

# Crystal Structure of Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub>: Reinvestigation

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Received December 14, 1999; in revised form March 7, 2000; accepted March 10, 2000

**In the context of a detailed investigation of the luminescent properties of the Na<sub>2-x</sub>Ag<sub>x</sub>ZnP<sub>2</sub>O<sub>7</sub> compounds, the structure of the pure sodium phosphates “revisited.” The crystal structure of Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> has been determined by X-ray diffraction using single crystals. A new model explaining the actual large unit cell ( $a = b = 2177.1(3)$  pm,  $c = 1028.5(2)$  pm,  $P4_2/n$ ,  $Z = 32$ ) was determined by assuming the existence of twins. The structure is made up of [ZnP<sub>2</sub>O<sub>7</sub>] layers consisting of corners sharing [P<sub>2</sub>O<sub>7</sub>] groups and [ZnO<sub>4</sub>] tetrahedra, and the sodium atoms are located between the layers in 7- or 8-fold coordinated sites. This model is discussed with respect to the crystal chemistry of the monovalent cation zinc phosphate. © 2000 Academic Press**

## 1. INTRODUCTION

The spectroscopic properties of silver(I) in insulators have been largely investigated in both crystalline and glassy forms due to the strong emission bands appearing in the UV–visible range (1–3). In the particular case of the “Ag<sub>2</sub>O–ZnO–P<sub>2</sub>O<sub>5</sub>” system the luminescent properties of the crystalline diphosphate Ag<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> were remarkable by the unusual silver(I) pair emission provided by Ag<sup>+</sup>–Ag<sup>+</sup> centers where the interatomic distance is comparable to the silver distance in metal. Actually such results have required the analysis of the optical properties of Na<sub>2-x</sub>Ag<sub>x</sub>ZnP<sub>2</sub>O<sub>7</sub> compounds in order to determine the influence of silver concentration on the luminescent parameters (4). In this context it was of interest to have an exact description of the structure of the pure sodium phosphate assuming a progressive replacement of Na<sup>+</sup> by Ag<sup>+</sup>.

Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> was originally mentioned by Klement (5), but single crystals were prepared by Majling *et al.* (6). These authors described the Weissenberg photographs by a system of strong reflections assuming a tetragonal cell ( $a_0 = 769.19$  pm,  $c_0 = 1027.26$  pm) in addition to a system of weak reflections corresponding to a larger unit cell

$a = 2\sqrt{2}a_0$ ,  $c = c_0$ . The first model of the crystal structure was published by Erragh *et al.* (7) using the small unit cell with the tetragonal space group  $P4_2/mmm$ . The atomic arrangement is made up of layers containing [ZnO<sub>4</sub>] tetrahedra sharing corners with [P<sub>2</sub>O<sub>7</sub>] groups. The sodium atoms are located between the layers. The refinement of the crystal structure was carried out by assuming a disordered position of the bridging oxygen of the diphosphate group about the mirror plane of the layer.

The present investigation presents a new structural model for Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub>. This model is discussed in the context of the large unit cell.

## 2. PREPARATION PROCESS

Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> compounds were synthesized by heating stoichiometric quantities of Na<sub>2</sub>CO<sub>3</sub>, ZnO, and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>. The reagents are carefully mixed and progressively heated up to 600°C to allow ammonia, water, and carbon dioxide vapors to evolve. After a final grinding, the powder is heated at 720°C for 36 h. The obtained powders are white. DTA performed on Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> shows a congruent melting point at about 796°C. Small single crystals of this phase were grown from samples melted at 850°C and slowly cooled (3°C h<sup>-1</sup>) to room temperature.

## 3. STRUCTURE STUDY

### 3.1. Preliminary Investigations

Single crystals of Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> were selected by optical examination. Weissenberg and Buerger photographs are consistent with  $4/mmm$  Laue class of tetragonal symmetry. Actually, all the mean reflections are compatible with a small cell (SC)  $a_1 = b_1 = 768.5$  pm and  $c_1 = 1026.5$  pm, but a great number of weak reflections need to consider a large cell (LC)  $a_2 = b_2 = 2a_1\sqrt{2}$  and  $c_2 = c_1$ , corresponding to the matrix transformation:  $\vec{a}_2 = 2\vec{a}_1 + 2\vec{b}_1$ ,  $\vec{b}_2 = -2\vec{a}_1 + 2\vec{b}_1$ , and  $\vec{c}_2 = \vec{c}_1$ .

Data collection with Bruker SMART CCD diffractometer using MoK $\alpha$  radiation and an LC was done for all the reciprocal space (12,670 reflections with  $I > 2\sigma(I)$ ). The

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**TABLE 1**  
Crystallographic Data and Data Collection Conditions for Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub>

Crystal data	
Formula	Na <sub>2</sub> ZnP <sub>2</sub> O <sub>7</sub>
Formula weight	285.29 g
Crystal system	Tetragonal
Space group	<i>P</i> 4 <sub>2</sub> / <i>n</i>
Unit cell dimensions	<i>a</i> = 2177.1(3) pm <i>b</i> = 2177.1(3) pm <i>c</i> = 1028.5(2) pm
Volume	4874.8 (14) × 10 <sup>6</sup> pm <sup>3</sup>
<i>Z</i>	32
Density (calculated)	3.110 Mg m <sup>-3</sup>
Wavelength	MoK $\alpha$ radiation (71.070 pm)
Cell parameters from	676 reflections ( $\theta = 5\text{--}23^\circ$ )
Temperature	293(1) K
Absorption coefficient	4.69 mm <sup>-1</sup>
<i>F</i> (000)	4416
Crystal size	0.075 × 0.075 × 0.175 mm
Color	Colorless
Data collection	
Diffractometer	Bruker SMART CCD
Scans	$\omega$ rotation with narrow frames (0.3°) for three $\phi$ values (0°, 88° and 180°)
Absorption correction	Empirical (SADABS; Sheldrick, 1997)
$\theta$ range for data collection	4.61–23.31°
Index range	–24 ≤ <i>h</i> ≤ 19, –23 ≤ <i>k</i> ≤ 24, –10 ≤ <i>l</i> ≤ 11
Reflections collected	18,168 (12,670 with <i>I</i> > 2 $\sigma$ ( <i>I</i> ))
Independent reflections	2833 (with <i>I</i> > 2 $\theta$ ( <i>I</i> ))
<i>R</i> <sub>INT</sub>	0.035
Refinement	
Program	SHELXL 93 (14)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	2833/0/215
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.054, w <i>R</i> <sub>2</sub> = 0.093
<i>S</i> (goodness-of-fit on <i>F</i> <sup>2</sup> )	0.994
( $\Delta/\sigma$ ) <sub>max</sub>	0.001
Extinction coefficient	0.00095(3)
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$	0.92 and –0.63 10 <sup>-6</sup> e pm <sup>-3</sup>

unit cell parameters were refined from 676 reflections in the range  $5^\circ < \theta < 23^\circ$ . Table 1 lists the crystal data and the experimental conditions for data collection and structure refinement. At this stage, after data reduction with SAINT (8) and empirical absorption correction with SADABS (9), *R*<sub>INT</sub> values were respectively 0.035 and 0.036 for the Laüé classes 4/*m* and 4/*mmm*.

### 3.2. Structural Approach in the Context of the “small cell” (SC)

From the 12,670 observed reflections in (LC)<sub>2</sub>, 2122 are compatible with (SC)<sub>1</sub>:  $h_1 = (h_2 - k_2)/4$ ;  $k_1 = (h_2 + k_2)/4$ ;

**TABLE 2**  
Atomic Coordinates (×10<sup>4</sup>) and Equivalent Displacement Parameters for the SC Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> Model

Atoms	Positions	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (pm <sup>2</sup> )
Zn	4 <i>d</i>	0	5000	2500	226(7)
Na1	4 <i>f</i>	3589(4)	3589(4)	0	283(12)
Na2	4 <i>g</i>	3024(4)	3024(4)	5000	324(13)
P	8 <i>j</i>	1364(2)	1364(2)	2117(2)	208(8)
O1	4 <i>e</i>	0	0	157(8)	810(5)
O2	8 <i>j</i>	1353(5)	1353(5)	3567(5)	272(14)
O3	16 <i>k</i>	0773(8)	3028(6)	1484(4)	590(2)

$l_1 = l_2$ . For these 2122 reflections the only extinction rule that can be considered is (0*kl*):  $k + l = 2n + 1$  (except for 58 weak reflections with  $2\sigma(I) < I < 15\sigma(I)$ ). The possible space groups in 4/*mmm* Laüé class are *P*4<sub>2</sub>/*mmm*, *P* $\bar{4}$ *n*2, and *P*4<sub>2</sub>*nm*. A solution can be found in the centric space group *P*4<sub>2</sub>/*mmm* with 259 unique reflections using Patterson function deconvolution and heavy atoms methods. Refinements with anisotropic atomic displacement parameters converged to *R*<sub>1</sub> = 0.034, w*R*<sub>2</sub> = 0.087, *S* = 1.203, and  $\Delta\rho_{\text{Max}} = 0.52 \times 10^{-6}$  e pm<sup>-3</sup>. The corresponding atomic parameters are reported in Table 2, and a projection view along  $\bar{c}$  is shown in Fig. 1.

These results can be compared with the model of Erragh *et al.* (7). The atomic coordinates are very close with deviations less than 2 $\sigma$  except for the bonding oxygen (O1)

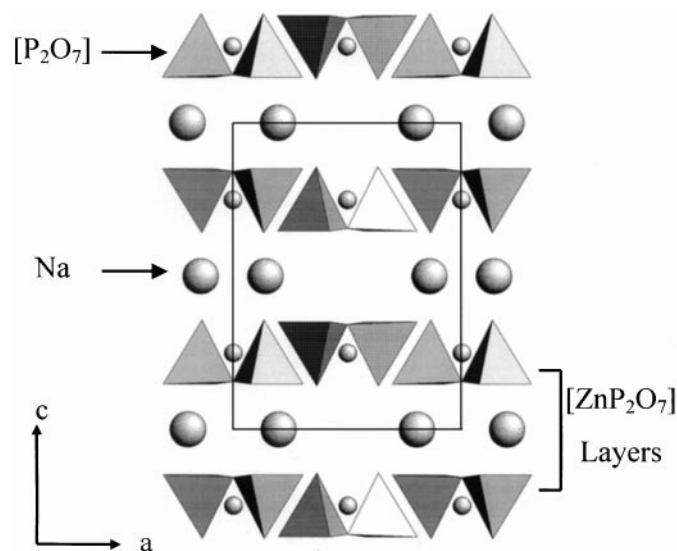


FIG. 1. Projection of the SC Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> structure on the (*a,c*) plane.

of the  $[\text{P}_2\text{O}_7]$  entity, which is located between the split position (with a site occupancy of 0.5) previously reported. Moreover, values of displacement parameters that are too high for O1 and O3 are also observed. Therefore it was necessary to consider a model involving the large unit cell.

### 3.3. Structure Determination with the "Large Cell" (LC)

The space group of the LC was determined assuming the following criteria:

(i) The only extinction rules taken into consideration are

$$(hk0) \quad h + k = 2n + 1$$

$$(00l) \quad l = 2n + 1$$

$$(0kl) \quad k = 2n + 1 \text{ (excepted for few weak reflections with } 2\sigma(I) < I < 4\sigma(I)\text{)}$$

(ii) The approximate model described in the previous paragraph with the SC excluded the presence of a 4-fold axis in the structure.

Accordingly, the only possible space group is  $P4_2/n$  (No. 86) in  $4/m$  Laüé class. From the reduced cell structural approach ( $P4_2/mnm$ ,  $Z = 4$ ), a new model was generated involving the (LC) cell, the  $P4_2/n$  space group and  $Z = 32$  (Table 3).

Assuming anisotropic displacement parameters for Zn atoms and isotropic ones for all others, refinement with 2833 independent reflections and 214 free parameters lead to  $R_1 = 0.096$  and  $wR_2 = 0.151$ . This result carried out with the  $P4_2/n$  space group is not consistent with the apparent  $4/mmm$  Laüé class and needs to introduce a new hypothesis: the existence of twins with a matrix twin 010, 100, 001 (or equivalent). Then the refinement converges with a division into equal parts of the two twinning entities ( $4/mmm$  appearance) and leads to  $R_1 = 0.053$ ,  $wR_2 = 0.093$ , and  $S = 0.994$ . Atomic coordinates and isotropic (or equivalent) displacement parameters are reported in Table 4. Figure 2 shows the

**TABLE 3**  
Transformation of the SC  $\text{Na}_2\text{ZnP}_2\text{O}_7$  into the LC  $\text{Na}_2\text{ZnP}_2\text{O}_7$  Model

Atoms	Number of independent positions		Number of total positions	
	SC	LC	SC	LC
Zn	1	6	4	32
Na	2	8	8	64
P	1	8	8	64
O	3	28	28	224

**TABLE 4**  
Atomic Coordinates ( $\times 10^4$ ) and Displacement Parameters

Atoms	Positions	x	y	z	$U_{\text{iso}}/U_{\text{eq}}$
Zn(1)	2a	2500	2500	2500	163(9)
Zn(2)	2b	7500	7500	2500	147(9)
Zn(3)	4e	7500	2500	2466(2)	156(5)
Zn(4)	8g	5074(1)	5039(1)	2500(2)	159(5)
Zn(5)	"	4944(1)	7486(1)	2509(2)	142(5)
Zn(6)	"	2534(1)	4949(1)	2499(2)	147(5)
Na(1)	"	4460(2)	6229(3)	0002(7)	26(1)
Na(2)	"	4733(2)	6270(3)	4930(8)	24(1)
Na(3)	"	3837(2)	2753(2)	0078(6)	18(1)
Na(4)	"	3743(3)	3044(2)	4995(8)	24(1)
Na(5)	"	6958(2)	3741(3)	0004(9)	27(1)
Na(6)	"	7243(2)	3689(3)	4906(8)	29(1)
Na(7)	"	3792(3)	4440(2)	4987(8)	22(1)
Na(8)	"	6280(3)	5263(2)	0063(7)	21(1)
P(1)	"	6979(2)	6213(2)	2163(4)	13(1)
O(12)	"	7130(4)	5599(5)	1484(10)	20(2)
O(13)	"	7380(4)	6709(4)	1624(9)	23(2)
O(14)	"	6941(5)	6195(4)	3601(11)	20(3)
OB12	"	6302(4)	6430(5)	1575(10)	17(2)
P(2)	"	5608(2)	6288(2)	2075(4)	16(1)
O(22)	"	5275(4)	6834(4)	1409(9)	15(2)
O(23)	"	5423(4)	5689(4)	1468(10)	17(2)
O(24)	"	5599(5)	6269(4)	3540(11)	20(3)
P(3)	"	6272(2)	4388(2)	2894(4)	17(1)
O(32)	"	6273(4)	4393(5)	1421(11)	21(3)
O(33)	"	5802(4)	4796(4)	3518(9)	18(2)
O(34)	"	6897(4)	4505(4)	3575(10)	23(2)
OB34	"	6070(5)	3715(4)	3410(10)	18(2)
P(4)	"	6212(2)	3022(2)	2836(4)	15(1)
O(42)	"	6239(4)	3042(5)	1416(11)	18(3)
O(43)	"	6827(4)	2861(4)	3473(9)	18(2)
O(44)	"	5693(4)	2651(4)	3478(9)	15(2)
P(5)	"	3704(2)	6882(2)	2927(4)	10(1)
O(52)	"	3672(4)	6889(5)	1466(11)	17(3)
O(53)	"	3177(5)	7209(4)	3571(10)	21(2)
O(54)	"	4309(4)	7099(4)	3576(10)	17(2)
OB56	"	3587(5)	6184(4)	3425(10)	19(2)
P(6)	"	3785(2)	5522(2)	2877(4)	13(1)
O(62)	"	3829(4)	5531(5)	1413(11)	20(3)
O(63)	"	3281(4)	5105(4)	3454(9)	18(2)
O(64)	"	4400(4)	5377(4)	3507(9)	16(2)
P(7)	"	4475(2)	3778(2)	2131(4)	13(1)
O(72)	"	4699(5)	3188(5)	1472(10)	25(3)
O(73)	"	4826(5)	4307(4)	1528(10)	19(2)
O(74)	"	4469(5)	3790(4)	3600(11)	19(3)
OB78	"	3798(4)	3857(4)	1564(10)	18(2)
P(8)	"	3114(2)	3708(2)	2113(4)	11(1)
O(82)	"	2719(4)	4220(4)	1446(9)	16(2)
O(83)	"	2988(4)	3097(4)	1504(9)	19(2)
O(84)	"	3111(4)	3683(4)	3534(10)	12(2)

Note. Isotropic ( $\times 10^{-1} \text{ pm}^2$ ) for Na, O, and P; equivalent isotropic ( $\text{pm}^2$ ) for Zn.  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor (LC  $\text{Na}_2\text{ZnP}_2\text{O}_7$  model).

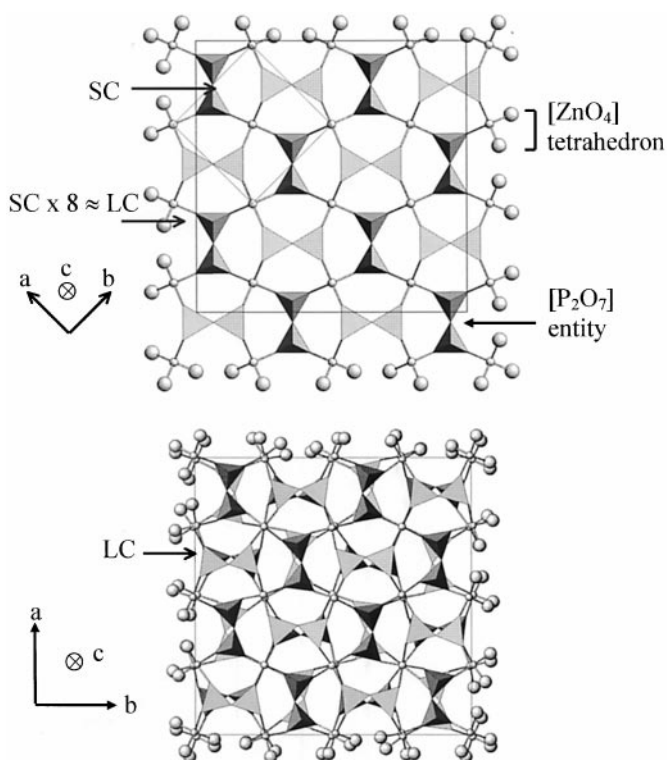


FIG. 2. Comparison between the ideal sheets of SC Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> with the actual sheets of the LC Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub>.

distortions of sheets from the SC model to the LC model. The oxygen atoms are labeled O<sub>ii'</sub> for “terminal atom” bond to P<sub>i</sub> (*i*' = 2, 3, 4) and O<sub>b<sub>ij</sub></sub> for “bridging atom” between P<sub>i</sub> and P<sub>j</sub>. The anisotropic displacement parameters of Zn atoms are given in Table 5. Selected bond lengths and angles are listed in Table 6.

TABLE 5  
Anisotropic Displacement Parameters ( $\times 10^{-1}$  pm)  
for Zn Atoms in Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub>

Atoms	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Zn(1)	146(13)	146(13)	199(20)	0	0	0
Zn(2)	153(13)	153(13)	135(19)	0	0	0
Zn(3)	116(14)	188(14)	165(14)	0	0	-2(16)
Zn(4)	153(9)	146(8)	176(10)	18(8)	10(8)	-13(6)
Zn(5)	162(11)	136(9)	128(10)	-7(8)	9(7)	-5(9)
Zn(6)	138(9)	122(10)	181(11)	5(8)	-7(8)	9(5)

Note. The anisotropic displacement factor exponent takes the form  $-2\pi^2[h^2a^{*2}U_{11} + \dots + 2hka^*b^*U_{12}]$ . (LC Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> model).

### 3.4. Pertinence of the Twinned LC Model

The pertinence of this LC model which has been determined from twinned single crystals can be tested by an investigation of the X-ray powder diffraction pattern. Obviously such investigation does not need the introduction of the twin hypothesis.

Diffraction powder data were collected at room temperature on a Philips PW3040 ( $\theta$ - $\theta$ ) diffractometer with the following experimental parameters: Bragg-Brentano geometry; diffracted-beam graphite monochromator; CuK $\alpha$  radiation (40 kV, 50 mA); steps of 0.02° ( $2\theta$ ) over the angular range 10–120° ( $2\theta$ ) with a fixed counting time of 30 s.

SC and LC models were compared using Rietveld method (FULLPROF program (10)) and atomic coordinates values obtained from single crystal study. Table 7 shows the improvement of the profile factors ( $R_p$ ,  $R_{wp}$ ,  $cR_p$ ,  $cR_{wp}$  and  $\chi^2$ ) and of the crystal structure indicators ( $R_B$  and  $R_F$ ) for the LC model. Moreover the LC-model explains very precisely the existence in location and intensities of several weak peaks of the powder diffraction pattern in the 25–45° ( $2\theta$ ) range (Fig. 3), which are not considered by the SC approach.

## 4. STRUCTURE DESCRIPTION

Basically the LC model preserves the [ZnP<sub>2</sub>O<sub>7</sub>] layers made up of [ZnO<sub>4</sub>] tetrahedra sharing corners with the [P<sub>2</sub>O<sub>7</sub>] groups. The sodium are located between the layers in oxygenated sites with 7-fold or 8-fold coordination. The structural evolution from the SC model to the LC model results from a slight shift of the P, Zn, and O atoms every other layer.

The P–O distances in the [P<sub>2</sub>O<sub>7</sub>] groups are typical of a diphosphate unity in which the longer distances P<sub>i</sub>–O<sub>b<sub>ij</sub></sub> <162.5 pm> characterize the P–O–P bridge, whereas the shorter P–O distances <151.7 pm> correspond to the external bonds. The [ZnO<sub>4</sub>] tetrahedra are almost regular with a small dispersion of the zinc oxygen distances which are included between 192.5 and 199.0 pm. The mean Zn–O distance (195.6 pm) is consistent with the table of Shannon (11) ( $d_{Zn-O} = 200.0$  pm). The actual coordination of sodium was determined by bond valence calculations. In order to achieve proper bond-valence sums ( $\sum s \approx 1$ ) a number of weaker bonds (Na–O  $\approx 300.0$  pm) must be taken into account (Table 6) which leads to an 8-fold coordination for Na(1) and Na(5) and a 7-fold coordination for the remaining sodium. All the sodium sites exhibit a large dispersion of the sodium–oxygen distances. The two shortest Na–O distances in each sodium sites (except Na(5)) are connected to two opposite [ZnP<sub>2</sub>O<sub>7</sub>] layers which contribute to the stability of the structure. Moreover the sodium atoms are

connected through common faces which implies short Na–Na distances ( $d_{\text{Na1–Na6}} = 308.0$  pm,  $d_{\text{Na7–Na4}} = 304.0$  pm) or through common edges giving rise to more longer distances ( $d_{\text{Na1–Na6}} = 337.0$  pm,  $d_{\text{Na1–Na8}} = 363.0$  pm,  $d_{\text{Na2–Na7}} = 356.0$  pm etc.).

## 5. CONCLUSIONS

The structure of the zinc phosphates containing an additional large size monovalent cations ( $r_{M^+} > 102.0$  pm if CN = 6) are mainly correlated by the P/Zn atomic

**TABLE 6**  
Selected Bond Lengths (pm) and Angles (°) in LC-Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub>

(a) Zn tetrahedra <sup>a</sup>									
Zn1	O83 <sup>i</sup>	O83	O83 <sup>ii</sup>	O83 <sup>iii</sup>	Zn2	O13 <sup>iv</sup>	O13 <sup>v</sup>	O13	O13 <sup>vi</sup>
O83 <sup>i</sup>	196.7(9)	117.3(5)	105.7(2)	105.7(2)	O13 <sup>iv</sup>	196.1(10)	102.2(2)	102.2(2)	125.3(6)
O83	336 (2)	196.7(9)	105.7(2)	105.7(2)	O13 <sup>v</sup>	305 (2)	196.1(10)	125.3(6)	102.2(2)
O83 <sup>ii</sup>	314 (2)	314 (2)	196.7(9)	117.3(5)	O13	305 (2)	348 (2)	196.1(10)	102.2(2)
O83 <sup>iii</sup>	314 (2)	314 (2)	336 (2)	196.7(9)	O13 <sup>vi</sup>	348 (2)	305 (2)	305 (2)	196.1(10)
Zn3	O53 <sup>ii</sup>	O53 <sup>iv</sup>	O43 <sup>vii</sup>	O43	Zn4	O23	O64	O73	O33
O53 <sup>ii</sup>	192.6(10)	112.8(6)	103.4(5)	110.7(4)	O23	192.5(9)	108.3(4)	115.2(4)	99.9(4)
O53 <sup>iv</sup>	332 (2)	192.6(10)	110.7(4)	103.4(5)	O64	313.4(14)	194.1(9)	111.9(4)	115.3(4)
O43 <sup>vii</sup>	304.8(14)	319.6(13)	195.8(10)	116.2(6)	O73	327.8(12)	386.3(14)	195.8(10)	105.9(4)
O43	319.6(13)	304.8(14)	332 (2)	195.8(10)	O33	298.4(14)	330.5(12)	313.7(14)	197.3(9)
Zn5	O12 <sup>vi</sup>	O22	O54	O34 <sup>vi</sup>	Zn6	O63	O44 <sup>iii</sup>	O82	O72 <sup>iii</sup>
O12 <sup>vi</sup>	194.9(10)	110.4(4)	113.8(4)	111.1(4)	O63	193.0(9)	106.9(4)	104.5(4)	116.5(4)
O22	320.4(13)	195.3(9)	105.8(4)	110.1(4)	O44 <sup>iii</sup>	311.5(13)	194.7(9)	115.5(4)	109.9(4)
O54	327 (2)	311.9(13)	195.8(9)	105.5(4)	O82	307.9(13)	330.6(13)	196.2(9)	103.7(4)
O34 <sup>vi</sup>	324.8(14)	323.1(13)	314.2(14)	199.0(10)	O72 <sup>iii</sup>	331.8(13)	320.9(14)	309.4(14)	197.1(10)
(b) P tetrahedra									
P1	OB12	O12	O13	O14	P2	OB12	O22	O23	O24
OB12	166.1(10)	105.8(5)	100.3(6)	108.8(6)	OB12	162.5(10)	98.6(6)	106.5(6)	109.5(6)
O12	255.7(13)	154.5(10)	109.4(6)	116.1(6)	O22	240.8(14)	155.2(10)	110.9(6)	117.1(6)
O13	242.6(14)	248.1(14)	149.5(10)	114.9(6)	O23	250.6(13)	251.5(14)	150.1(10)	112.9(6)
O14	256 (2)	257 (2)	251.1(14)	148.2(12)	O24	256 (2)	261.0(14)	250.7(14)	150.8(13)
P1–OB12–P2 = 131.0(7)									
P3	OB34	O32	O33	O34	P4	OB34	O42	O43	O44
OB34	161.9(10)	109.6(6)	102.1(6)	103.9(6)	OB34	165.2(10)	109.7(6)	102.7(5)	100.8(5)
O32	256 (2)	151.5(13)	115.2(6)	116.6(6)	O42	255 (2)	146.3(13)	113.5(6)	118.2(6)
O33	242.5(13)	254 (2)	149.8(10)	107.9(6)	O43	248.7(14)	250.5(14)	154.1(10)	109.9(6)
O34	249.6(13)	261.0(14)	246.6(14)	155.2(11)	O44	245.9(13)	258 (2)	251.3(14)	153.8(10)
P3–OB34–P4: 131.3(7)									
P5	OB56	O52	O53	O54	P6	OB56	O62	O63	O64
OB56	162.4(10)	108.5(6)	100.7(6)	106.3(6)	OB56	160.4(10)	110.8(6)	101.7(6)	105.8(5)
O52	254.0(14)	150.4(12)	113.6(6)	117.8(6)	O62	256 (2)	150.9(12)	115.9(6)	111.9(5)
O53	240.9(14)	252 (2)	150.4(10)	108.3(6)	O63	244.2(14)	258.7(14)	154.3(9)	109.9(5)
O54	254.0(14)	261.6(14)	248 (2)	155.0(10)	O64	249.3(13)	250.9(14)	250.7(13)	152.0(10)
P5–OB56–P6 = 133.4(7)									
P7	OB78	O72	O73	O74	P8	OB78	O82	O83	O84
OB78	159.3(10)	103.0(6)	103.6(6)	110.8(6)	OB78	162.6(10)	102.1(5)	101.6(6)	110.9(6)
O72	244.6(14)	153.2(11)	107.1(7)	117.3(6)	O82	248.4(12)	156.7(10)	110.5(6)	117.5(6)
O73	244.2(14)	245 (2)	151.5(10)	113.7(6)	O83	241.9(13)	251.5(13)	149.4(10)	112.6(6)
O74	255.6(14)	260 (2)	253 (2)	151.2(12)	O84	254.7(13)	259.0(14)	246.0(13)	146.3(11)
P7–OB78–P8: 134.3(7)									

TABLE 6—Continued

(c) Na polyhedra			
Na(1)–O(73)	250.2(12)	Na(5)–O(52)	245.9(13)
Na(1)–O(62)	251.0(12)	Na(5)–O(44)	250.2(11)
Na(1)–O(32)	255.5(12)	Na(5)–O(32)	252.1(13)
Na(1)–O(42)	263.9(12)	Na(5)–O(42)	262.1(13)
Na(1)–O(22)	264.2(11)	Na(5)–O(53)	263.6(12)
Na(1)–O(72)	269.4(12)	Na(5)–O(62)	275.1(12)
Na(1)–O(52)	269.7(12)	Na(5)–O(43)	280.7(12)
Na(1)–O(23)	283.7(11)	Na(5)–O(54)	280.7(12)
$\Sigma s = 0.87^b$		$\Sigma s = 0.90$	
Na(2)–O(74)	230.7(13)	Na(6)–O(42)	233.7(13)
Na(2)–O(24)	236.6(13)	Na(6)–O(52)	235.9(12)
Na(2)–OB34	244.3(12)	Na(6)–O(34)	236.6(12)
Na(2)–O(54)	245.8(12)	Na(6)–O(43)	249.9(12)
Na(2)–O(64)	254.0(11)	Na(6)–OB56	250.8(12)
Na(2)–OB56	294.1(12)	Na(6)–O(53)	266.7(12)
Na(2)–O(44)	301.0(11)	Na(6)–OB34	298.3(12)
$\Sigma s = 1.06$		$\Sigma s = 1.12$	
Na(3)–O(14)	233.1(12)	Na(7)–O(63)	241.2(11)
Na(3)–O(84)	238.5(11)	Na(7)–O(33)	243.1(12)
Na(3)–O(83)	247.7(11)	Na(7)–O(74)	249.2(12)
Na(3)–OB12	247.9(11)	Na(7)–O(24)	253.6(12)
Na(3)–O(72)	254.4(12)	Na(7)–O(14)	256.3(13)
Na(3)–O(22)	262.2(11)	Na(7)–O(84)	267.4(11)
Na(3)–OB78	285.0(11)	Na(7)–O(64)	286.8(11)
$\Sigma s = 1.07$		$\Sigma s = 0.96$	
Na(4)–O(13)	242.2(12)	Na(8)–O(62)	231.4(12)
Na(4)–O(82)	245.6(12)	Na(8)–O(32)	235.4(13)
Na(4)–O(84)	246.7(12)	Na(8)–O(12)	246.9(12)
Na(4)–O(24)	256.1(13)	Na(8)–O(23)	253.6(11)
Na(4)–O(14)	265.4(12)	Na(8)–OB78	255.0(11)
Na(4)–O(74)	268.0(12)	Na(8)–O(82)	290.3(11)
Na(4)–O(12)	289.1(12)	Na(8)–OB12	297.8(11)
$\Sigma s = 1.05$		$\Sigma s = 1.00$	

<sup>a</sup>(i)  $-x + \frac{1}{2}, -y + \frac{1}{2}, z$ ; (ii)  $y, -x + \frac{1}{2}, -z + \frac{1}{2}$ ; (iii)  $-y + \frac{1}{2}, x, -z + \frac{1}{2}$ ; (iv)  $-y + \frac{3}{2}, x, -z + \frac{1}{2}$ ; (v)  $-x + \frac{3}{2}, -y + \frac{3}{2}, z$ ; (vi)  $y, -x + \frac{3}{2}, -z + \frac{1}{2}$ ; (vii)  $-x + \frac{3}{2}, -y + \frac{1}{2}, z$ .

<sup>b</sup>The bond valence values are calculated using the following formula:  $s = \exp[(1.803 - di)/0.37]$  (15).

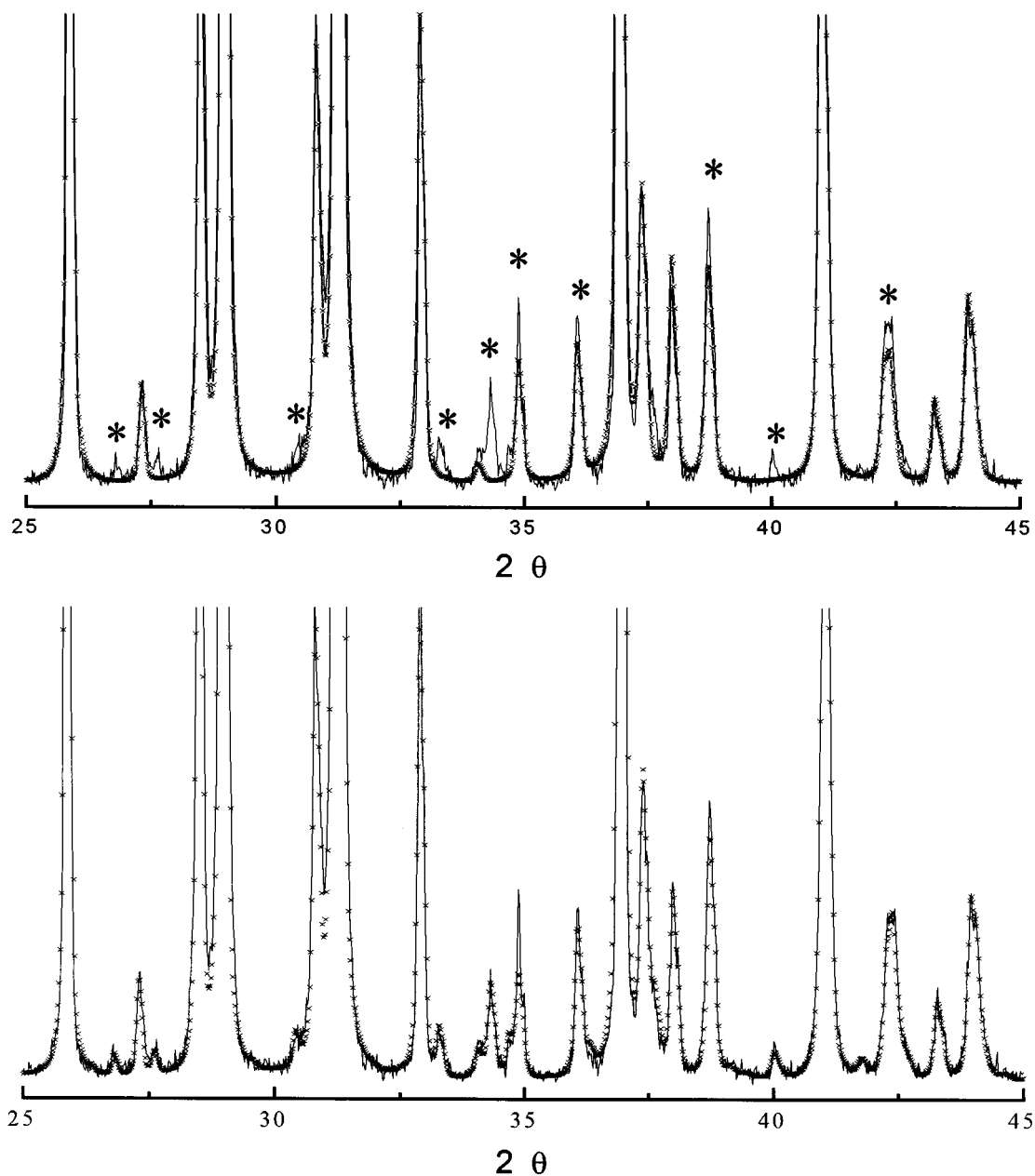
ratio. Assuming  $P/Zn = 3$ , e.g., in  $ZnAg(PO_3)_3$  or  $Na_4Zn_4(P_4O_{12})_3$  the phosphate subnetwork is made up of  $(PO_3)_\infty$  long chains or  $P_4O_{12}$  ring anions and the zinc in

octahedral sites belongs clearly to the cationic subnetwork (12). In the case  $M^+ZnPO_4$  monophosphates ( $M = Ag$ ) ( $P/Zn = 1$ ) (13), the compounds belong to the large structural family of tridymite derivative with a three-dimensional covalent network made up of fully ordered  $[ZnO_4]$  and  $[PO_4]$  corner-sharing. The cations  $M^+$  ( $Na^+ \rightarrow Cs^+, Ag^+, NH_4^+$ ) are located in the large cavities created by the  $[ZnPO_4]$  network with large coordination number (e.g., CN can reach 10 in  $\beta$ - $AgZnPO_4$  (13)). In the intermediate case of the sodium zinc diphosphate ( $P/Zn = 2$ ) the covalent network is two dimensional with full ordering between the  $[ZnO_4]$  tetrahedra and the diphosphate groups. Only the sodium atoms are located between the layers with also large CN (7 or 8). Finally the short Na–Na distances observed between the layers can explain the aptitude of silver pair

TABLE 7  
Comparison Between Reliability Factors

Structural approach	$R_p$	$R_{wp}$	$cR_p$	$R_B$	$R_F$	$\chi^2$
SC Na <sub>2</sub> ZnP <sub>2</sub> O <sub>7</sub>	13.3	18.3	16.5	7.34	5.81	4.87
LC Na <sub>2</sub> ZnP <sub>2</sub> O <sub>7</sub>	11	14.8	13.1	4.74	3.79	3.07

Note. The Rietveld profilation method was used on the X-ray diffraction pattern of Na<sub>2</sub>ZnP<sub>2</sub>O<sub>7</sub> powders according to the SC and LC structural approaches.



**FIG. 3.** Parts of the experimental and calculated powder diffraction pattern in the context of the SC and LC  $\text{Na}_2\text{ZnP}_2\text{O}_7$  models. The small peaks (\*) are accurately described by the LC  $\text{Na}_2\text{ZnP}_2\text{O}_7$  model. (—) Experimental diagram; (x) calculated diagram.

formation in such structural arrangement which was evidenced for the compounds  $\text{Na}_{2-x}\text{Ag}_x\text{ZnP}_2\text{O}_7$  (4).

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