

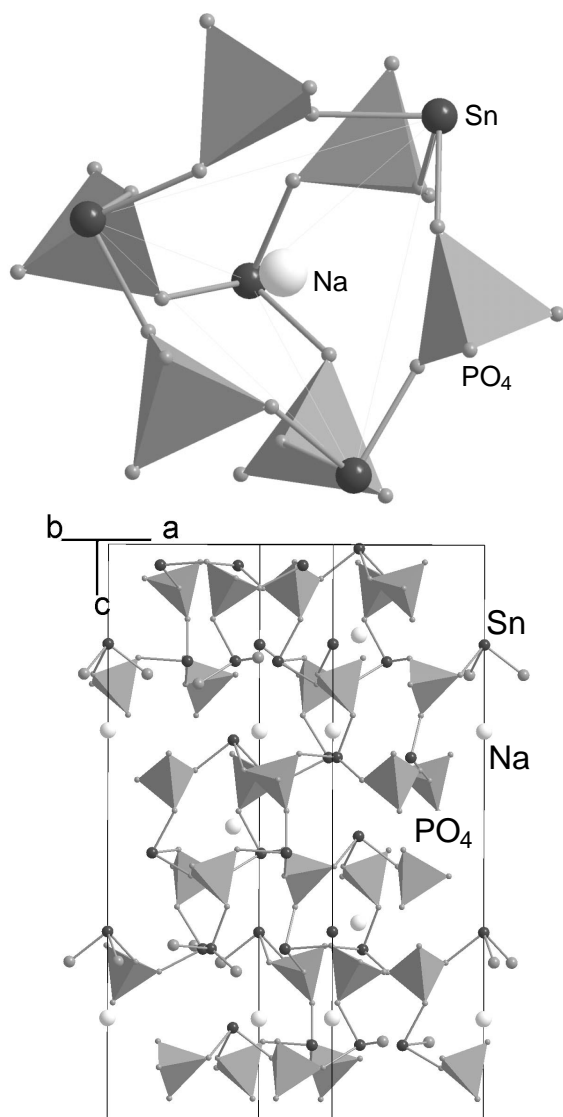
# Crystal structure of sodium tetratin(II) triphosphate, $\text{NaSn}_4(\text{PO}_4)_3$

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## Abstract

$\text{NaO}_{12}\text{P}_3\text{Sn}_4$ , trigonal,  $R3c$  (no. 161),  $a = 9.594(1) \text{ \AA}$ ,  $c = 24.186(5) \text{ \AA}$ ,  $V = 1927.8 \text{ \AA}^3$ ,  $Z = 6$ ,  $R_{\text{gt}}(F) = 0.023$ ,  $wR_{\text{ref}}(F^2) = 0.056$ ,  $T = 293 \text{ K}$ .

## Source of material

The titled compound was obtained by mild hydrothermal method. Starting materials were of analytical grade and used without further purification. The mixtures of 0.226 g  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , 0.432 g

$\text{H}_3\text{BO}_3$ , 2.147 g  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  were prepared and dissolved in distilled water with the molar ratio of 1:7:6. The pH value of the solution was about 1.5. The mixtures were sealed in glass tubes of about 20 cm in length. The filling of the solution was about 30 % of the tube volume. The glass tubes were placed in an oven and the temperature was increased slowly to about 140 °C and reacted for 2 weeks before cooling to room temperature. The reaction was under autogenous pressure. The colorless crystals with trigonal prism shape were grown from solution in a glass tube.

## Discussion

The compounds in alkali metal-tin phosphate systems have attracted great interest due to their diverse properties such as non-linear optical properties. Although quite some compounds have been reported in potassium and ammonium system [1-4], there is only one in sodium system, namely  $\text{NaSn}_2(\text{PO}_4)_3$  with Sn(IV) valence and there is no Sn(II) compound reported up to now to our knowledge. However, the analogous Pb(II) compound,  $\text{NaPb}_4(\text{PO}_4)_3$ , was published in  $P6_3/m$  [5], differently from the space group reported here.

The title compound with a Sn(II) valence represents a new structure type. Sodium shows nine-fold coordination with oxygen atoms (figure, top). The coordination tetrahedron around the P atom is quite regular with the average interatomic distance of 1.534 Å. The average bond angle is 109.5° (range from 107.8° to 111.3°). All the average P—O bond distances and O—P—O bond angles are consistent with those typical values observed in phosphates. The coordination number of tin is 3 with the mean distances of Sn—O as 2.088 Å and 2.108 Å. On the basis of bond strength calculations [6], the bond valence sums for P and Sn atoms are all close to +5 and +2, respectively. The structure can be described as  $[\text{NaO}_{12}]\text{Sn}_4$  groups linked by isolated phosphates into a three-dimensional structure (figure, bottom). The  $[\text{NaO}_{12}]\text{Sn}_4$  group forms a tetrahedral arrangement, and  $\text{PO}_4$  groups form octahedral arrangement with each capping the six edges of the former tetrahedron. The Flack  $x$  parameter of  $-0.03(4)$  confirms the absolute structure.

**Table 1.** Data collection and handling.

Crystal:	colorless trigonal prism, size $0.04 \times 0.07 \times 0.07 \text{ mm}$
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
$\mu$ :	$81.47 \text{ cm}^{-1}$
Diffractometer, scan mode:	Rigaku AFC7-CCD, $\varphi/\omega$
$2\theta_{\text{max}}$ :	$55.94^\circ$
$N(hkl)_{\text{measured}}$ , $N(hkl)_{\text{unique}}$ :	1540, 796
Criterion for $I_{\text{obs}}$ , $N(hkl)_{\text{gt}}$ :	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$ , 786
$N(\text{param})_{\text{refined}}$ :	62
Programs:	SHELXL-97 [7], DIAMOND [8]

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**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
Na(1)	6 <i>a</i>	0	0	0.0426(2)	0.025(1)	<i>U</i> <sub>11</sub>	0.026(3)	0.0126(7)	0	0
Sn(1)	6 <i>a</i>	2/3	1/3	0.02428(3)	0.0239(3)	<i>U</i> <sub>11</sub>	0.0160(4)	0.0119(1)	0	0.0
Sn(2)	18 <i>b</i>	0.59256(4)	0.73008(4)	0.99030(2)	0.0155(2)	0.0131(2)	0.0218(2)	0.0062(2)	-0.0008(2)	0.0007(2)
P(1)	18 <i>b</i>	0.6726(2)	0.7885(2)	0.11802(7)	0.0126(6)	0.0115(6)	0.0163(7)	0.0055(5)	0.0034(5)	0.0007(5)
O(1)	18 <i>b</i>	0.8119(6)	0.7300(6)	0.9942(2)	0.028(2)	0.032(2)	0.015(2)	0.021(2)	-0.001(2)	-0.007(2)
O(2)	18 <i>b</i>	0.8391(5)	0.8218(6)	0.1371(3)	0.015(2)	0.022(2)	0.044(3)	0.010(2)	-0.005(2)	-0.007(2)
O(3)	18 <i>b</i>	0.7126(6)	0.9409(5)	0.9427(2)	0.031(2)	0.014(2)	0.024(3)	0.013(2)	0.002(2)	0.003(2)
O(4)	18 <i>b</i>	0.6895(6)	0.8726(5)	0.0621(2)	0.029(2)	0.015(2)	0.019(2)	0.010(2)	0.007(2)	0.001(2)

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