

## The Structure of $\text{Na}_5\text{Ti}(\text{PO}_4)_3$

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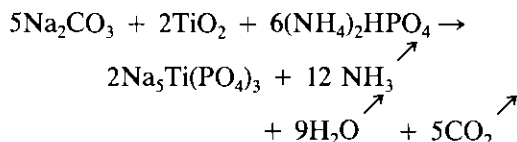
The sodium titanium phosphate  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$  crystallizes in the trigonal space group  $R\bar{3}2$  ( $a = 9.0607(2)$  Å,  $c = 21.734(1)$  Å,  $V = 1545.3$  Å<sup>3</sup>,  $d_m = 2.84(2)$ ,  $d_c = 2.89$  Mg · m<sup>-3</sup>,  $Z = 6$ ).  $R = 0.022$  and  $R_w = 0.023$  for 831 reflections. The structure belongs to the Nasicon-type family and is characterized by a 2-2 titanium-sodium ordering along the  $c$  axis. The four crystallographically independent sodium atoms show coordination numbers 6 and 8. The cell parameters and the cationic distribution are consistent with the rules governing the structural evolution of such types of material © 1993 Academic Press, Inc.

The recent development of all-optical communication systems makes new optical devices necessary. In this context transparent glasses with large nonlinearities are promising materials (1). The choice of composition is dictated by the possibility of an increase of the nonlinear coefficient index  $n_2$ , which is induced by the presence of highly hyperpolarizable entities. From the recent analysis of the nonlinear index in crystals by Adair *et al.* (2), the most significant result is the high value of  $n_2$  for titanium oxides containing  $\text{TiO}_6$  octahedral group. Within this scope we have recently described the conditions of glass formation in the  $\text{Na}_2\text{O}-\text{TiO}_2-\text{P}_2\text{O}_5$  system (3). The investigation of the recrystallization process of these glasses had led to the identification of a new Nasicon type phosphate  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ . The single crystal structure determination of this phosphate is reported here.

### Experimental

The crystalline form of  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$  can be prepared by calcination of a mixture of

$\text{Na}_2\text{CO}_3$ ,  $\text{TiO}_2$ , and  $(\text{NH}_4)_2\text{HPO}_4$  in stoichiometric proportion. The reaction



is completely achieved after two thermal treatments of 15 hr at 300 and 500°C and a final treatment of 24 hr at 750°C.

Single crystals were grown by slow cooling (5°C/hr) between 850°C and room temperature of the previous mixture initially heated to 600°C for 15 hr.

The obtained crystals are transparent, colorless, and enclosed in right parallelepipeds limited by the {110},  $\{1\bar{1}0\}$ , and {001} faces.

Preliminary oscillation and Weissenberg photographs show the crystal to be trigonal. The unit cell parameters (Table I) were refined by the Rietveld method using the following experimental conditions:  $\text{CuK}_\alpha$  radiation;  $2\theta$  range and step (°): 5-110, 0.02; 280 reflections; pseudo-Voigt profile function

TABLE I  
CRYSTALLOGRAPHIC AND EXPERIMENTAL DATA

1. Crystal data	
Space group	<i>R</i> 32
<i>a</i> (Å)	9.0607 (2)
<i>c</i> (Å)	21.734 (1)
<i>V</i> (Å <sup>3</sup> )	1545.3 (1) Å <sup>3</sup>
<i>Z</i>	6
<i>D<sub>m</sub></i> (g · cm <sup>-3</sup> )	2.84 (2)
<i>D<sub>calc</sub></i> (g · cm <sup>-3</sup> )	2.89
$\mu$ (MoK $\alpha$ )(cm <sup>-1</sup> )	15.5
<i>F</i> (000)	1308
2. Intensity measurement	
<i>T</i>	298 (2) K
Crystal size (mm)	0.250 × 0.150 × 0.100
Automatic diffractometer	Enraf–Nonius CAD4
Radiation (Å)	MoK $\alpha$ , $\lambda$ = 0.7107
Monochromator	graphite
Scan mode	$\omega$
Scan width (°)	1.00 + 0.35 tan $\theta$
Counter slit width (mm)	2.50 + 3.00 tan $\theta$
Recording angular range ( $\theta^\circ$ )	$\theta < 35^\circ$
Miller indices ranges	-14 ≤ <i>h</i> ≤ +14 -14 ≤ <i>k</i> ≤ +14 -34 ≤ <i>l</i> ≤ +34
Recorded intensities (in <i>R</i> lattice)	9065
Number of unique reflections with <i>I</i> > 3 $\sigma$ ( <i>I</i> )	831
<i>R</i> (int)	0.013
3. Refinement results	
Number of parameters	68
Secondary extinction parameter	167(4) · 10 <sup>-5</sup>
<i>S</i>	2.78
Residual electronic density range ( <i>e</i> Å <sup>-3</sup> )	-0.48 to +0.65 (maximum near Ti atoms)
Final <i>R</i> value	0.022
Final <i>R<sub>w</sub></i> value ( $\omega$ = 1/ $\sigma^2$ )	0.023

( $\eta$  = 0.42 (1)) background correction with a polynomial function (degree 5 in  $2\theta$ ); 48 parameters refined,  $R_p$  = 0.089,  $R_{wp}$  = 0.122,  $R_B$  = 0.064.

Systematic absences  $-h + k + l \neq 3n$  for (*hkl*) and observed equivalent intensities are compatible with rhomboedral lattice mode and  $\bar{3}m1$  Laue group. Data collection, with  $-h + k + l = 3n$  rule, was done with an Enraf–Nonius CAD-4 diffractometer (Table I). Corrections were made for Lorentz-polarization effects and for absorption based on azimuthal scans of 10 reflections spanning the  $\theta$  range ( $\Delta T/T$ )<sub>Max</sub> = 0.04.

Observation of a positive nonlinear optical test of second harmonic generation (SHG = (1.064/0.523) $\mu$ m), which is about 80% that of the K.D.P., indicates a non-centrosymmetric space group: *R3m* or *R32*. The *R32* group is selected as a subgroup of the *R3c* Nasicon reference group. Atomic scattering factors for Na<sup>+</sup>, Ti<sup>4+</sup>, P<sup>5+</sup>, and O<sup>-</sup> and anomalous dispersion correction are found from the International Tables for X-Ray Crystallography (4).

### Structure Determination

The structure is solved by heavy-atom methods with the SHELX 76 program (5). Transposition of the Nasicon model in the *R32* space group lead to a very high refinement factor *R* = 0.47.

Successive difference Fourier synthesis indicate important displacement for PO<sub>4</sub> tetrahedral groups and for sodium sites. Refinements including the isotropic thermal parameter lead to *R* = 0.07.

The following notation has been used for sodium atoms:

—Na(0) for sodium located in octahedral sites alternatively with titanium along the threefold axis with a 2–2 ordering,

—Na(1) for sodium located in the sites of the Nasicon model usually labelled *M*<sub>1</sub>,

—Na(2) and Na(3) for sodium found in the sites usually labelled *M*<sub>2</sub> respectively associated with [Ti<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] and [Na(0)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] entities.

Refinement with individual anisotropic thermal parameter show a strong anisotropy for Na(3) with a greater displacement along the *c* axis:  $U_{33} = \bar{r}_{001}^2 = 0.115 \text{ \AA}^2$ .

The residual electronic density around this site can also be interpreted, assuming a partial statistical delocalization of the Na(3) atoms out of the binary axis at the 9*e* site. A refinement calculated with this hypothesis leaves 53% Na atoms (Na(31)) in the initial site but 47% (Na(32)) are statistically distributed over the 18*f* site, i.e., with a  $\Delta z$  translation from the former center (Table II). This result is obtained with a relevant value of

TABLE II  
 FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS

Atom	Position	Occupancy rate	x	y	z	$B_{\text{eq}}$ ( $\text{\AA}^2$ ) or $B_{\text{iso}}^*$
Na(0)	6c	6	$\frac{1}{2}$	$\frac{2}{3}$	0.0683(1)	1.39(4)
Ti	6c	6	0	0	0.09952(3)	0.53(2)
P(1)	9d	9	0.7200(1)	0	0	0.61(3)
P(2)	9e	9	0.3285(1)	0	$\frac{1}{2}$	0.69(3)
O(11)	18f	18	0.4493(2)	0.2925(2)	0.0134(1)	1.19(7)
O(12)	18f	18	0.1548(2)	0.1945(2)	0.0549(1)	1.91(8)
O(21)	18f	18	0.5474(2)	0.6215(2)	0.1113(1)	1.83(8)
O(22)	18f	18	0.1815(2)	0.0271(2)	0.1555(1)	1.33(7)
Na(1)	6c	6	0	0	0.2505(1)	1.61(4)
Na(2)	9d	9	0.3875(2)	0	0	1.45(5)
Na(31)	9e	4.8(1)	0.6788(4)	0	$\frac{1}{2}$	1.51(5)*
Na(32)	18f	4.2(1)	0.6789(7)	0.0021(6)	0.5202(4)}	

the usual isotropic thermal parameter (1.5  $\text{\AA}^2$ ) and is compatible with the  $M_2$  site environment. Final refinements done in this context with the introduction of anisotropic thermal parameters for all the other atoms, of a weighting scheme  $\omega = 1/\sigma^2(F_0)$ , and of an empirical isotropic secondary extinction correction  $x [F_c = F(1 - 10^{-4} \times F^2/\sin \theta)]$  leads to  $R = 0.022$  and  $R_w = 0.023$  (Table I).

The final atomic parameters are given in Table II and selected bond lengths are listed in Table III.

### Description of the Structure

Na<sub>5</sub>Ti(PO<sub>4</sub>)<sub>3</sub> belongs to the Nasicon-type family. The 3D framework is made up of PO<sub>4</sub> tetrahedra sharing corners with TiO<sub>6</sub> and NaO<sub>6</sub> octahedra. Actually a 2–2 ordered distribution of titanium and sodium occurs along the *c* axis giving rise to two different units [Ti<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] and [Na(0)<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>] (Fig. 1). Each phosphate group is connected with both Na(0)O<sub>6</sub> and TiO<sub>6</sub> octahedra. As expected, in the P–O–Ti connection the P–O bond is longer (P(1)–O(12) = P(2)–O(22) = 1.560  $\text{\AA}$ ) than in the P–O–Na(O) one (P(1)–O(11) = 1.509  $\text{\AA}$ ; P(2)–O(21) = 1.505  $\text{\AA}$ ). Thus the PO<sub>4</sub> group is more distorted than in NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>, where the P–O dis-

tances are respectively 1.519 and 1.501  $\text{\AA}$  (6). Within these units the Ti–Ti distance, 4.325  $\text{\AA}$ , is larger than the Na(0)–Na(0) distance of 4.20  $\text{\AA}$ .

This [Na(0)TiP<sub>3</sub>O<sub>12</sub>]<sup>4-</sup> framework encloses two different kinds of site for the remaining sodium atoms:

(i) the first type,  $M_1$ , is a strongly distorted antiprism elongated along the *c* axis and sharing common faces with one TiO<sub>6</sub> and one Na(0)O<sub>6</sub> octahedron. In this cluster (Fig. 2), the cations are located in off-center positions (in the direction indicated by the arrows) in order to reduce their mutual electrostatic repulsion. Consequently, in each of these polyhedra, two types of cation–oxygen distances are observed:

(1) in the sodium–oxygen octahedron, Na(0)–O(21) = 2.366  $\text{\AA}$  < Na(0)–O(11) = 2.536  $\text{\AA}$ ;

(2) in the  $M_1$  site, Na(1)–O(11) = 2.358  $\text{\AA}$  < Na(1)–O(22) = 2.575  $\text{\AA}$  (in NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> the corresponding Na–O distance is 2.472  $\text{\AA}$  (6));

(3) in the TiO<sub>6</sub> octahedron Ti–O(12) = 1.881  $\text{\AA}$  < Ti–O(22) = 1.960  $\text{\AA}$  (the corresponding distances are 1.912 and 1.983  $\text{\AA}$  in NaTi<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>).

(ii) The second type  $M_2$ , where Na(2) and Na(3) are found, are irregular eight-coordi-

TABLE III  
SELECTED BOND LENGTHS AND ANGLES OF Na<sub>5</sub>Ti(PO<sub>4</sub>)<sub>3</sub>

Na(0)O <sub>6</sub> octahedron						
Na(0)	O(11 <sup>i</sup> )	O(11 <sup>ii</sup> )	O(11 <sup>iii</sup> )	O(21)	O(21 <sup>iv</sup> )	O(21 <sup>v</sup> )
O(11 <sup>i</sup> )	2.538(2)	3.140	3.140	3.393	4.820	3.365
O(11 <sup>ii</sup> )	76.5(1)	2.538(2)	3.140	4.820	3.365	3.393
O(11 <sup>iii</sup> )	76.4(1)	76.5(1)	2.538(2)	3.365	3.393	4.820
O(21)	87.5(1)	158.8(1)	86.6(1)	2.366(2)	3.764	3.764
O(21 <sup>iv</sup> )	158.9(1)	86.6(1)	87.5(1)	105.4(1)	2.365(2)	3.764
O(21 <sup>v</sup> )	86.6(1)	87.5(1)	158.9(1)	105.4(1)	105.4(1)	2.366(2)
TiO <sub>6</sub> octahedron						
Ti	O(12)	O(12 <sup>vi</sup> )	O(12 <sup>vii</sup> )	O(22)	O(22 <sup>viii</sup> )	O(22 <sup>ix</sup> )
O(12)	1.882(2)	2.794	2.794	2.740	2.651	3.833
O(12 <sup>vi</sup> )	95.9(1)	1.882(2)	2.794	3.833	2.740	2.652
O(12 <sup>vii</sup> )	95.9(1)	95.9(1)	1.882(2)	2.652	3.833	2.740
O(22)	91.0(1)	172.2(1)	87.3(1)	1.960(2)	2.661	2.661
O(22 <sup>viii</sup> )	87.3(1)	91.0(1)	172.2(1)	85.5(1)	1.960(2)	2.661
O(22 <sup>ix</sup> )	172.2(1)	87.3(1)	91.0(1)	85.5(1)	85.5(1)	1.960(2)
Na(1)O <sub>6</sub> octahedron						
Na(1)	O(11 <sup>xiii</sup> )	O(11 <sup>xiv</sup> )	O(11 <sup>xv</sup> )	O(22)	O(22 <sup>xvi</sup> )	O(22 <sup>xvii</sup> )
O(11 <sup>xiii</sup> )	2.359(2)	3.140	3.140	3.778	4.156	4.870
O(11 <sup>xiv</sup> )	83.5(1)	2.359(2)	3.140	4.156	4.870	3.778
O(11 <sup>xv</sup> )	83.5(1)	83.5(1)	2.359(2)	4.870	3.778	4.156
O(22)	99.9(1)	114.8(1)	161.7(1)	2.574(2)	2.661	2.661
O(22 <sup>xvi</sup> )	114.8(1)	161.7(1)	99.9(1)	62.3(1)	2.574(2)	2.661
O(22 <sup>xvii</sup> )	161.7(1)	99.9(1)	114.8(1)	62.3(1)	62.3(1)	2.574(2)
P(1)O <sub>4</sub> tetrahedron						
P(1)	O(11 <sup>xix</sup> )	O(11 <sup>xx</sup> )	O(11 <sup>xxi</sup> )	O(12 <sup>xxii</sup> )	O(12 <sup>xxiii</sup> )	O(12 <sup>xxiv</sup> )
O(11 <sup>xix</sup> )	1.509(2)	2.529	2.529	2.521	2.492	2.492
O(11 <sup>xx</sup> )	113.8(1)	1.509(2)	2.529	2.492	2.521	2.521
O(12 <sup>xxi</sup> )	110.4(1)	108.6(1)	110.4(1)	1.560(2)	2.466	2.466
O(12 <sup>xxii</sup> )	108.6(1)	110.4(1)	108.6(1)	104.5(1)	1.560(2)	1.560(2)
P(2)O <sub>4</sub> tetrahedron						
P(2)	O(21 <sup>xxv</sup> )	O(21 <sup>xxvi</sup> )	O(21 <sup>xxvii</sup> )	O(22 <sup>xxviii</sup> )	O(22 <sup>xxix</sup> )	O(22 <sup>xxx</sup> )
O(21 <sup>xxv</sup> )	1.505(2)	2.509	2.509	2.463	2.566	2.566
O(21 <sup>xxvi</sup> )	112.9(1)	1.505(2)	2.509	2.566	2.463	2.463
O(22 <sup>xxvii</sup> )	106.9(1)	113.7(1)	113.7(1)	1.560(2)	2.432	2.432
O(22 <sup>xxviii</sup> )	113.7(1)	106.9(1)	106.9(1)	102.4(1)	1.560(2)	1.560(2)
Na(2)O <sub>8</sub> polyhedron						
Na(2)—O(11) : 2.437(2) × 2						
—O(11 <sup>iii</sup> ) : 2.528(2) × 2						
—O(12 <sup>i</sup> ) : 2.984(2) × 2						
—O(21 <sup>iii</sup> ) : 2.501(2) × 2						
Na(31)O <sub>8</sub> polyhedron						
Na(31)—O(22 <sup>xvii</sup> ) : 2.511(2) × 2						
—O(22 <sup>xviii</sup> ) : 2.840(2) × 2						
—O(21 <sup>xvii</sup> ) : 2.572(2) × 2						
—O(12 <sup>xvii</sup> ) : 2.859(2) × 2						
Na(32)O <sub>8</sub> polyhedron						
Na(32)—O(22 <sup>xvii</sup> ) : 2.576(2)						
—O(22 <sup>xvii</sup> ) : 2.507(2)						
—O(22 <sup>xvii</sup> ) : 2.895(2)						
—O(22 <sup>xvii</sup> ) : 2.853(2)						
—O(21 <sup>xvii</sup> ) : 2.392(2)						
—O(21 <sup>xvii</sup> ) : 2.819(2)						
—O(12 <sup>xvii</sup> ) : 2.505(2)						

Note. Symmetry code: (i)  $y, x, \bar{z}$ ; (ii)  $x - y, \bar{y} + 1, \bar{z}$ ; (iii)  $\bar{x} + 1, \bar{x} + y, \bar{z}$ ; (iv)  $\bar{y} + 1, x - y + 1, z$ ; (v)  $\bar{x} + y, \bar{x} + 1, z$ ; (vi)  $\bar{y}, x - y, z$ ; (vii)  $\bar{x} + y, \bar{x}, z$ ; (viii)  $\bar{x} + \frac{1}{2}, \bar{x} + y + \frac{1}{2}, \bar{z} + \frac{1}{2}$ ; (ix)  $y - \frac{1}{2}, x - \frac{3}{2}, \bar{z} + \frac{1}{2}$ ; (x)  $x - y - \frac{1}{2}, \bar{y} + \frac{1}{2}, \bar{z} + \frac{1}{2}$ ; (xi)  $\bar{y} + 1, x - y, z$ ; (xii)  $x - y + \frac{1}{2}, \bar{y} + \frac{3}{2}, \bar{z} + \frac{1}{2}$ ; (xiii)  $x - \frac{1}{2}, y - \frac{3}{2}, z + \frac{1}{2}$ ; (xiv)  $\bar{x} + y + \frac{3}{2}, \bar{x} + \frac{1}{2}, z + \frac{1}{2}$ ; (xv)  $y + \frac{1}{2}, x - \frac{1}{2}, \bar{z} + \frac{1}{2}$ ; (xvi)  $x + \frac{3}{2}, y + \frac{1}{2}, z + \frac{1}{2}$ ; (xvii)  $x - y + \frac{1}{2}, \bar{y} - \frac{1}{2}, \bar{z} + \frac{1}{2}$ .

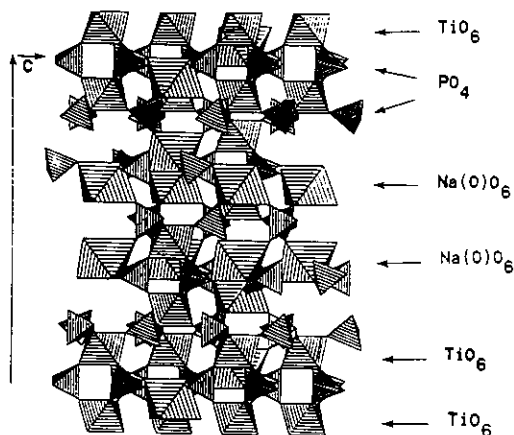


FIG. 1. A perspective view of the  $\text{Na}(0)\text{TiP}_3\text{O}_{12}$  framework illustrating the 2-2 titanium-sodium (0) ordering.

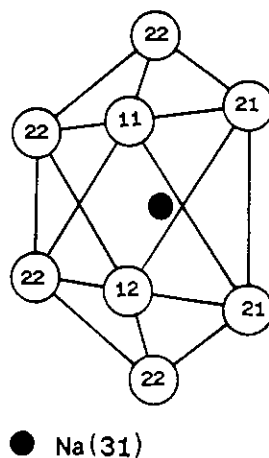


FIG. 3. Oxygenated environment of the  $\text{Na}(31)$  atom.

nated sites with a wide distribution of the sodium-oxygen distances (Fig. 3).  $\text{Na}(2)$  has six oxygen neighbors at about  $2.50 \text{ \AA}$ , whereas the two other oxygens are  $2.984 \text{ \AA}$  distant. In the site of  $\text{Na}(3)$  ( $\text{Na}(31)$ ) or

$\text{Na}(32)$  the cations have four oxygen neighbors also at about  $2.50 \text{ \AA}$  and the four remaining anions at  $2.85 \text{ \AA}$ .

### Discussion

These structural results can be analyzed in the context of the evolution of the

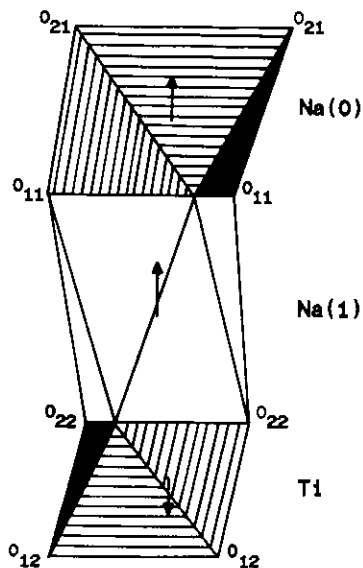


FIG. 2. Environment of the  $M_1$  site in  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ .

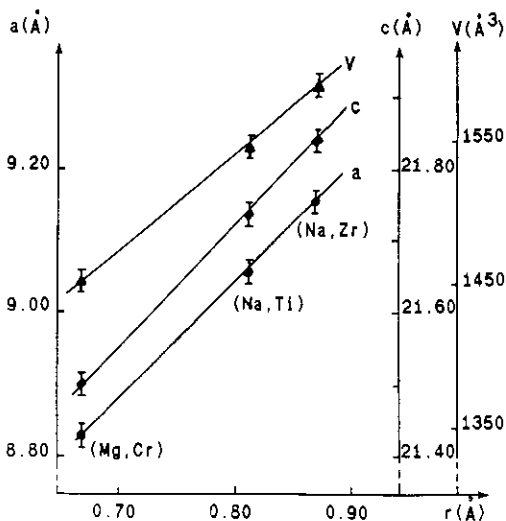


FIG. 4. Evolution of the crystallographic parameters of various Nasicon-type phosphates for which the mean charge of the cation in the octahedral site is 2.5. Ionic radii are given by (8)  $\text{MgCr} = \text{Na}_4\text{MgCr}(\text{PO}_4)_3$  (7),  $\text{NaTi} = \text{Na}_5\text{Ti}(\text{PO}_4)_3$  (this work),  $\text{NaZr} = \text{Na}_5\text{Zr}(\text{PO}_4)_3$  (9).

Nasicon-type phosphate. Assuming the cationic distribution found in  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ , the structural formula can be written as  $\text{Na}_3(M_2)\text{Na}(M_1)A_2(\text{PO}_4)_3$ , where  $A$  represents the cations in octahedral sites.

The rule governing the cell parameters of such materials has been already established (7):

(i) the  $a$  parameter is directly correlated with the size of the  $A^{n+}$  cations, here  $\text{Na}(0)^+$  and  $\text{Ti}^{4+}$ , and with the proportion of sodium in  $M_2$  position;

(ii) the  $c$  parameter also increases with the strength of the  $\text{Na}^+(M_1) - A^{n+}$  electrostatic repulsion.

Figure 4 compares some structural data for Nasicon-type phosphates for which the mean charge of the  $A$  cations is 2.5. The linear variations of these parameters versus the mean  $A$  cation radius are consistent with the atomic distribution found for  $\text{Na}_5\text{Ti}(\text{PO}_4)_3$ .

The sodium–titanium ordering has two consequences:

—a marked distortion of the  $\text{PO}_4$  group;  
 —the displacement of the sodium  $\text{Na}(1)$  from the center of the  $M_1$  site, which can explain the relatively high value of the SHG signal.

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