SYNTHESIS AND STRUCTURAL STUDY OF NaTi$_2$(PO$_4$)$_3$-NaSn$_2$(PO$_4$)$_3$ SOLID SOLUTIONS. I.THE EFFECT OF COMPOSITION ON LATTICE PARAMETERS.

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ABSTRACT

Compounds NaM$_2^{IV}$(PO$_4$)$_3$ with NZP-type structure present a different behavior depending on the nature of M^{IV}. For M^{IV} = Ti and Zr the structure shows the space group R$\bar{3}$c, whereas for M^{IV} = Sn the space group is R$\bar{3}$. Differences in behavior of NaTi$_2$(PO$_4$)$_3$ - NaSn$_2$(PO$_4$)$_3$ solid solutions are discussed in relation to the composition.

The variation of the lattice parameters with composition in NaTi$_{2-x}$Sn$_x$(PO$_4$)$_3$ (0<x<2) solid solutions, prepared by ceramic method, has been studied. A sharp change in the lattice parameter "a" is observed between the compositions with x = 1 and 1.2. The lattice parameter "c" increases as the Sn content increases in the whole range of composition. The space group R$\bar{3}$c becomes to R$\bar{3}$ for the composition with x > 1.

The structure of the compound with x = 1 (NaSnTi(PO$_4$)$_3$) has been determined applying the Rietveld method to deconvolute the powder x-ray diffraction profile.

MATERIALS INDEX : sodium, tin, titanium, phosphates, NZP structure.

1. INTRODUCTION

The NaZr$_2$(PO$_4$)$_3$ type structure (NZP) is formed by an extraordinary range of discrete compositions and crystalline solutions (1). Several ionic substitutions have been reported since NZP-type compounds of composition M^{I}M$_2^{IV}$(PO$_4$)$_3$, with M^I = Li, Na, K, Rb, Cs and M^{IV} = Zr, Hf, were synthesized in 1967 by Sljukic et al. (2).

In 1968, Hagman and Kierkegaard (3) solved first the crystal structure for the $NaZr_2(PO_4)_3$ composition and the titanium and germanium analogues. They obtained the compound $NaTi_2(PO_4)_3$ from a mixture of sodium metaphosphate and titanium dioxide heated in a platinum crucible for 24 h at 1200°C.

The hexagonal unit cell dimensions calculated by these authors for this compound from Guinier-Hägg powder photographs were: $a_h = 8.4924 \pm 0.0005$ Å and $c_h = 21.7788 \pm 0.0015$ Å.

Later, the synthesis of the compound $NaSn_2(PO_4)_3$ and its unit cell parameters were reported in two papers. In 1976 it was obtained by Perret et al. (4) by calcining homogeneous mixtures of Na_2CO_3, SnO_2, and $(NH_4)_2HPO_4$, in stoichiometric amounts, at 950°C for 20 h. The parameters calculated from powder diffractograms for the rhombohedral unit cell were: $a = 8.981 \pm 0.004$ Å and $\alpha = 56° 33'$. Slobodyanik et al. in 1981 (5) studied the reaction of tin dioxide with molten sodium metaphosphate finding that the complete conversion of tin dioxide into $NaSn_2(PO_4)_3$ at 1000-1100°C took about 20 h. The hexagonal unit cell dimensions calculated by these authors were: $a_h = 8.37$ Å and $c_h = 22.63$ Å

J.L. Rodrigo et al. (6) calculated the hexagonal unit cell parameters for $NaM_2(PO_4)_3$, with M = Ti, Sn, Zr, at room temperature, by least squares fitting. The values are shown in Table 1.

TABLE 1.

Lattice parameters "a" and "c" (Å) for $NaM_2(PO_4)_3$, with M = Ti, Sn, Zr at room temperature.

Sample	a(Å)	c(Å)	r_M (Å) [7]
$NaTi_2(PO_4)_3$	8.4876(3)	21.8008(1)	0.745
$NaSn_2(PO_4)_3$	8.5002(8)	22.5415(3)	0.83
$NaZr_2(PO_4)_3$	8.8103(3)	22.762(2)	0.86

It can be seen in this table that as the larger M atom is, larger "a" and "c" parameters are, which appears normal, i.e. substitution of a M atom by a larger cation expands the structure. However, it can be appreciated a value of "a" for Sn closer to that for Ti than for Zr; this would appear rather unexpected in view that the proximity between the radius of Sn and Zr which should lead closer parameters.

The purpose of the present work has been to study the evolution in the lattice parameters by indexing method, for the compositions $NaTi_{2-x}Sn_x(PO_4)_3$, with x = 0 to 2, in order to try to explain the "irregularity" observed. After that, the x-ray diffraction profiles of some compositions were deconvoluted following the Rietveld method.

The Rietveld method (8,9,10) was originally developed for the refinement of structures from neutron diffraction data, but it had been extended and applied (11,12,13) using powder x-ray diffraction data, and so solving the structure of those compounds that cannot be synthesized in the form of single crystals.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of the reaction mixtures

The compositions $NaTi_{2-x}Sn_x(PO_4)_3$, with x = 0, 0.5, 0.8, 1, 1.2, 1.5, and 2, were prepared following the ceramic method. Starting materials were industrial or C.P. grade titanium dioxide (anatase), tin dioxide, sodium carbonate and ammonium dihydrogenphosphate.

The preparation of the reaction mixtures was carried out by two stages. Firstly, amounts of TiO_2 and SnO_2 in the desired composition ratio were thoroughly homogenized in distilled water in a ball mill for 30 minutes. Afterwards, these mixtures were dried first at 110°C for two hours and then at 500°C for two hours. This previous mixing provides the homogeneous distribution of titanium and tin in the reaction mixtures; if the reaction mixture is prepared by a single stage unreacted oxides remain after calcining. In a second stage the titanium-tin oxides mixtures were added to the stoichiometric amounts of the other starting materials and all them were mixed and ground in acetone, in order to avoid the solution of reactants solubles in water, in a ball mill for 30 minutes. The wet homogenized mixtures were allowed to dry under the air for an hour.

2.2. Heat treatments

The reaction mixtures thus prepared were preheated in a refractory crucible with a Bunsen flame, until the evolution of gases stopped, and then heated at 800°C for 16 h. After being cooled to room temperature the materials formed were reground in a mortar with a pestle to ensure breaking of any aggregates and heated to 1100°C, where they were held for 16 hours. After each calcination, the samples, ground to a fine powder, were studied by x-ray diffraction to check the progress of the reaction. The peaks that did not match with those of NZP-type structure (3) were searched for the possible impurities such as TiO_2, SnO_2, TiP_2O_7 and SnP_2O_7 on JCPDS cards. In view of the results of this study some of the samples were heated at 1200°C for 16 h.

2.3. X-ray data collecting and treatment

The x-ray diffraction was carried out by powder method using monochromatic CuKα radiation.

For phases identification, the diffraction patterns were obtained at the scanning rate of 2° (2θ) per minute and interpreted by comparing with the data from literature. For accurate measurements the diffractograms were recorded at 1° or 0.5° (2θ) per minute between 10 and 160°(2θ).

All the samples were indexed for NZP-type structures on the basis of Hagman-Kierkegaard's data for $NaTi_2(PO_4)_3$ (3) from 10 to 60°(2θ). Rough cell parameters were calculated based on the indexed peaks (10 to 60° 2θ values). From these lattice parameters, diffraction patterns were calculated, which were used in the indexing of higher angle peaks (2θ = 60° and above). Then, accurate cell parameters were calculated on all the peaks by least-squares fitting.

After that, the x-ray diffraction profiles for the intermediate composition, $NaTiSn(PO_4)_3$, was deconvoluted following the Rietveld method. This method was already applied to the compound $NaTi_2(PO_4)_3$ (14) and $NaSn_2(PO_4)_3$ (15).

2.4. Structure analysis by Rietveld method

The XRPD pattern was collected using a step of 0.05° (2θ) between 10° and 150°(2θ) and a time of 8 seconds.

The x-ray diffraction pattern was analyzed by the Rietveld method (10), using the Wiles & Young (13) profile refinement program, which employs a Newton-Raphson algorithm to minimize the function $R = \sum w_i [y_i - y_{ci}]^2$ where y_i and y_{ci} are, respectively, the observed and calculated data points, and w_i is the statistical weight ($w_i = 1/\sigma_i$) .

For the refinement of the profile at room temperature the program was fed with the lattice parameters and the atomic positions calculated by J.L. Rodrigo et al.(14) for the compound $NaTi_2(PO_4)_3$.

A Pseudo-Voight function was chosen to generate the shape of the diffraction peaks. The background was estimated by linear interpolation between points corresponding to regions without reflections. The original Rietveld program had to be modified in order to handle the eccentricity of the sample.

The profile refinement was performed in the space group $R\bar{3}c$ (No.167). Ti and Sn atoms were considered to be statistically distributed [1:1] over the same crystallographic positions. The refinement process was developed in sequential steps: i) the scale factor, ii) the eccentricity and the hexagonal lattice parameters a and c, iii) the atomic positions, iv) the FWHM parameters (U, V, W) and the asymmetry factor, v) the isotropic temperature factors and, finally, vii) the anisotropic temperature factors. In the final stage, the complete structure was refined with 37 parameters.

3. RESULTS and DISCUSSION

The calcination at 800°C of the samples with compositions corresponding to x = 0.5 to 1.5 yields a NZP type phase as the major phase and SnP_2O_7, TiP_2O_7 and unreacted SnO_2 as minor phases. The samples with x = 0, $NaTi_2(PO_4)_3$, and x = 2, $NaSn_2(PO_4)_3$, subjected to the same heat treatment also contain these major and minor phases depending on its composition.

After calcination at 1100°C/16h, for the samples with x = 0, 0.5, 0.8, 1, and 1.5, and at 1200°C/16h, for the sample 1.2 and 2, an only phase is present, with NZP-type structure and composition $NaTi_{2-x}Sn_x(PO_4)_3$. It was indexed as rhombohedral and the hexagonal lattice parameters calculated by least squares fitting. Figure 1 shows the variation of these lattice parameters, obtained by indexing method, with composition.

As can be seen in figure 1 the value of parameter "a" increases with the Sn content reaching to a sharp change in the sample with x = 1, $NaTiSn(PO_4)_3$, from which it decreases of the Sn content increases until the value for the compound

$NaSn_2(PO_4)_3$. With regard to parameter "c", its value increases as the Sn proportion does throughout all the compositions, although the value for the compound $NaTiSn(PO_4)_3$ deflect from the straight line made by the other values of parameter "c".
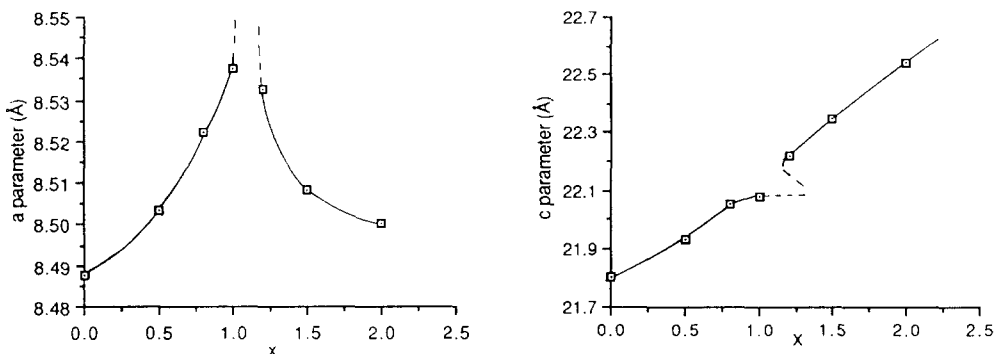

Fig. 1.Lattice parameters of $NaTi_{2-x}Sn_x(PO_4)_3$ with x = 0 to 2.

The Rietveld refinement of the sample $NaTiSn(PO_4)_3$ yielded the hexagonal lattice parameters a_h = 8.5302 ± 0.0002 Å, c_h = 22.1053 ± 0.0001 Å. These cell parameters and those obtained by indexing method (a = 8.5369(1) and c = 22.084(3)) are in good agreement, although there is some difference between both values for parameter c, which could be attributed to intrinsic characteristics of Rietveld method.

Final atomic positions appear in table 2 and anisotropic thermal parameters are given in table 3. From atomic positions the interatomic distances and angles were calculated, the most representative of which are listed in table 4.

Comparing interatomic distances and angles for the studied compound, $NaTiSn(PO_4)_3$, with those for the compound $NaTi_2(PO_4)_3$ (14) it can be observed that the [Ti/Sn]06 octahedron has been elongated. Effectively, the height of TiO6 octahedron is DC = 2.278 Å whereas that of [Ti/Sn]O6 octahedron is DC = 2.3166 Å.

TABLE 2

Atomic positions and occupancy factors for $NaTiSn(PO_4)_3$ at room temperature with e.s.d in parenthesis

	x	y	z	N
Na	0	0	0	0.1667
Ti/Sn	0	0	0.1456(1)	0.1667
P	0.2882(5)	0	0.2500	0.5000
O1	0.1784(8)	-0.0306(10)	0.1933(3)	1.0000
O2	0.1906(7)	0.1652(7)	0.0885(3)	1.0000

TABLE 3

Anisotropic thermal parameters ($\mathring{A}^2$) with e.s.d.'s in parenthesis and R-factors.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Na	0.009(1)	B_{11}	0.0006(3)	0.0045(8)	0	0
Ti/Sn	0.0008(1)	B_{11}	0.00012(3)	0.0004(8)	0	0
P	0.002(1)	0.004(9)	0.0004(1)	0.0008(7)	0.0002(1)	0.0004(2)
O1	0.003(1)	0.009(2)	0.0007(2)	0.004(2)	0.0007(5)	0(5)
O2	0(1)	0(2)	0.0003(2)	-0.004(1)	0.0009(5)	0.0006(4)

R_p= 9.50 R_{wp}= 12.33 R_e= 5.81 R_f= 2.95 R_B= 3.97

TABLE 4.

The interatomic distances ($\mathring{A}$) with e.s.d´s in parenthesis and angles for $NaTiSn(PO_4)_3$. (The labels used in the table are indicated in figure 2)

6(Na-O2)	= 2.483(6)
3(Ti/Sn-O1)	= 1.973(7)
3(Ti/Sn-O2)	= 1.983(6)
2(P - O1)	= 1.507(7)
2(P - O2)	= 1.530(6)

O_{2a} - Na - O_{2b} = 64.5	
O_{2a} - Na - O_{2g} = 115.5	

O_{1h} - Ti/Sn - O_{1d} = 94.1	
O_{2a} - Ti/Sn - O_{2b} = 83.8	
O_{1d} - Ti/Sn - O_{2a} = 91.2	
O_{1d} - Ti/Sn - O_{2b} = 172.7	
O_{1d} - Ti/Sn - O_{2c} = 90.4	

O_{1d} - P - O_{1k} = 115.3	
O_{1d} - P - O_{2l} = 111.6	
O_{1d} - P - O_{2m} = 104.5	
O_{2l} - P - O_{2m} = 109.3	
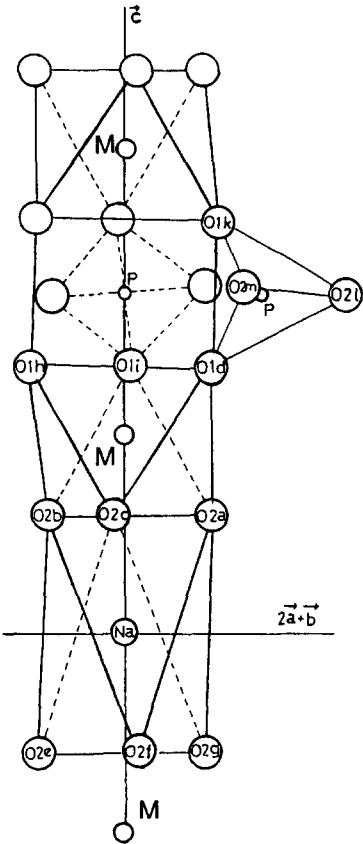
Fig.2 Projection of the $NaM_2^{IV}(PO_4)_3$, M^{IV} = Ti, Sn, showing the polyhedra along the axis c .

As Sn content increases (values x >1), the solid solutions behavior is similar to the compound with x = 2, $NaSn_2(PO_4)_3$, which presents the space group $R\overline{3}$ at room temperature. For the compound with x = 1.2, $NaTi_{0.8}Sn_{1.2}(PO_4)_3$, the Rietveld method applied with the space group $R\overline{3}c$ or $R\overline{3}$ doesn't give good results. In the execution with $R\overline{3}$ space group some isotropic temperature factors are negative, whereas the atomic positions exhibit values which induces to think about the possibility of that both $R\overline{3}c$ and $R\overline{3}$ phases be present at room temperature.

4. CONCLUSIONS

The variation of the lattice parameter "a" of $NaTi_{2-x}Sn_x(PO_4)_3$ with the composition presents a sharp change between the compositions with x values 1 and 1.2. This change divides solid solutions in two parts, one part rich in Ti(IV), $x \leq 1$, with a similar behavior that of the compound $NaTi_2(PO_4)_3$, and another part rich in Sn(IV), x>1, with the behavior similar that of the compound $NaSn_2(PO_4)_3$. This change doesn't take place in the lattice parameter "c" ingreasing its value as the Sn(IV) content increases in the two parts of the series.

The lattice parameters refined by Rietveld method, that is deconvoluting the x-ray diffraction profile, match very well those calculated by indexing method which implies least-squares fitting from the peak positions.

The results obtained by the Rietveld method confirm that, on the one hand, the behavior of the compound $NaTiSn(PO_4)_3$ is similar to that of the compound $NaTi_2(PO_4)_3$ with analogous interatomic distances and angles (14) and, on the other hand, the Ti(IV) and Sn(IV) atoms are statistically distributed over the same crystallographic position. The [Ti/Sn]O6 octahedra have been elongated in relation to the TiO6 octahedra due to the ionic radius of Sn(IV) (0.83 Å Shannon and Prewitt) somewhat greater than that of Ti(IV) (0.745 Å). The study of the compound $NaTiSn(PO_4)_3$ by x-ray diffraction doesn't show the existence of a superstructure, this results being confirmed by electrons diffraction.

In conclusion, the compositions $NaTi_{2-x}Sn_x(PO_4)_3$ with x = 0 to 2 present two structures which are related each other, one of them with $R\overline{3}c$ symmetry for the compositions rich in Ti(IV) ($0 \leq x \leq 1$) and the other with $R\overline{3}$ symmetry for the compositions rich in Sn(IV) ($1 < x \leq 2$).

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