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A new structure type of phosphate: Crystal structure of $Na_2Zn_5(PO_4)_4$

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Abstract

A new compound, $Na_2Zn_5(PO_4)_4$, was identified in the system $ZnO–Na_2O–P_2O_5$ and high-quality crystal was obtained by the melt method. The crystal structure of this compound was solved by direct method from single crystal X-ray diffraction data. The structure was then refined anisotropically using a full-matrix least square refinement on F^2 and the refinement converged to $R_1 = 0.0233$ and $wR_2 = 0.0544$. This compound crystallizes in the orthorhombic system with space group *Pbcn*, lattice parameters $a = 10.381(2)$ Å, $b = 8.507(1)$ Å, $c = 16.568(3)$ Å and $Z = 4$. The structure is made up of 3D $[Zn_5P_4O_{16}]_n^{2n-}$ covalent framework consisting of $[Zn_4P_4O_{16}]_n^{4n-}$ layers. The powder diffraction pattern of $Na_9Zn_{21}(PO_4)_{17}$ is explained by simulating a theoretical pattern with $NaZnPO_4$ and $Na_2Zn_5(PO_4)_4$ in the molar ratio of 1:4 and then by Rietveld refinement of experimental pattern. $Na_2Zn_5(PO_4)_4$ melts congruently at 855 °C and its conductivity is 5.63×10^{-9} S/cm.

Keywords: $Na_2Zn_5(PO_4)_4$; Structure determination; Single-crystal diffraction; X-ray powder diffraction

1. Introduction

The II–VI semiconductor zinc oxide (ZnO) has important applications in many functional devices [1,2]. Several methods, such as hydrothermal [3,4], vapor transport [5–7] and melt methods [8–11] are used to obtain excellent ZnO crystals. A suitable flux is needed to grow ZnO crystals at a lower temperature due to the high melting point (1975 °C) and serious volatilization of ZnO at high temperature. PbF_2 was used as a flux to grow ZnO crystals, but it is noxious. In order to search for a suitable flux, the phase relations in the $ZnO–Na_2O–P_2O_5$ system are investigated.

In the pseudo-ternary system of $ZnO–Na_2O–P_2O_5$, six compounds were reported, i.e., $NaZnPO_4$ [12,13], $Na_2ZnP_4O_{12}$ [14], $NaZn(PO_3)_3$ [14–16], $Na_2ZnP_2O_7$ [17–19], $Na_9Zn_3(PO_4)_5$ [20] and $Na_9Zn_{21}(PO_4)_{17}$ [20]. These compounds were prepared by flux method [12,14], solid-state reaction [16] or melt method [17]. The luminescence properties of silver doped $NaZn(PO_3)_3$ [16] and emission characteristics of the rare-earth-containing $Na_2ZnP_2O_7$ materials [18] were also reported. For $Na_9Zn_3(PO_4)_5$ and $Na_9Zn_{21}(PO_4)_{17}$ compounds, only unindexed powder diffraction patterns were reported. Our X-ray powder diffraction pattern of the nominal chemical composition compound $Na_9Zn_{21}(PO_4)_{17}$ is similar to the one reported in Ref. [20] and does not match well. In addition, the indexing result of the diffraction pattern was not convincing for the low figures of merit. In order to solve the structure, we tried to grow single crystals of this phase from $Na_9Zn_{21}(PO_4)_{17}$ melt by slowly cooling method. However, a single crystal with composition $Na_2Zn_5(PO_4)_4$ was obtained and its crystal structure and properties are reported in this paper. Obviously, $Na_9Zn_{21}(PO_4)_{17}$ is very similar to $4 \cdot (Na_2Zn_5(PO_4)_4)$.

2. Experimental section

2.1. Preparation of sample

The raw materials are analytical pure ZnO, Na_2CO_3 and $NH_4H_2PO_4$. These materials were weighed in the molar ratio of 62:13:50, then were mixed and ground

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homogeneously in an agate mortar. The mixture was heated to 900 °C in a platinum crucible and kept at this temperature for 1 h to make the melt homogeneous. Then the melt was cooled to 800 °C at a rate of 1 °C/h and to 400 °C at a rate of 20 °C/h, and afterwards rapidly cooled to room temperature by switching off the furnace. Transparent irregular grains could be found on the surface of the crucible. A single crystal was selected under microscope for structure determination.

2.2. *Structure determination of the compound*

A suitable single crystal was mounted on a thin glass fiber for structural determination. The room temperature intensity data were collected on a Rigaku R-Axis Rapid IP diffractometer with graphite-monochromated MoK_α radiation. Semi-empirical absorption correction based on multi-scan was applied.

2.3. *Differential thermal analysis (DTA) measurement*

Thermal analysis of the title compound was conducted on a RSZ-type high-temperature μ-DTA apparatus with Pt-PtRh thermocouples. Alumina crucibles were used as vessels and reference standard. The heating rate was 10 °C/min and the precision of the measurement is ±3 °C.

2.4. *Conductivity of the compound*

The raw materials weighted in the nominal chemical composition of $Na_2Zn_5(PO_4)_4$ were preheated at 700 °C for 10 h with slow heating rate, then were melt at 900 °C in a platinum crucible and quenched on a copper plate. Then the obtained sample was annealed at 600 °C for 48 h and identified by X-ray diffraction. After cutting and polishing, it was conducted in the hp 4192 A resistant spectroscopy for measuring the conductivity.

3. Results and discussions

3.1. *Structure description and discussion*

The structure was solved by direct method with SHELX97 [21] and refined using a full-matrix refinement on F^2. All atoms were refined anisotropically. $Na_2Zn_5(PO_4)_4$ crystallizes in the orthorhombic system with space group *Pbcn*, lattice parameters $a = 10.381(2)$ Å, $b = 8.507(1)$ Å, $c = 16.568(3)$ Å and $Z = 4$. Crystallographic data and structure refinement are listed in Table 1. The coordinates and equivalent atomic displacement parameters of the 14 crystallographically independent atoms are listed in Table 2.

Both Zn and P atoms are tetrahedrally coordinated by oxygen atoms. The bond lengths and angles for each tetrahedron are listed in Table 3. [ZnO_4] tetrahedrons deviate from the ideal one while the [PO_4] tetrahedrons are close to the regular one. The Zn–O bond lengths and O–Zn–O bond angles vary in the range of 1.898(2)–1.997(2) Å and 95.31(9)°–127.49(9)° with average values of 1.951(2) Å and 109.40(9)°, respectively. The corresponding value for [PO_4] tetrahedrons are 1.507(2) Å–1.571(2) Å and 107.49(13)°–112.83(12)° with average values of 1.536(2) Å and 109.44(12)°, respectively.

Table 1
Crystallographic data and structure refinement for $Na_2Zn_5(PO_4)_4$

Empirical formula	$Na_2Zn_5P_4O_{16}$
Formula weight	752.71
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system space group	Orthorhombic *Pbcn*
Unit cell dimensions	$a = 10.381(2)$ Å alpha = 90°
	$b = 8.507(1)$ Å beta = 90°
	$c = 16.568(3)$ Å gamma = 90°
Volume	1463.2(5) Å
Z calculated density	4 3.417 kg/m^3
Absorption coefficient	8.664 mm^{-1}
F(0 0 0)	1440
Crystal size	0.31 × 0.15 × 0.11 mm
Theta range for data collection	2.46–27.41°
Limiting indices	$-13 < = h < = 13$
	$-10 < = k < = 11$
	$-21 < = l < = 21$
Reflections collected/unique	13565/1663 [*R*(int) = 0.0179]
Completeness to theta = 27.41	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.4491 and 0.1743
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1663/0/123
Goodness-of-fit on F^2	1.063
Final R indices [$I > 2$sigma(I)]	$R_1 = 0.0233$ w$R_2 = 0.0544$
R indices (all data)	$R_1 = 0.0288$ w$R_2 = 0.0560$
Largest diff. peak and hole	0.795 and −0.628 e.Å^{-3}

By sharing two corners, the [$Zn(1)O_4$] and [$Zn(2)O_4$] tetrahedrons form a $[ZnO_3]_n^{4n-}$ zigzag chain running along the *b*-axis (Fig. 1a), which is distinguished from all the other reported sodium zincophosphates. Again by sharing corner oxygen atoms, two parallel $[ZnO_3]_n^{4n-}$ zigzag chains are connected by [PO_4] polyhedrons to build a $[Zn_4P_4O_{16}]_n^{4n-}$ layer perpendicular to the *c*-axis (Fig. 1b). [$Zn(3)O_4$] polyhedrons link the neighbor layers by sharing apex oxygen atom with the [PO_4] polyhedron to form a 3D $[Zn_5P_4O_{16}]_n^{2n-}$ zincophosphate covalent framework with channels along the *b*-axis in which the sodium atoms are located (Fig. 1c). Within a radius of 3 Å, Na is coordinated by 5 oxygen atoms. Four of the 5 Na–O bond lengths are in the range of 2.278(3) Å–2.542(3) Å while the other one is 2.938(3) Å. The average bond lengths and angles of the 4 shorter bonds are 2.389 Å and 108.41°, respectively, which are in close agreement with the corresponding repoted values in ICSD [22].

Based on the accurate bond geometries of a large number of compounds, the bond valence sum V_i for a given atom *i* and bond distances r_{ij} between atom *i* and atom *j* follows the equation:

$$V_i = \sum_{j=1}^{N} \exp\left(\frac{r_0 - r_{ij}}{0.37}\right),$$

Table 2
Atomic coordinates ($\times 10^4$), equivalent isotropic and anisotropic displacement parameters (Å$^2 \times 10^3$) for Na$_2$Zn$_5$(PO$_4$)$_4$

Atom	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Zn(1)	3393(1)	3887(1)	4204(1)	12(1)	14(1)	10(1)	11(1)	0(1)	2(1)	1(1)
Zn(2)	3344(1)	802(1)	5539(1)	11(1)	11(1)	11(1)	11(1)	1(1)	1(1)	−1(1)
Zn(3)	0	6949(1)	7500	10(1)	11(1)	11(1)	10(1)	0	1(1)	0
P(1)	882(1)	9049(1)	6057(1)	9(1)	9(1)	8(1)	10(1)	1(1)	1(1)	0(1)
P(2)	943(1)	4460(1)	8672(1)	9(1)	9(1)	9(1)	8(1)	0(1)	0(1)	1(1)
Na(1)	1672(1)	2606(2)	7057(1)	31(1)	25(1)	46(1)	22(1)	−10(1)	10(1)	−8(1)
O(1)	3675(2)	3037(3)	5314(1)	14(1)	24(1)	10(1)	10(1)	0(1)	−3(1)	−2(1)
O(2)	4453(2)	5650(3)	3976(2)	20(1)	10(1)	16(1)	32(1)	5(1)	−1(1)	−1(1)
O(3)	1203(2)	8037(3)	6795(1)	16(1)	16(1)	19(1)	12(1)	8(1)	0(1)	−1(1)
O(4)	1677(2)	563(2)	6055(1)	14(1)	14(1)	11(1)	17(1)	−1(1)	4(1)	−3(1)
O(5)	1746(2)	4994(3)	4420(1)	13(1)	12(1)	16(1)	11(1)	−1(1)	−1(1)	2(1)
O(6)	1291(2)	5530(3)	7971(1)	15(1)	14(1)	18(1)	13(1)	7(1)	0(1)	1(1)
O(7)	4509(2)	−503(3)	6128(1)	15(1)	11(1)	18(1)	16(1)	3(1)	−2(1)	1(1)
O(8)	3696(2)	2234(3)	3444(1)	15(1)	22(1)	13(1)	11(1)	−1(1)	−2(1)	5(1)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (deg) for Na$_2$Zn$_5$(PO$_4$)$_4$

Zn(1)–O(2)	1.898(2)	P(1)-O(2)#5	1.507(2)
Zn(1)–O(8)	1.914(2)	P(1)-O(4)#6	1.530(2)
Zn(1)–O(5)	1.984(2)	P(1)-O(3)	1.532(2)
Zn(1)–O(1)	1.997(2)	P(1)-O(1)#3	1.571(2)
Zn(2)–O(7)	1.910(2)	P(2)–O(6)	1.520(2)
Zn(2)–O(4)	1.941(2)	P(2)–O(7)#4	1.525(2)
Zn(2)–O(1)	1.968(2)	P(2)–O(8)#7	1.536(2)
Zn(2)–O(5)#1	1.980(2)	P(2)–O(5)#8	1.565(2)
Zn(3)–O(3)	1.945(2)	Na(1)–O(3)#1	2.278(3)
Zn(3)–O(3)#2	1.945(2)	Na(1)–O(8)#7	2.332(3)
Zn(3)–O(6)#2	1.965(2)	Na(1)–O(4)	2.405(3)
Zn(3)–O(6)	1.965(2)	Na(1)–O(7)#3	2.542(3)
		Na(1)–O(6)	2.938(3)
O(2)–Zn(1)-O(8)	110.73(10)	O(3)–Zn(3)–O(6)	95.31(9)
O(2)–Zn(1)-O(5)	99.23(9)	O(3)#2–Zn(3)–O(6)	119.49(9)
O(8)–Zn(1)-O(5)	127.49(9)	O(6)#2–Zn(3)–O(6)	104.22(14)
O(2)–Zn(1)-O(1)	112.62(10)	O(2)#5–P(1)–O(4)#6	112.83(12)
O(8)–Zn(1)-O(1)	108.42(9)	O(2)#5–P(1)–O(3)	109.81(13)
O(5)–Zn(1)-O(1)	97.59(9)	O(4)#6–P(1)–O(3)	110.96(13)
O(7)–Zn(2)-O(4)	106.19(9)	O(2)#5–P(1)–O(1)#3	110.70(14)
O(7)–Zn(2)-O(1)	123.25(9)	O(4)#6–P(1)–O(1)#3	107.53(12)
O(4)–Zn(2)-O(1)	109.88(9)	O(3)–P(1)–O(1)#3	104.68(12)
O(7)–Zn(2)–O(5)#1	107.83(10)	O(6)–P(2)–O(7)#4	112.72(13)
O(4)–Zn(2)–O(5)#1	109.50(9)	O(6)–P(2)–O(8)#7	108.44(13)
O(1)–Zn(2)–O(5)#1	99.60(9)	O(7)#4–P(2)–O(8)#7	108.14(12)
O(3)–Zn(3)–O(3)#2	123.15(14)	O(6)–P(2)–O(5)#8	107.49(13)
O(3)–Zn(3)–O(6)#2	119.49(9)	O(7)#4–P(2)–O(5)#8	109.94(12)
O(3)#2–Zn(3)–O(6)#2	95.31(9)	O(8)#7–P(2)–O(5)#8	110.09(12)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1/2,y-1/2,z$; #2 $-x,y,-z+3/2$; #3 $-x+1/2,y+1/2,z$; #4 $x-1/2,y+1/2,-z+3/2$; #5 $x-1/2,-y+3/2,-z+1$; #6 $x,y+1,z$; #7 $-x+1/2,-y+1/2,z+1/2$; #8 $x,-y+1,z+1/2$; #9 $x+1/2,y-1/2,-z+3/2$; #10 $x+1/2,-y+3/2,-z+1$; #11 $x,y-1,z$; #12 $x,-y+1,z-1/2$; #13 $-x+1/2,-y+1/2,z-1/2$.

where r_0 is the bond valence parameter. For Na–O, Zn–O and P–O ion pairs, r_0 is 1.803, 1.704 and 1.617, respectively [14]. Bond valence sums for all the unique atoms are calculated and listed in Table 4.

Obviously, the positive and negative charges compensate each other with an acceptable tolerance. The bond valence sum for sodium atom is 0.895, having more than 10% deviations from unit. The reported results show that the bond valence sum for sodium is greater than unit when the coordination number is large while less than unit when the coordination number is small. As mentioned above, one of the Na–O bond (Na(1)–O(6), 2.938 Å) is radically longer than the other four bonds (2.278–2.542 Å), it thus contributes little (0.047 v.u.) to the bond valence sum. The bond valence sum for sodium atom in regular tetrahedral site is 0.790 [15], which is close to the bond valence value for sodium in the title compound. The bond valence deviation of sodium atom from unit can be easily understood by the distorted theorem of bond valence theory [16].

As shown in Table 2, the equivalent atomic displacement parameters of Na are 2–3 times larger than those of the other atoms. In addition, $U_{22} \approx 2U_{11} \approx 2U_{33}$ of Na indicates large vibration amplitude in the direction of the *b*-axis. Thus, ion conductivity along the channels which run parallel to the *b*-axis is expected.

As briefly mentioned by Belharouak et al. [18], the structure of the covalent frameworks has close relation with the P/Zn atomic ratio. The changes of zincophosphate framework with the decreasing of P/Zn atomic ratio is the result of a compromise between the decomposing of polyphosphate groups and the concentrating of [ZnO$_4$] polyhedrons. In compounds NaZn(PO$_3$)$_3$ ($I\bar{4}3d$, $Pa\bar{3}$ and $Pbca$), P/Zn = 3:1, the building blocks are either polypospate rings [14,15] or chains [16] made up of corner-sharing [PO$_4$] tetrahedrons. The polyphosphate anions are then connected by [ZnO$_6$] octahedrons to make the zinc phosphate framework. With the decreasing of P/Zn atomic ratio to 2:1, the polyphosphate rings or chains decompose into diphosphate groups [P$_2$O$_7$] and the coordination number of Zn decreases from 6 to 4. [P$_2$O$_7$] groups and [ZnO$_4$] groups are then arranged in a fully ordered way to build the covalent layer of Na$_2$ZnP$_2$O$_7$ [17–19]. In the

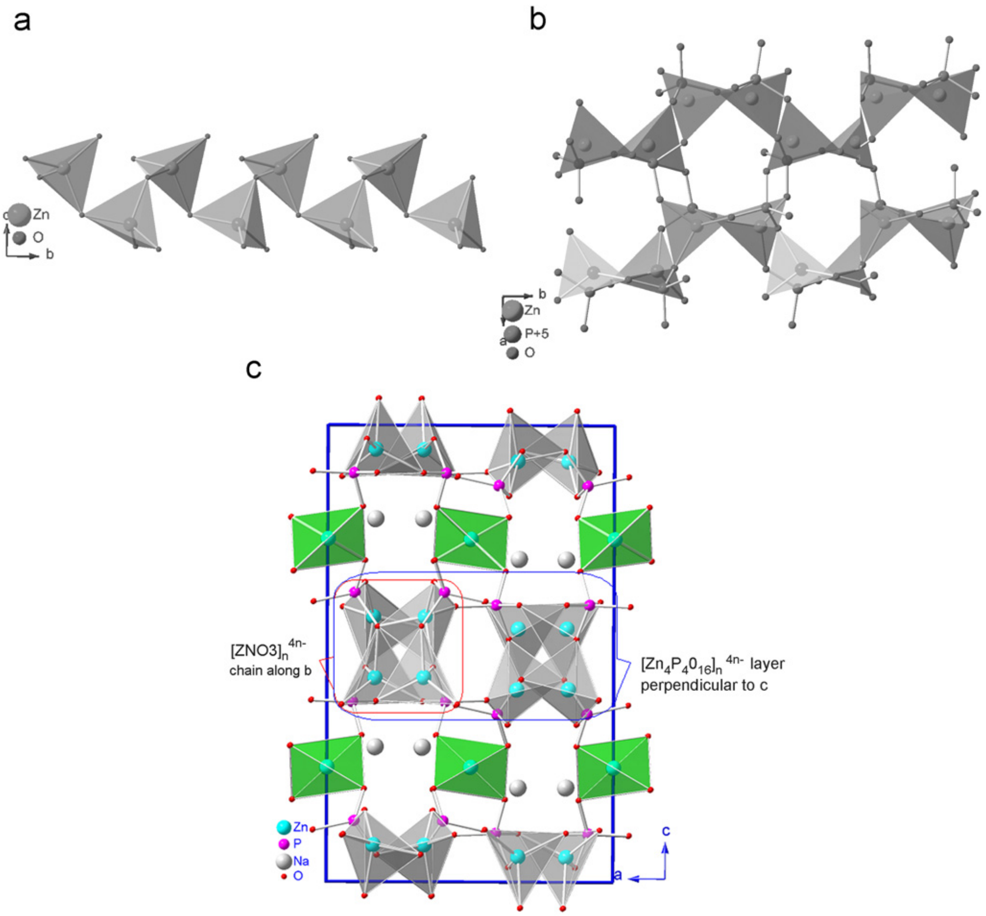

Fig. 1. (a) [ZnO_4] shares two corners with each other to build a $[ZnO_3]_n^{4n-}$ zigzag chain along b. (b) $[ZnO_3]_n^{4n-}$ chains are linked by [PO_4] to form $[Zn_4P_4O_{16}]_n^{4n-}$ layer perpendicular to c. (c) $[Zn_4P_4O_{16}]_n^{4n-}$ layers are linked by [Zn(3)O_4] to build a covalent framework with channels along b, in which the sodium atoms are located.

Table 4
Bond valence calculation for $Na_2Zn_5(PO_4)_4$

Central atom	Coordinate atoms	Bond valence sum
Zn(1)	O(1), O(2), O(5), O(8)	2.081
Zn(2)	O(1), O(4), O(5)#1, O(7)	2.064
Zn(3)	O(3), O(3)#2, O(6), O(6)#2	2.030
P(1)	O(1)#3, O(2)#5, O(3), O(4)#6	5.002
P(2)	O(5)#8, O(6), O(7)#4, O(8)#7	4.978
Na(1)	O(3)#1, O(4), O(6), O(7)#3, O(8)#7	0.895
O(1)	Zn(1), Zn(2), P(1)#1	2.075
O(2)	Zn(1), P(1)#10	1.938
O(3)	Zn(3), P(1), Na(1)#3	2.057
O(4)	Zn(2), P(1)#11, Na(1)	1.989
O(5)	Zn(1), Zn(2)#3, P(2)#12	2.094
O(6)	Zn(3), P(2), Na(1)	1.840
O(7)	Zn(2), P(2)#9, Na(1)#1	1.991
O(8)	Zn(1), P(2)#13, Na(1)#13	2.051

Note: See footnote of Table 3 for symmetry transformations.

structure of $NaZnPO_4$ [13] (P/Zn = 1:1), the coordination number of Zn is 4, which is the lowest plausible value for Zn–O polyhedrons. The phosphate group is the smallest phosphate groups [PO_4]. Fully ordered corner-sharing [ZnO_4] and [PO_4] tetrahedrons make up the 3D covalent framework, a member of the large structural family of tridymite. In the title compound, the P/Zn atomic ratio is further lowered to a value of 0.8, which is the lowest value in pseudo-ternary compounds obtained in the P_2O_5–ZnO–Na_2O system. The [PO_4] polyhedron is the smallest P–O clusters and the coordination number of Zn cannot be lowered too. To accommodate the large number of zinc atoms, like [PO_4] tetrahedrons, some [ZnO_4] tetrahedrons link to each other by sharing two common apex oxygen atoms to form infinite $[ZnO_3]_n^{4n-}$ chains. Again by sharing corners, [PO_4] polyhedrons link the $[ZnO_3]_n^{4n-}$ chains to build zincophosphate layers. The layers are then connected by [Zn(3)O_4] polyhedrons to form a 3D covalent framework.

3.2. *Powder diffraction pattern*

As mentioned in Section 1, the powder diffraction pattern of our sample is similar to Ref. [20], an unindexed pattern, but does not match it well. In addition, $Na_2Zn_5(PO_4)_4$ was obtained in an effort to grow $Na_9Zn_{21}(PO_4)_{17}$ single crystals. During the investigation of the phase relations in the system $Na_2ZnP_2O_7$–$Zn_2P_2O_7$, Grebenshchikov et al. [23] found that the previously

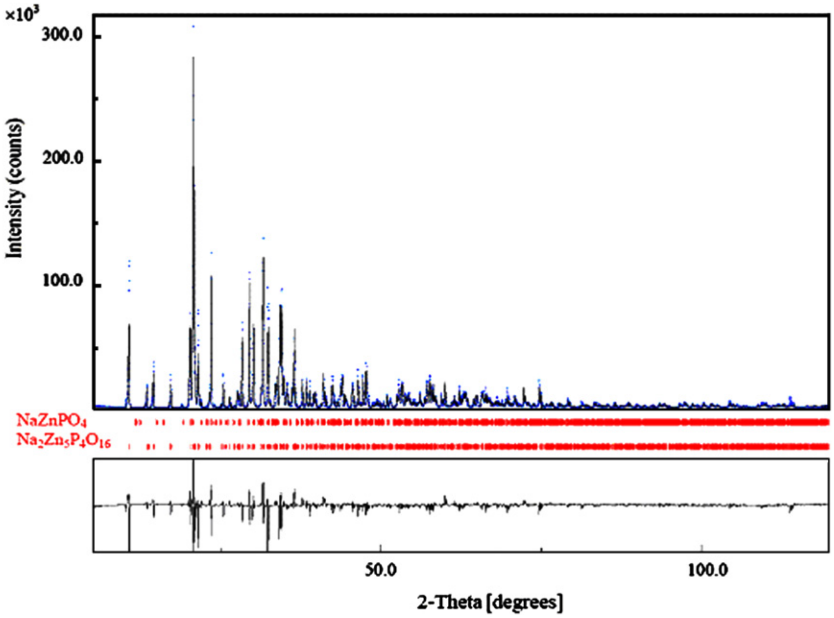

Fig. 2. Rietveld Refinement of powder mixtures of $Na_2Zn_5(PO_4)_4$ and $NaZnPO_4$ (measured pattern: cross; calculated pattern: solid lines. $Rp = 15.20\%$, $Rwp = 19.33\%$).

reported phase $Na_8Zn_6(P_2O_7)_5$ could not be confirmed. In fact, the “phase” may present a mixture of $Na_2ZnP_2O_7$ and $Zn_2P_2O_7$ in 4:1 molar ratio. In our work, if $Na_2Zn_5(PO_4)_4$ mixes with $NaZnPO_4$ in 4:1 molar ratio, which is a highly possible phase in the $ZnO–Na_2O–P_2O_5$ system at 400–900 °C, the “formula” of the mixture is then $Na_9Zn_{21}(PO_4)_{17}$. As a matter of fact, both $Na_2Zn_5(PO_4)_4$ and $NaZnPO_4$, which are the major and minor phases, respectively, are identified on the powder diffraction pattern of $Na_9Zn_{21}(PO_4)_{17}$. We simulated the theoretical powder diffraction patterns of a mixture of $Na_2Zn_5(PO_4)_4$ and $NaZnPO_4$ in the molar ratio of 4:1 with PowderCell [24]. The theoretical curve is in good agreement with the measured pattern. The actual weight percentage of each phase is then determined from Rietveld refinement of the measured pattern by using the program MAUD [25] (Fig. 2). The weight fraction of $Na_2Zn_5(PO_4)_4$ and $NaZnPO_4$ is 95.26 and 4.74 wt%, respectively, which is in close agreement with the 4:1 molar ratio.

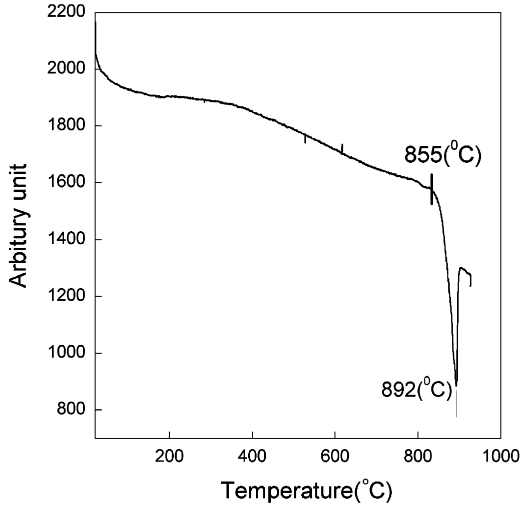

Fig. 3. Thermal analysis curve of $Na_2Zn_5(PO_4)_4$ with heating rate of 10 °C/min.

3.3. *DTA analysis*

As shown in Fig. 3, the extrapolated onset point 855 °C on the DTA curve is the melting point of the compound. The only one endothermal peak in the heating curve indicates that no phase transition happens during the course. This compound is easily to be obtained from the melt due to the character of congruent melting. The crystals are being grown for measurement of other properties.

3.4. *Conductivity analysis*

The sample for conductivity measurement is 10 mm in diameter and 0.3 mm in thickness. XRD confirmed the samples were $Na_2Zn_5(PO_4)_4$ after they were annealed at 600 °C. The resistance is $6.7842 \times 10^6\,\Omega$, and the conductivity is about 5.63×10^{-9} S/cm at room temperature.

4. Conclusions

The structure of a new compound $Na_2Zn_5(PO_4)_4$ was determined by single crystal X-ray diffraction method. The structure is made up of 3D $[Zn_5P_4O_{16}]_n^{2n-}$ covalent framework consisting of $[Zn_4P_4O_{16}]_n^{4n-}$ layers. It belongs to the orthorhombic system with space group *Pbcn* and lattice parameters $a = 10.381(2)$ Å, $b = 8.507(1)$ Å, $c = 16.568(3)$ Å. The powder diffraction pattern of $Na_9Zn_{21}(PO_4)_{17}$ is explained by simulating a theoretical pattern with $NaZnPO_4$ and $Na_2Zn_5(PO_4)_4$ in the molar ratio of 1:4 and then by Rietveld refinement of the experimental data. The compound $Na_2Zn_5(PO_4)_4$ melts congruently at 855 °C and its conductivity is 5.63×10^{-9} S/cm at room temperature.

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