HIGH TEMPERATURE NEUTRON DIFFRACTION STUDY
OF SODIUM DI-TIN TRI-PHOSPHATE

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ABSTRACT

High temperature high resolution neutron diffraction study of the crystal chemistry of $NaSn_2(PO_4)_3$ has been completed, at four different temperatures, applying the Rietveld method to the experimental neutron diffraction profile of a synthetic crystalline powder.

Below the phase transition (~860 K) the space group has been determined to be $R\bar{3}$ which changes to $R\bar{3}c$ in the high temperature phase. No chemical bond breaks through the transition.

The change in temperature makes the SnO_6 polyhedra rotate around the three fold axis in both structures. The PO_4 polyhedra rotate strictly around the two fold axis in the high temperature phase, but around the [0001] direction in the low temperature form.

MATERIALS INDEX: sodium, tin, phosphates, [NZP] structure.

1. INTRODUCTION.

$NaSn_2(PO_4)_3$ presents a fast and reversible second order phase transition about 860 K (1). Both phases above and below the transition point are rhombohedral and, as the lattice thermal expansion of the high temperature phase is like those of $NaTi_2(PO_4)_3$ and $NaZr_2(PO_4)_3$, it has been suggested that these three phases are isostructural (1), with [NZP] structure (2). Lattice thermal expansion studies on a lot of compounds has already carried out in this family because of their application to ceramics with adjustable and very low thermal expansion (3-6). Although the mechanism that controls the expansion coefficients for some [NZP] materials is very well known, and the model has been tested for $NaTi_2(PO_4)_3$ (6) using a computer model (2, 7), the low temperature form of $NaSn_2(PO_4)_3$ presents a different thermal expansion behaviour and no explanation has been given for it, nor for its structure.

This transition does not show up in the analogous compounds of Ti and Zr, at least in the range of the temperatures studied (RT to 1100°C). Being the size of the Sn^{4+} ion between those of Ti^{4+} and Zr^{4+}, it has been suggested that their different electronic configuration is, probably, responsible for the existence of such a phase transition.

2. EXPERIMENTAL RESULTS.

Powder crystalline samples of $NaSn_2(PO_4)_3$ have been prepared from mixtures of SnO_2, $NH_4H_2PO_4$ and Na_2CO_3 in stoichiometric proportions and heated, as described elsewhere (1). X ray diffractograms showed a single phase and no difference with those prepared earlier.

The first attempts to solve the structure from X-ray diffraction profiles at room temperature, using the structural parameters of the analogous compounds of Ti and Zr as a model, were fruitless. The only known fact about the structure was that the c-glide plane, present above the transition point, is lost in the low temperature form. After having adjusted the background, the scale factor, the zero point, the eccentricity, and the lattice parameters (hexagonal axes), only the position of Na, Sn and P atoms could be accepted. Regardless the number of cycles of refinement, the lighter atoms, the oxygens, never got to reliable positions. Negative isotropic factors and big statistic deviations appeared again and again in the final cycle. This way, only the centre of the polyhedra NaO_6, SnO_6, PO_4 were known. As the thermo-mechanical properties in these materials lye mainly in the rotations of such polyhedra, we have had to look for a more sensible technique able to locate precisely the oxygens.

Neutron diffraction has been carried out using the **D2B** instrument at the Institute Laue Langevin (8). This machine is a high resolution, high intensity diffractometer installed on the thermal neutron beam H11 (cut-off 0.60 Å). Incident and focusing 5' Soller collimators provide the high resolution without loosing intensity on the beam. The monochromator is a crystal of Ge that selects a wavelength of 1.594 Å. The 64 ^3He detectors are located at intervals of 2.5° covering 160°.

The neutron diffraction profile was collected from 10° to 160° (2θ) at intervals of 0.05°. The sample was kept in a high temperature furnace and four profiles have been taken at 299 K, 673 K, 873 K and 1073 K.

Neutron diffraction profiles have been fitted according to the Rietveld method using the STRAP program at ILL computers and an improved version at the CIUV IBM 3090. The structural model used in the starting parameters came from the approximated results obtained from the previous studies.

Only the high temperature data from the compound above their transition point have been easily refined in the $R\bar{3}c$ space group. At the first trials, data from the low temperature form, below their transition point, could not be refined in the $R\bar{3}$, R3m nor the R32 space groups. Instead, the only group that started yielding a lower Bragg R-factor was the R3 space group. When the convergence was reached under this space group, an analysis of the output structural parameters showed the existence of a very probable inversion centre. So, remodelling the input structure, according to this possibility, the final refinement has been carried out using the $R\bar{3}$ space group, improving the fitting sensibly. The parameters obtained are in Table 1. The derived r.m.s. of the atoms (better than the anisotropic thermal parameters) have been collected in Table 2.

TABLE. 1. Structural refinement results for $NaSn_2(PO_4)_3$ neutron diffraction data, at different temperatures. T= Temperature(°C), S.P.= Space Group, R_B= Bragg R-factor (in %), a/c=hexagonal axes parameters. The atomic coordinates, x,y,z, are given with the σ of the last figure between parenthesis.

T (°C)	26			400			600			800		
S.G.	$R\bar{3}$			$R\bar{3}$			$R\bar{3}c$			$R\bar{3}c$		
R_B	3.44			4.73			5.79			6.18		
a(Å)	8.51324(8)			8.5481(1)			8.5704(1)			8.5659(1)		
c(Å)	22.5106(3)			22.5772(4)			22.6173(4)			22.6902(5)		
Na1	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000	.0000
Na2	.0000	.0000	.5000	.0000	.0000	.5000						
Sn1	.0000	.0000	.1478(2)	.0000	.0000	.1480(4)	.0000	.0000	.1472(1)	.0000	.0000	.1474(1)
Sn2	.0000	.0000	.6453(2)	.0000	.0000	.6458(4)						
P	.2909(3)	-.0010(3)	.2496(2)	.2909(4)	.0004(6)	.2498(3)	.2904(2)	.0000	.2500	.2902(2)	.0000	.2500
O1	.1644(4)	-.0542(3)	.1966(1)	.1692(7)	-.0462(6)	.1961(2)	.1775(2)	-.0327(2)	.1948(1)	.1761(2)	.0345(3)	.1952(1)
O12	.0076(3)	-.1941(4)	.6924(1)	.0181(6)	-.1866(6)	.6935(2)						
O2	.2065(3)	-.1468(3)	.0910(1)	.2015(5)	.1522(5)	.0912(2)	.1914(2)	.1678(2)	.0900(1)	.1921(2)	.1685(2)	.0907(1)
O22	-.1889(3)	-.1741(3)	.5876(1)	-.1835(5)	-.1805(5)	.5884(2)						

TABLE. 2. The three r.m.s. (Å) for each atom in $NaSn_2(PO_4)_3$ as calculated from the anisotropic thermal parameters, at every temperature. The orientation of these ellipsoid principal axes are omitted. Significantly small r.m.s. of flattened ellipsoids are underlined.

T (°C)	26			400			600			800		
Na1	.2402	.2402	_.0848_	.3608	.3608	_.0663_	.3883	.3883	.1726	.4574	.4574	.1694
Na2	.2125	.2125	.1451	.3334	.3334	_.2114_						
Sn1	.0883	.0883	.0734	.1123	.1123	.1102	.1300	.1300	.1257	.1391	.1391	.1399
Sn2	.0857	.0857	.1110	.1228	.1228	.1325						
P	.0805	.1029	.0584	.0816	.1419	.1063	.1202	.1543	.0957	.1338	.1603	.1084
O1	.1577	.1727	_.0534_	.2200	.2479	_.0810_	.2618	.2296	.0965	.2820	.2443	.1103
O12	.1280	.1587	_.0582_	.1967	.2168	_.0787_						
O2	_.0470_	.1025	.1520	_.0841_	.2049	.1559	.1036	.2446	.1873	.1111	.2639	.2047
O22	.1244	_.0535_	.1007	.1967	_.0750_	.1582						

3. DISCUSSION.

The phase transition in $NaSn_2(PO_4)_3$ occurs with relatively little change inside the Na, Sn and P polyhedra, the main change lies outside. Particularly, the phosphate group looses its 2-fold symmetry during the transition from the $R\bar{3}c$ to the $R\bar{3}$ space group. In the high temperature form, the two-fold axes $[2\bar{1}\bar{1}0]$ fix the possible rotation of the phosphate groups to such axes(6), but in the low temperature form, there is no restriction and the rotation of the O21-O22 edge has a component around the [0001] direction nine times bigger than the component around the $[\bar{2}110]$ direction (the only rotation present in the $NaTi_2(PO_4)_3$ and $NaZr_2(PO_4)_3$ compounds). In figure 1, the projection of a fragment of the structure ($0 \le z \le 1/4$) in the [0001] direction shows the rotation of the phosphate groups around this direction in the low temperature form.
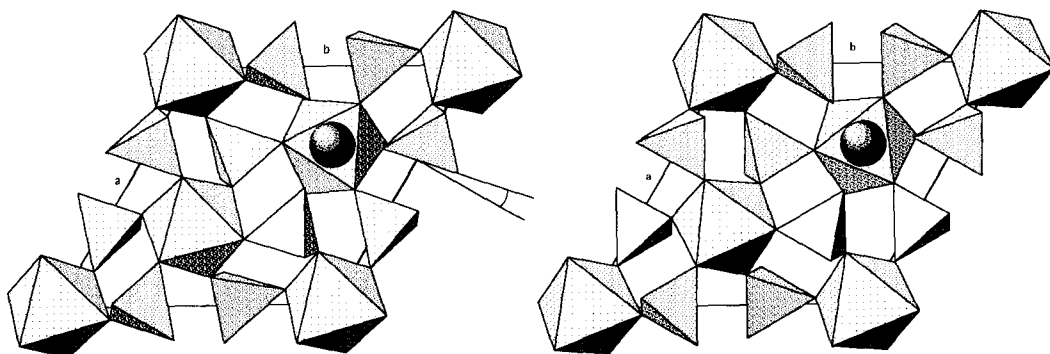
Figure 1. Projection of the structures of $NaSn_2(PO_4)_3$ at 26°C showing the tilting of the edge O21-O22 of the phosphate (to the left) and at 800°C (to the right).

The magnitude of the rotations is plotted vs. the temperature in figure 2. The component of the rotation of the edge O11-O12 in the phosphate group out of the $(\bar{2}110)$ plane is very small, but that of the edge O21-O22, around the [0001] direction is big. This rotation takes place along with the rotation of the octahedra around the three-fold axes. In figure 3, the variation of the $\phi1$ and $\phi2$ angles are represented for the second SnO_6 octahedra in $NaSn_2(PO_4)_3$ together with the corresponding values found for $NaTi_2(PO_4)_3$ (6) and $NaZr_2(PO_4)_3$ (9). Rotations in the first SnO_6 octahedra are somewhat smaller. These rotations explain the nature of the phase transition, but they are not enough to understand why it occurs in the Sn compound and not in the Ti and Zr analogs.

In figures 4 and 5, the distortions inside the octahedra are plotted versus the temperature to show how regular the TiO_6, SnO_6 and ZrO_6 polyhedra are. The departure of the O-M-O angles from 90° in the octahedra can be taken as a measure of the distortion, and the mean value used in figure 4 has been calculated using the formula:

$$D=(\sum_{i,j} |\alpha_{ij}\text{-}90| \;)/12$$

The derived distortion, D, in the high temperature form of the Sn material decreases with the temperature in the same way as in the Ti and the Zr materials, but the values do not interpolate according to the way the M-O bonds do. It is apparent that the SnO_6 octahedra present a higher distortion. In the low temperature form of the Sn material, both SnO_6's (no longer related by the two-fold axis) behaves very differently. In one, Sn1, the distortion is smaller and in the other bigger.

In figure 5, the axial torsions in the octahedra, $\phi2$-$\phi1$, show a similar behaviour. Torsion in the high temperature form of the Sn material increases with the temperature in the same way as in the Ti and the Zr materials, but the values do not interpolate according to the way the M-O bonds do. Torsions, in fact, suffer an inversion after they reach a zero value, following a regular variation. In the low temperature form of the Sn material, both SnO_6's suffer different and opposite torsions.

The anisotropy of the thermal vibrations of sodium atoms in $NaSn_2(PO_4)_3$ at room temperature is described by two different flattened ellipsoids. The ratio of the r.m.s. for Na1 is, .2402/.0848=2.833, and that of the Na2 is, .2125/.1451=1.465. The constriction along the [0001] direction over the vibrations in Na1 is bigger than over the vibrations in Na2. The ratio of the r.m.s. for the Na in $NaZr_2(PO_4)_3$, .252/.122=2.066, is in between. Also other flattened ellipsoids appear in O1 and O12 in [0001] direction, and in O2 and O22 in [$2\bar{1}10$] direction. This constrictions go along the principal tensions or driving forces responsible for the thermal expansion.

CONCLUSION.

The present work has proved that a close model of the structure is not enough to get a convergency in the refinement following the Rietveld method. To solve the structure of the low temperature form of $NaSn_2(PO_4)_3$, it has been necessary to obtain the Neutron diffraction profile because it depends on the oxygens contribution much more than what the X-ray diffraction profile does. Even in the refinement of the neutron data, it has been necessary to start with a model with lower symmetry than that used in the last refinement, i.e., a bigger freedom in the atom parameters has been required in order to achieve suitable changes during the first cycles of refinement. Nevertheless, the Rietveld method is a unique method to study the structural aspects of the powder and polycrystalline materials.
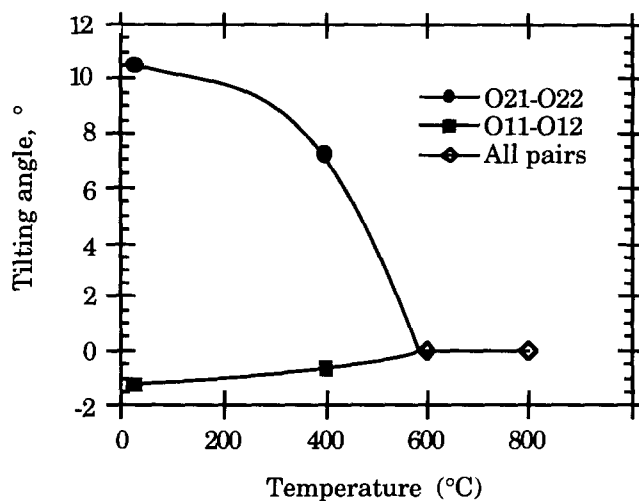
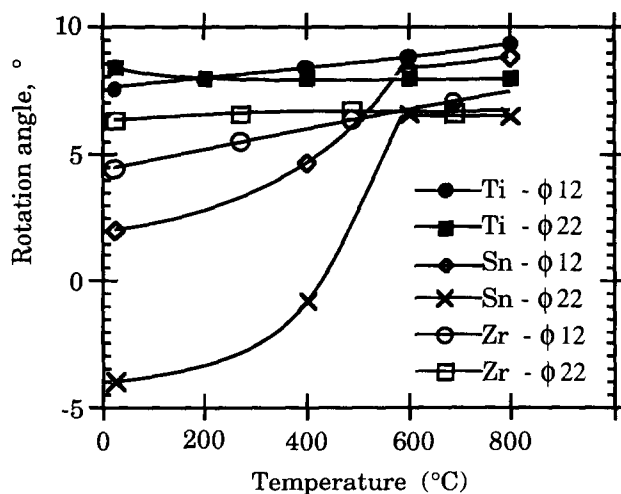Figure 2.   Tilting of the PO_4 tetrahedron edges out of the $(2\bar{1}\bar{1}0)$ plane,   in $NaSn_2(PO_4)_3$.

Figure 3. Rotation of the octahedra edges in the $NaM_2(PO_4)_3$ with M={Ti,Sn,Zr}. $\phi 2$ and $\phi 1$ were defined for $NaTi_2(PO_4)_3$ in reference (6), here, the second index applies to the two non-symmetric SnO_6 below the transition point.
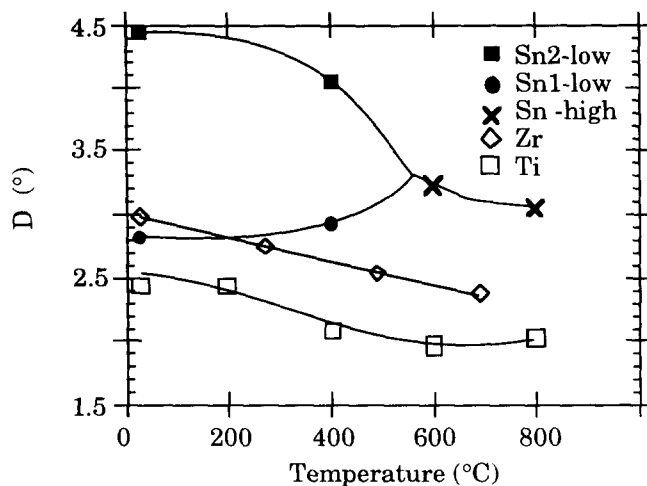
Figure 4. Mean distortion of the O-M-O angles in the octahedra for the NaM$_2$(PO$_4$)$_3$ materials with M={Ti,Sn,Zr}.
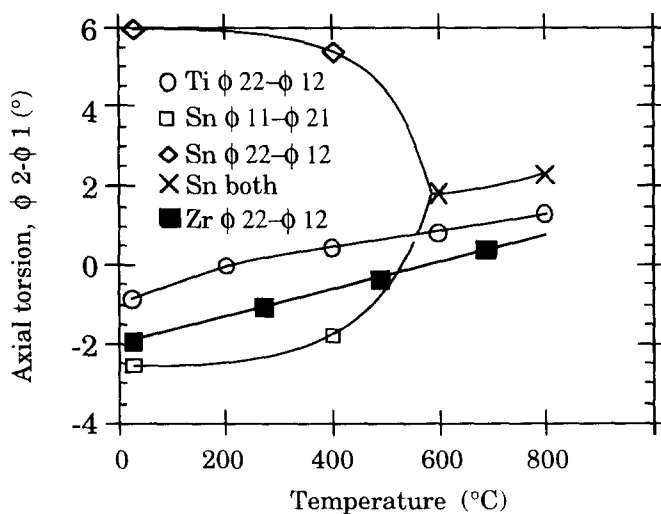
Figure 5. Axial torsions in the octahedra of the NaM$_2$(PO$_4$)$_3$ with M={Ti,Sn,Zr}.

The global analysis of the structure at the four temperatures reveals that the structural transition is due to a fast rotation of the SnO$_6$ and PO$_4$ polyhedra around axes along the [0001] direction breaking the two fold axis in the R$\bar{3}$c space group that exists in the structure above the transition point.

The fact that the distortions in the TiO_6 and ZrO_6 octahedra are lower than those present in the SnO_6 octahedron, together with the ability of this octahedron to increase its distortion below the transition point are the key to understand the chemical nature of this phase transition. They suggest that the chemical bond between the metal and the oxygens, based in the d^2sp^3 hybridization of the metal, gets a bigger contribution from the 'd orbitals' in the case of Ti^{4+} and Zr^{4+} than in the case of Sn^{4+}, which is a post-transition metal with all the 'd orbitals' occupied and unable to help in the bond to the neighbouring oxygens. The 'd orbital' contribution helps the bonds to keep directed towards the corners of a regular octahedron. And so, the bigger rigidity of the O-M-O bond angles in the case of Ti^{4+} and Zr^{4+} than in the case of Sn^{4+}, is the driving force that avoids the phase transition in the two first cases. In the case of Sn^{4+}, it is easier to bend the O-Sn-O and Sn-O-P bonds to get a somewhat close-packed structure below the transition point.

Apparently, the usability of $NaTi_2(PO_4)_3$ and $NaZr_2(PO_4)_3$ compounds to build ceramics with very low thermal expansion lies not only in the topology of bonds in the [NZP] structure, but also in the relative rigidity of the O-M-O bond angles, to prevent the skeleton to distort and become closer-packed.

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