THERMAL EXPANSION OF $NaTi_2(PO_4)_3$ STUDIED BY RIETVELD METHOD FROM X-RAY DIFFRACTION DATA.

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ABSTRACT

Previous disagreement about the thermal expansion of the rhombohedral compound, NZP-type, $NaTi_2(PO_4)_3$ has been clarified. It is shown that thermal stresses affect the thermal expansion, but they relax after some time of storage. Its anisotropic thermal expansion, has been calculated from high temperature X-ray diffraction, and it is linear in the range from room temperature up to 800°C. Coefficients are $\alpha(a)=-4.4 \times 10^{-6}$ °C^{-1} and $\alpha(c)=20\times10^{-6}$°C^{-1}.

The predictability of thermal expansion and the tailoring of the composition of NZP ceramics require to check whether the thermal effect on the rotations and distortions of the atomic polyhedra in this structure is the responsible for the high anisotropy in the thermal expansion. This effect has been determined experimentally by solving the chemical structure at five different temperatures, applying the Rietveld method to deconvolute the powder X-ray diffraction profiles. The Rietveld computer program was modified to include and refine a coefficient relating to the eccentricity of the sample in the X-ray high-temperature camera.

MATERIALS INDEX: sodium, titanium, phosphates, NZP.

1. INTRODUCTION.

Single crystals of the double phosphate $NaTi_2(PO_4)_3$ were prepared by Hagman and Kierkegaard (1) in 1968, and it has shown that they were isomorphous to $NaZr_2(PO_4)_3$, NZP-type of structure. One of the authors had calculated its thermal expansion (2) from room temperature up to 500°C, finding a negative thermal expansion coefficient of -5.5×10^{-6} °C^{-1} by dilatometry, and a strong anisotropy, from high temperature X ray diffraction, with coefficients $\alpha(a)=-5.61 \times 10^{-6}$ °C^{-1} (25°C to 500°C) and $\alpha(c) = 12.8 \times 10^{-6}$ °C^{-1} (25°C to 200°C) and 28.1×10^{-6} °C^{-1}(200°C to 500°C) showing a deflection in the expansion along the hexagonal "c" axis. So the volume expansion coefficient was 5.27×10^{-7} °C^{-1}(25°C to 200°C) and 5.63×10^{-6} °C^{-1} (200°C to 500°C). Three questions raised by these results. (i) What is the structural mechanism that yields its anisotropic thermal expansion?. (ii) What is the

structural meaning of the deflection at 200°C, not being present in the isomorphous $NaZr_2(PO_4)_3$ (3) neither in the dilatometric curve?. (iii) Why is the dilatometric expansion coefficient so close to the lattice expansion in the direction of the "a" axis, instead of being close to the mean volume expansion?.

The answer to the first question was provided by Alamo in the form of a computer model (4,5), based on the rotations of polyhedra that are connected by corners and that depend on the expansion of the weakest bonds. The experimental data to verify it, came from Hazen's structure analysis from high temperature X ray diffraction on a single crystal of $Na_{1+x}Zr_{2-x}(SiO_4)_x(PO_4)_{3-x}$ with x=.11 (6). According to that model, the thermal effect of enlarging the weakest bonds is similar, but smaller, than the crystal chemistry effect of the Na substitution by a larger atom like K, Rb, or Cs(4).

Oota et al. (7) studying the thermal expansion of $NaTi_2(PO_4)_3$, among other compounds, from room temperature up to 1000°C found similar results but no deflection at 200°C.

Thus, there is a lack of concordance in previous works, and in this work, we have studied again the lattice thermal expansion of the same sample that was used before (2), as well as the expansion of a new prepared sample, determining the lattice parameters at five temperatures from room temperature up to 800°C.

Also, in materials with a flexible skeleton and a high anisotropy, single crystals use to show a crystal structure that is slightly different from that present in the ceramics. In which, grains are under anisotropic tensions. Thus, in order to solve the atomic structure in poly-crystalline samples, the X ray diffraction profiles at the same five different temperatures were deconvoluted using the Rietveld method. This method (8,9,10) was originally developed for the refinement of structures from neutron diffraction data, but it has been extended and applied in the last decade in many cases (11,12,13), using powder X ray diffraction, and so solving the structure of those compounds that cannot be synthesized in the form of single crystals. The method requires an starting model, as it follows a non-linear least squares procedure to deconvolute the powder diffraction profile, but more implementations allow the use of direct methods as well (14,15), and the study of microstrains and particle size of ceramic materials. It allows users to get the most about the structural information of polycrystalline samples.

In our case, applying the Rietveld method to $NaTi_2(PO_4)_3$ at different temperatures gives direct information on how the structure changes with the temperature, particularly, how the octahedra TiO_6 and the tetrahedra PO_4 rotate in the structure and yield a contraction in the "a" direction. This knowledge will help to establish the structure-properties relationships.

2. EXPERIMENTAL.

2.1. SYNTHESIS AND CHARACTERIZATION.

The compound $NaTi_2(PO_4)_3$ was prepared following a ceramic route using stoichiometric amounts of Na_2CO_3, TiO_2 and $NH_4H_2PO_4$. The mixture was homogenized and heated to 200°C, in order to decompose the ammonium phosphate, and then, calcined in two steps of 800°C/12 hours and 1100°C/12 hours separated by a grinding. The product was allowed to cool slowly.

2.2. LATTICE EXPANSION FROM X RAY DIFFRACTION.

The lattice thermal expansion was determined from the high temperature diffractograms taken on a HT Parr camera, by indexing and fitting the peaks between 100° and 160°(2θ), by least squares. The temperatures were 25, 200, 400, 600 and 800°C. Then the dependence of a and c with the temperature, a = f(t) and c = f(t), was fitted to a polynomial expression by least squares. The thermal expansion coefficients were calculated from the following expressions:

$$\alpha_t(a) = (da/dt)/a_t \quad \alpha_t(c) = (dc/dt)/c_t \quad \beta_t = (2\alpha_t(a) + \alpha_t(a))/3$$

were $\alpha_t(a)$ and $\alpha_t(c)$ are the thermal expansion coefficients in the direction of a and c respectively. And β_t is the volume thermal expansion.

2.3. STRUCTURE ANALYSIS BY RIETVELD METHOD.

The diffraction profiles of the new sample of $NaTi_2(PO_4)_3$ were taken automatically, under the control of a computer, by setting the high temperature camera at RT, 200°, 400°, 600° and 800°C, and using a step of 0.05°(2θ) between 10° and 100°(2θ), and a time of 2 seconds. For the refinement of the profile at RT, the program was fed with the lattice parameters we had calculated before and with the atomic positions calculated by Hagman (1) for the $NaZr_2(PO_4)_3$, and space group symmetry $R\bar{3}$
fed were those got for the closer lower temperature.
The Pseudo-Voigt function was elected to simulate the X-ray diffraction profile, although this was the worst adjusting part in the refinements. The original Rietveld program had to be modified in order to handle the eccentricity of the sample that is variable and appears at high temperature due to the kind of sample holder in the high temperature camera.
The refinement process was developed in sequential steps: i) The scale factor. ii) The zeropoint, the eccentricity and the hexagonal lattice parameters a and c. iii) The atomic positions and occupancy factors and the overall temperature factor. iv) The FWHM parameters (U, V, W), and the Asymmetry. And finally, v) The anisotropic temperature factors.

3. RESULTS.

The reaction product after calcination at 800°C yield $NaTi_2(PO_4)_3$ as the major phase and TiP_2O_7 as a minor phase. After calcination at 1100°C only the $NaTi_2(PO_4)_3$ phase was present. It was indexed as rhombohedral, type NZP, and fitted by least squares giving the hexagonal lattice parameters a=8.4876(3) Å and c= 21.801(1) Å.
The high temperature parameters of this sample and its thermal expansion appear in Table 1. The higher the temperature the shorter "a" and the larger "c". But, the absolute values of the thermal expansion parameters decrease with the temperature. The volume expansion is very anisotropic with an average value of 3.7×10^{-6} °C^{-1}.

TABLE 1.
Thermal expansion of $NaTi_2(PO_4)_3$ calculated from high temperature diffractograms by least squares fitting.

T(°C)	a (Å)	c (Å)	V (Å^3)	$\alpha_t(a) \times 10^6$	$\alpha_t(c) \times 10^6$	$\beta_t \times 10^6$
25	8.4876(3)	21.801(1)	1360.10	−6.81	21.24	2.54
200	8.4786(3)	21.882(1)	1362.26	−5.77	21.95	3.47
400	8.4698(3)	21.977(1)	1365.38	−4.55	21.49	4.13
600	8.4631(3)	22.068(1)	1368.86	−3.33	19.66	4.33
800	8.4585(3)	22.149(1)	1372.36	−2.11	16.49	4.09

The $NaTi_2(PO_4)_3$ sample, that was used before (2), was restudied again in the high temperature camera giving practically the same results as the new sample. Checking the records it showed up that the old sample was originally quenched. So, it appears that the deflection at 200°C (2) was due to microstructural stresses and also, that they relax after some years of storage.
The Rietveld refinement yielded the atomic positions in Table 2, from which the most representative bond lengths and angles have been calculated, appearing in Table 3.

TABLE 2.
Structural parameters obtained from Rietveld refinements.

T(°C)	25	200	400	600	800
a(Å)	8.4854(2)	8.4754(3)	8.4671(3)	8.4594(3)	8.4561(3)
c(Å)	21.7994(8)	21.8871(9)	21.9778(9)	22.0668(11)	22.1512(10)
V(Å³)	1359.33	1361.58	1364.52	1367.52	1371.71
Ti z	.1455(2)	.1461(2)	.1458(2)	.1462(2)	.1466(2)
P x	.2879(6)	.2874(7)	.2860(6)	.2847(8)	.2853(7)
01 x	.1736(9)	.1727(10)	.1714(9)	.1690(11)	.1681(10)
01 y	-.0285(10)	-.0303(12)	-.0318(11)	-.0330(12)	-.0350(12)
01 z	.1930(4)	.1931(4)	.1932(4)	.1934(5)	.1935(4)
02 x	.1955(9)	.1950(10)	.1960(9)	.1963(9)	.1970(10)
02 y	.1648(9)	.1659(10)	.1668(9)	.1670(10)	.1675(10)
02 z	.0885(4)	.0890(4)	.0900(4)	.0911(5)	.0921(4)
Rp	13.01	13.15	12.72	13.89	12.97
Rwp	18.52	19.65	17.71	19.20	19.25
Re	12.91	12.81	12.94	12.92	12.86

TABLE 3.
Bond lengths and angles of $NaTi_2(PO_4)_3$ at different temperatures.

T(°C)	25	200	400	600	800
6(Na-02)	2.472(7)	2.486(8)	2.513(7)	2.538(7)	2.566(8)
3(Ti-01)	1.912(8)	1.908(8)	1.912(8)	1.899(8)	1.899(8)
3(Ti-02)	1.983(8)	1.987(8)	1.977(8)	1.973(8)	1.970(8)
2(P-01)	1.519(8)	1.521(8)	1.520(8)	1.524(8)	1.531(8)
2(P-02)	1.501(8)	1.501(8)	1.500(8)	1.505(8)	1.499(8)
02a-Na-02b	65.6	65.1	64.6	63.9	63.4
02a-Na-02g	114.4	114.9	115.4	116.1	116.6
01h-Ti-01d	93.5	93.7	93.1	92.8	92.9
02a-Ti-02b	84.9	84.6	85.6	85.9	86.4
01d-Ti-02a	90.2	90.7	90.8	91.0	91.0
01d-Ti-02b	173.9	173.6	174.7	175.1	175.2
01d-Ti-02c	91.2	90.7	90.3	90.1	89.5
01d-P-01k	112.1	112.6	113.3	113.2	113.2
01d-P-02l	111.4	111.5	111.0	110.7	110.2
01d-P-02m	105.1	105.3	105.7	106.3	106.6
02l-P-02m	111.9	110.8	110.2	109.6	110.2

TABLE 4.
Internal parameters used in Alamo's model in TiO_6 and PO_4 polyhedra

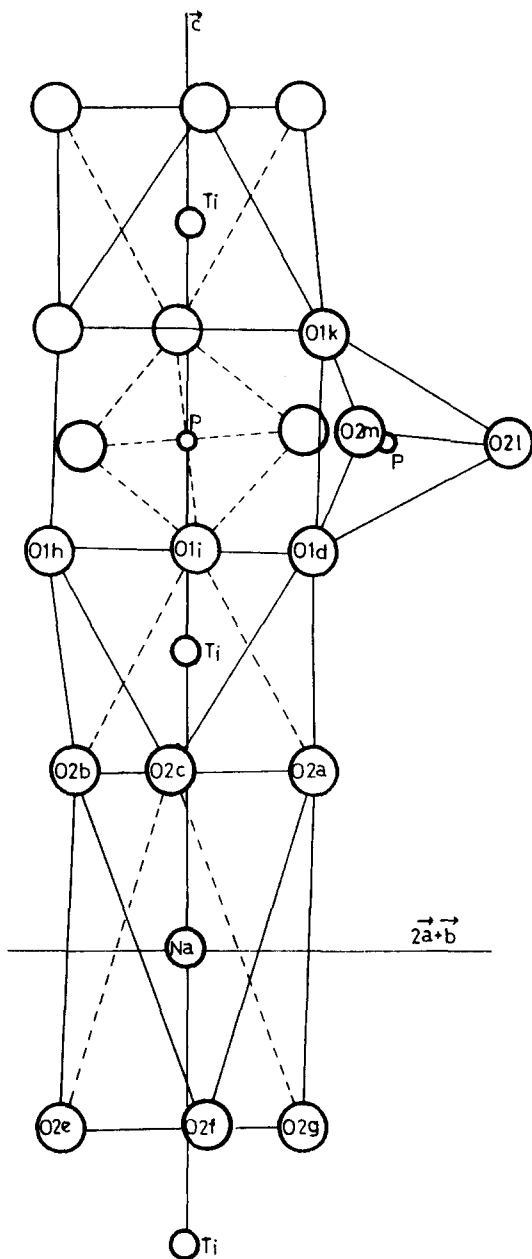| T(°C)	25	200	400	600	800
$\phi 1$	7.5	8.0	8.4	8.8	9.3
$\phi 2$	8.4	8.0	7.9	8.0	8.0
Ω	59.1	60.0	60.5	60.8	61.3
$\theta 1$	9.6	10.1	10.6	11.0	11.6
$\theta 2$	5.2	5.8	6.9	7.9	9.1
Δ	85.6	85.7	86.3	86.9	87.5
RZ1(Å)	1.6077	1.6076	1.6029	1.5877	1.5902
RZ2(Å)	1.5452	1.5442	1.5508	1.5516	1.5562
RP1(Å)	1.2601	1.265	1.2699	1.2722	1.2775
RP2(Å)	1.2432	1.235	1.2298	1.2299	1.2298
DC(Å)	2.278	2.278	2.268	2.257	2.244

FIG. 1
Projection of the $NaTi_2(PO_4)_3$, showing the polyhedra aligned along axis $\vec{c}$

From data in Table 3, it is apparent that the Na-O bonds are those with the greatest expansion, i. e., from 2.472 Å at 25°C to 2.566 Å at 800°C . And the Ti-O and P-O bonds remain practically constant within the experimental error limits.

The internal angles O2-Na-O2 in the elongated octahedron are related each other by the symmetry $\overline{3}$

O2 with the same z coordinate, decreases from 65.6° at 25°C to 63.4° at 800°C. So, both facts makes the face to face distance in the NaO_6 octahedron, along the "c" axis direction, to enlarge from 3.86 Å at 25°C to 4.08 Å at 800°C. (Figure 1).

The face to face distance in the TiO_6 octahedron, along the "c" axis direction, is nearly constant with a small contraction from 2.28 Å at 25°C to 2.25 Å a 800°C. The O-Ti-O angles show also small variations with just an irregularity at 200°C, probably it may be due to an extra source of error and to the fact that we are not far from the limits of precision in the method applied. In general, the angles O1-Ti-O1 decrease when the temperature increases, while the angles O2-Ti-O2 increase when the temperature increases (Table 3).

In the tetrahedron PO_4, the angle O1-P-O1 increases from 112.1° up to 113.3° at 400°C, and then staying constant up to 800°C. This makes the height of the prismatic hole increase slightly from 2.48 Å at 25°C to 2.50 Å at 800°C. The angle O2-P-O2 closes from 111.9° to 110.2° when the temperature increases.
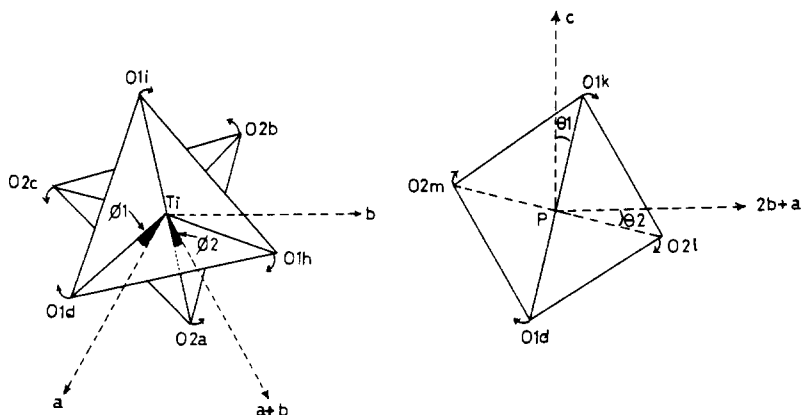
FIG. 2
Octahedron around the Titanium ions (to the left) and tetrahedron around the Phosphor (to the right) showing the internal angles and sign criteria.

   In Table 4 the values of the angles $\phi 1$, $\phi 2$, $\theta 1$ and $\theta 2$ are shown, as they are defined in Figure 2. They show clearly the degree of rotation and distortion in both coordination polyhedra.

   The angle $\phi 1$ increases with the temperature from 7.5° up to 9.3°, whereas $\phi 2$ keeps practically constant at 8°. It appears that the oxygen O1d belongs simultaneously to an octahedron TiO_6 and to a tetrahedron PO_4, while the oxygen O2a belongs to three polyhedra (NaO_6, TiO_6 and PO_4) so it shows a lesser degree of freedom. The global result is that the distortion angle Ω given by the projection of O1d, O2a and Ti along the "c" direction, increases with the temperature from 59.1° at 25°C up to 61.3° at 800°C.

   In the tetrahedron PO_4 both angles $\theta 1$ and $\theta 2$ increase with the temperature. $\theta 2$ increases faster than $\theta 1$ and this makes the angle Δ (projection along the "a" direction of the oxygen O1k, O2l and P) to increase with the temperature getting closer to 90°. So both angles Ω and Δ keep close to the ideal angles of 60° and 90°, but the angle Ω becomes, each step, slightly bigger, while Δ gets closer to 90°.

   Hazen's structure analysis from high temperature X ray diffraction on a single crystal of $Na_{1+x}Zr_{2-x}(SiO_4)_x(PO_4)_{3-x}$ with x=.11 (6) at the temperatures of 25°, 270°, 490° and 690°C yielded very similar results. The lattice thermal expansion follows a similar slope, and the atomic coordinates change in the same way; for instance, coordinate "z" of both the tetravalent atom increases and the coordinate "x" of the Phosphor decreases. Also, the rotations and angles of the polyhedra (sign criteria are the opposite) are very close in spite of the different size of the ZrO_6 and TiO_6 octahedra. All these facts point to the isostructurality in both crystals, and to the similar freedom of the polyhedra to rotate. Nevertheless, there is a difference in the precision of the structural parameters got by the two techniques.

Finally, the thermal expansion data of $NaTi_2(PO_4)_3$ has been applied in order to check Alamo's proportional distortion model (11). The starting parameters have been the atomic positions and the cell dimensions as refined by the Rietveld program from room temperature data. In this model, it was assumed that the distances: RP1, RP2, RZ1, RZ2 and DC would keep constant and that the equilibrium from the interatomic bonds would make any distortions in the octahedra and the tetrahedra proportional each other (U) with the residual effect (T) due to the fact that the structure cannot be built by perfect octahedra and tetrahedra. So, the equation proposed was:

$$\theta 1 - \theta 2 = U(\phi 2 - \phi 1 - T)$$

From our data (Table 4), the variations between 25°C and 800°C are: for RZ1 −1.1%, for RZ2 +0.7%, for RP1 +1.4%, for RP2 −1.1% and for DC −1.5%. These variations are reasonably small, but the calculated values for U and T are not comparable to those fitted from the $NaZr_2(PO_4)_3$ (1) and $KZr_2(PO_4)_3$ (16) structural data. The effect of the temperature on the NaO_6 octahedra is to enlarge it, but not so much as to get the size of the KO_6. Also, the temperature affects not only to the bonds in the NaO_6 group, but to all other bonds in the crystal as well, and so, the crystal chemistry substitution effect and the thermal expansion effect are not strictly equivalent, although both have a common dependence on the same atom connectivities in this structure. Also, the physical meaning of these values are not clear and they are under study at this moment. Nevertheless, two conclusions can be advanced:

i) the equation relating the angles θ and ϕ must be more complex and

ii) more experimental work and structural analysis are necessary to establish a general relation in this structural family.

4.CONCLUSIONS.

Using the Rietveld method to analyze the structural thermal expansion of $NaTi_2(PO_4)_3$ has allowed us to extend our understanding of its thermo-mechanical properties.

The lattice parameters refined by this method, deconvoluting the X rays diffraction peaks, match very well those calculated by least squares from the peak positions, and it could have been even better, if the profile would have been taken up to 160°(2θ).

The results do not match entirely the Alamo model (4-5), but they show it is an excellent approximation. In particular, the expression relating the octahedra and tetrahedra distortions is shown from this work to be chemically reasonably, i.e. that the Ti-O bonds bend about 10 times more than the P-O bonds, in conformity with the different steric restrictions. Also, we find conformity with the main lines of the model:

i) The contraction in the "a" direction from 25°C to 800°C, that is −0.0291Å, is due in −0.0824Å to the rotation of the phosphate group and in +0.0533Å to the rotation of the TiO_6 octahedron.

ii) The expansion in the "c" direction, that is +0.652Å, is due in +0.686Å to the rotations and distortions in the PO_4 group and in −0.034Å to the face-to-face distance contraction of the TiO_6 octahedron.

Other qualitative results are:

iii) TiO_6 becomes a more perfect octahedron increasing the temperature.

iv) PO_4 distorts mainly because of the O1 that build up the prismatic polyhedron O_6.

v) The NaO_6 polyhedra becomes more distorted. The Na-O2 distance increases and the O2 − Na-O2 angle decreases from 65.6 at 25°C to 63.4° at 800°C, so the NaO_6 octahedron distort more, away from 90°, the angle of the perfect octahedron.

Nevertheless, it is necessary to obtain more experimental data from other compounds in this family in order to predict closely the crystal chemistry substitution and the thermal expansion effects.

From these findings, it follows that the process applied in preparing materials is important to the final properties. At least in materials like this, where the flexibility of its structural skeleton allows hysteresis and distortions induced by microstructural stresses. Authors should describe the processing parts that can disturb the structures and properties like thermal quenching, pressing, final grinding and so on.

It follows also that, the Rietveld method is very convenient for crystal chemistry analysis in polycrystalline samples: powders, ceramics and natural rocks, <u>when the structure must be studied in its microstructural environment.</u> And it is unique, when the material cannot be prepared in the form of single crystals.

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