)–S(22) 81.3(2)		
	S(24)–Ti(2)–S(12) 156.9(2)		
	S(21)–Ti(2)–S(23) 81.6(2)		
	S(21)–Ti(2)–S(22) 164.9(2)		
	S(21)–Ti(2)–S(12) 100.8(2)		
	S(23)–Ti(2)–S(22) 85.3(2)		
		PS ₄ tetrahedra	
Distances	P(1)–S(11) 2.021(6)	P(2)–S(21) 2.006(6)	⟨P–S⟩ = 2.032 Å
	P(1)–S(12) 2.026(6)	P(2)–S(22) 2.035(6)	
	P(1)–S(13) 2.039(6)	P(2)–S(23) 2.036(6)	
	P(1)–S(14) 2.042(6)	P(2)–S(24) 2.049(6)	
Angles	S(11)–P(1)–S(12) 112.6(3)	S(21)–P(2)–S(22) 112.5846(3)	
	S(11)–P(1)–S(13) 105.4576(2)	S(21)–P(2)–S(23) 103.3179(2)	
	S(11)–P(1)–S(14) 110.3143(3)	S(21)–P(2)–S(24) 114.5850(3)	
	S(12)–P(1)–S(13) 111.6942(3)	S(22)–P(2)–S(23) 110.8714(3)	
	S(12)–P(1)–S(14) 103.4987(2)	S(22)–P(2)–S(24) 101.6966(2)	
	S(13)–P(1)–S(14) 113.4635(2)	S(23)–P(2)–S(24) 114.1151(3)	
		Na–S distances (≤5Å)	
	Na(1)–S(12) 2.88(4)	Na(2)–S(22) 2.7(1)	
	Na(1)–S(22) 2.95(3)	Na(2)–S(22) 2.8(1)	
	Na(1)–S(11) 3.11(4)	Na(2)–S(12) 3.23(6)	
	Na(1)–S(22) 3.12(4)	Na(2)–S(12) 3.29(6)	
	Na(1)–S(12) 3.41(4)	Na(2)–S(12) 3.47(6)	
	Na(1)–S(23) 3.42(4)	Na(2)–S(11) 3.56(5)	
	Na(1)–S(12) 3.56(4)	Na(2)–S(12) 3.61(6)	
	Na(1)–S(14) 3.98(4)	Na(2)–S(23) 4.01(8)	
	Na(1)–S(13) 4.32(4)	Na(2)–S(11) 4.27(6)	
	Na(1)–S(12) 4.42(4)	Na(2)–S(23) 4.31(8)	
	Na(1)–S(13) 4.45(4)	Na(2)–S(14) 4.43(8)	
	Na(1)–S(23) 4.68(4)	Na(2)–S(13) 4.92(6)	
		Na(2)–S(14) 4.97(8)	
	Na(3)–S(24) 4.13(8)		
	Na(3)–S(21) 4.29(8)	Na(4)–S(24) 3.88(8)	
	Na(3)–S(21) 4.33(8)	Na(4)–S(24) 3.97(9)	
	Na(3)–S(24) 4.41(8)	Na(4)–S(21) 3.99(7)	
	Na(3)–S(24) 4.46(7)	Na(4)–S(21) 4.7(1)	
		Na(4)–S(24) 4.93(7)	

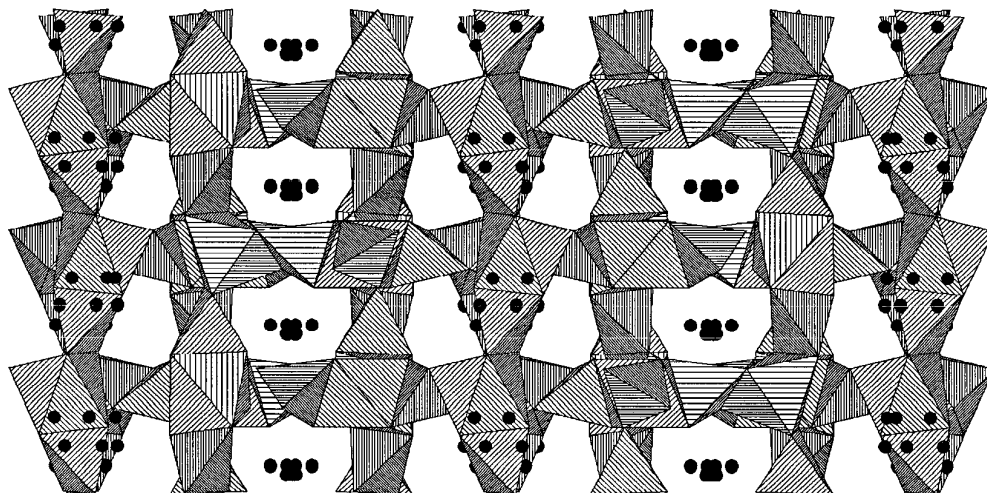


FIG. 3. Projection of the structure on (110). Na atoms are black dots.

in contrast, Na(3) to Na(6) atoms are located in the wide tunnels with weak Na–S bonds ($d > 3.8 \text{ \AA}$).

DISCUSSION

The value of the shortest S–S distance (3.12 \AA) excludes polyanionic species, for example $(S_2)^{2-}$ with a usual interatomic distance of about 2.05 \AA . Considering the ionic radius value $r_{S^{2-}} = 1.84 \text{ \AA}$ (7) and mean distances P–S and Ti–S, 2.03 \AA and 2.42 \AA , respectively, the cationic radii are $r_{P^{5+}} = 0.19 \text{ \AA}$ and $r_{Ti^{4+}} = 0.58 \text{ \AA}$, in good agreement with usual values (0.17 \AA and 0.605 \AA , respectively) in chalcogenide surrounding. Besides, NMR measurements on the single crystal are in agreement with the absence of Ti^{3+} . These results and the nature of the atomic arrangement justify the writing of oxidation state charge balance: $Na^+(Ti^{4+})_2(P^{5+})_3(S^{2-})_{12}$.

The structure can be viewed as $Ti(1)\square S_6$ and $Ti(2)P(2)S_6$ chains (in the ratio 1:3) parallel to c axis and linked by P(1) atoms in tetrahedral sites (Fig. 4). The threefold axis $Ti(1)\square S_6$ chains can be related to the TiS_2 structure (8), with $c_{NaTi_2(PS_4)_3} \approx 2c_{TiS_2}$, and the powder diffraction diagrams of two compounds present similarities (9). The $Ti(2)P(2)S_6$ chains constitute the sides of the tunnels along the c axis.

Another important fact is the Nasicon-type transformation. It has been reported in the literature that the phosphorotetrathioic acids and their salts are not stable in air and lead to the corresponding phosphoric compounds (10). Concerning $NaTi_2(PS_4)_3$ powders, a hydrolyzed amorphous phase is quickly obtained. A slight heating of this phase (400°C for 12 hr) leads to the Nasicon compound $NaTi_2(PO_4)_3$, characterized by X-ray powder diffraction (11). Many other Nasicon compounds were synthesized by this method (for example Ge, Sn, Nb, ...) always at lower

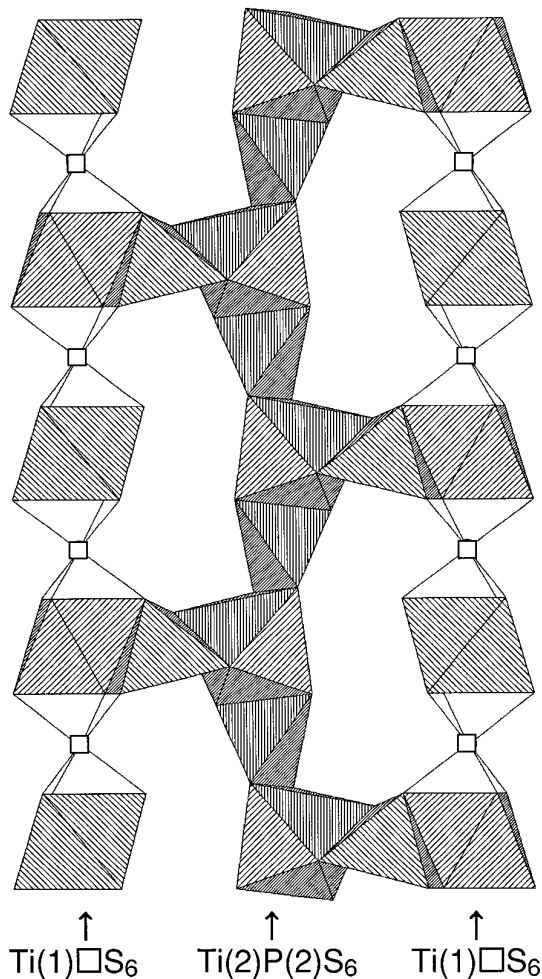


FIG. 4. $Ti(2)P(2)S_6$ and $Ti(1)\square S_6$ chains linked by $P(1)S_4$ tetrahedra.

temperatures (400 to 800°C) than the conventional methods using oxide reactants (800 to 1200°C).

CONCLUSION

$\text{NaTi}_2(\text{PS}_4)_3$ has been synthesized with the same stoichiometry as Nasicon-type $AM_2(\text{PO}_4)_3$. The final compound has not the Nasicon structure but an original one unrelated to known thiophosphate structures. The most attractive feature of this structure is its opened character with very wide tunnels in which some Na^+ cations are located. According to these geometrical factors and the high values of the ADPs, particularly for Na^+ cations, $\text{NaTi}_2(\text{PS}_4)_3$ seems to be a good compound concerning ionic conduction or intercalation, as it is confirmed by our first results.

Many other compounds with the same stoichiometry have been synthesized; among them $A^I\text{Ti}_2(\text{PS}_4)_3$ compounds are isotopic with $\text{NaTi}_2(\text{PS}_4)_3$. Syntheses of new compounds $A^I\text{MM}'(\text{PS}_4)_3$ or with different stoichiometry in the $A-M-P-S$ family are in progress. Besides the transformation in Nasicon-type oxides can be interesting to

synthesize compounds at low temperatures or to obtain new ones which are not accessible from oxide reactants.

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