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NOVEL ROUTES OF ADVANCED MATERIALS PROCESSING AND APPLICATIONS

Preparation of new zirconium phosphates by solvothermal reaction

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Abstract Two types of new zirconium phosphates, $[enH_2]Zr(OH)(PO_4)(HPO_4)$ (en; ethylene diamine) and $(NH_4)_5[Zr_3(OH)_9(PO_4)_2(HPO_4)]$ were prepared under solvothermal condition using diethylene glycol as a solvent and their crystal structures were determined by using single crystal X-ray diffraction data. The former compound has the layer structure similar to that of γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$, and protonated ethylene diamines were located in the interlayer space. At elevated temperatures, this compound decomposed by releasing protonated ethylene diamines and finally changed to ZrP_2O_7. The interlayer space was soft-chemically inactive unlike α-$Zr(HPO_4)_2 \cdot H_2O$ and γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$. The later compound has the tunnel structure built up by corner-sharing ZrO_6 octahedra and PO_4 tetrahedra, and NH_4^+ ion was located in the tunnel.

Introduction

α-$Zr(HPO_4)_2 \cdot H_2O$ and γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$, representative zirconium phosphates, are well known to have a layer type structure with soft-chemically active interlayer space [1, 2]. These zirconium phosphates have been used as an ion-exchanger, ion-conductor, and support of catalyst, etc. A variety of compounds based on a zirconium phosphate have been synthesized by adding organic compounds and fluorine under solvothermal reaction; for example, $[enH_2]_{1.5}[Zr(PO_4)(HPO_4)F_2]$ [3], $[enH_2]_{0.5}[Zr_2(HPO_4)(PO_4)F]$ [4], $[enH_2]_{0.5}$ $[Zr(HPO_4)_3]$ [5], $[enH_2]_{0.5}[Zr(PO_4)(HPO_4)]$ [5] (en; ethylene diamine), $[amH_2]_{0.5}[Zr_2(PO_4)$ $(HPO_4)_2F_2] \cdot 0.5H_2O$ (am; trans-1,4-diaminocyclohexane) [6], $[amH_2]_{0.5}[Zr_3(PO_4)_3F_6] \cdot 1.5H_2O$ (am; trans-1,4-diaminocycrohexane) [6], $[amH_2]_{0.5}[Zr_3(PO_4)_3(HPO_4)F_2] \cdot 1.5H_2O$ (am; 2,2-dimethyl-1,3-diaminopropane) [6]. The common structural feature for these inorganic–organic complexes is that the 1-D, 2-D or 3-D structure is built up by connecting inorganic part (edge-sharing of ZrO_6 octahedra and PO_4 tetrahedra) and organic one (protonated templates). Diversity of phosphates and organic compounds must produce much more new compounds based on ZrO_6 octahedra and PO_4 tetrahedra.

We have found three types of zirconium phosphates, 2-D $[NH_4]_2[enH_2]_2Zr_3(OH)_6(PO_4)_4$ [7] (hereafter, ZrPO-1), 2-D $[NH_4]_2Zr(OH)_3(PO_4)$ [8] (ZrPO-2), and 1-D $[NH_4]_3Zr(OH)_2$ $(PO_4)(HPO_4)$ [9] (ZrPO-3) and clarified their crystal structures by using single crystal X-ray diffraction data. In the course of this investigation, two types of zirconium phosphates, $[enH_2]Zr(OH)(PO_4)(HPO_4)$ (hereafter ZrPO-4) and $(NH_4)_5[Zr_3(OH)_9(PO_4)_2(HPO_4)]$ (ZrPO-5) could be synthesized under solvothermal condition using diethylene glycol. Here, we will describe the synthesis and crystal structure of these new zirconium phosphates.

Experimental

Plate-like single crystals of $[enH_2]Zr(OH)(PO_4)(HPO_4)$ (ZrPO-4) were prepared under the condition of $ZrOCl_2 \cdot 8H_2O:H_3PO_4:H_2N(CH_2)_2NH_2:NH_4F:(HOCH_2CH_2)_2O = 1.0:1.8:0.83:4.0:30$ with the molar ratio. Needle-like single crystals of $(NH_4)_5[Zr_3(OH)_9(PO_4)_2$ $(HPO_4)]$(ZrPO-5) were

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prepared under the condition of $ZrOCl_2 \cdot 8H_2O$:H_3PO_4:n-$(CH_3CH_2CH_2)_3N$:NH_4F:$(HOCH_2CH_2)_2O$ = 1.0:2.2:0.42:4.0:30 with the molar ratio. In a typical synthesis procedure, $ZrOCl_2 \cdot 8H_2O$ was dissolved in $(HOCH_2CH_2)_2O$ to form a solution, to which H_3PO_4 was added, then the mixture gelled. NH_4F was added to the gel to form a sol under stirring with a glass stick, and then $H_2N(CH_2)_2NH_2$ for ZrPO-4 or n-$(CH_3CH_2CH_2)_3N$ for ZrPO-5 was added dropwise to the sol under vigorous stirring. After stirred with a magnetic stirrer for 2 h, the reaction mixture was transferred into a Teflon-lined stainless steel autoclave to a fill fraction of 60%, and solvothermal-treated at 180 °C for 4 days. The solid product was filtered and washed with deionized water and ethanol, and then dried in air at 70 °C. The product was identified by X-ray powder diffraction using monochromated CuKα radiation. The thermal stability was investigated by TG-DTA with a heating rate of 10 °C/min from room temperature to 1,000 °C.

Single crystal X-ray diffraction data were collected by using a Rigaku AFC-7R four-circle diffractometer with graphite monochromated MoKα radiation using the ω-2θ scan technique ($D\omega = (1.73 + 0.30\tan\theta)°$). The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by using ψ scans. The crystal structure was solved and refined with the computer programs from the Crystal Structure crystallographic software package [10]. Details of the data collection and refinement are summarized in Table 1. The positional and thermal parameters, and bond valence sum [11] are summarized in Tables 2 and 3. Selected interatomic distances are listed in Table 4.

ZrPO-4 was crystallized in the monoclinic cell of $a = 12.281(3)$, $b = 6.577(2)$, $c = 6.575(1)$ Å and $\beta = 102.10(2)°$ with the space group of $P2_1$ (#4) and the final R-factors were $R = 0.053$ and $R_w = 0.058$ for 4874 unique reflections. ZrPO-5 was also crystallized in the monoclinic cell of $a = 19.108(4)$, $b = 7.547(2)$, $c = 15.492(4)$ Å and $\beta = 102.62(2)°$ with the space group of $P2_1/n$ (#14) and the final R-factors were $R = 0.050$ and $R_w = 0.060$ for 19085 unique reflections.

Table 1 Crystal data and intensity collections for ZrPO-4 and 5

Empirical formula	$H_{12}ZrP_2O_9N_2C_2$ (ZrPO-4)	$H_{30}Zr_3P_3O_{21}N_5$ (ZrPO-5)
Formula weight	361.29	802.84
Crystal color	Colorless	Colorless
Crystal dimensions	0.10 × 0.10 × 0.01 mm	0.10 × 0.20 × 1.00 mm
Crystal system	Monoclinic	
Space group	$P2_1$ (#4)	$P2_1/n$ (#14)
Lattice parameters	$a = 12.281(3)$ Å	$A = 19.108(4)$ Å
	$b = 6.577\ (2)$ Å	$B = 7.547(2)$ Å
	$c = 6.575(1)$ Å	$C = 15.492(4)$ Å
	$\beta = 102.10(2)$ Å	$\beta = 102.62(2)$ Å
Volume	519.3(2) $Å^3$	2,179(1) $Å^3$
Z value	2	4
Calculated density	2.310 g/cm^3	2.446 g/cm^3
Diffractometer	Rigaku AFC-7	
Radiation	Graphite monochromated	
Mo $K\alpha$	$\lambda = 0.71069$ Å	
Temperature	23.0°C	
μ(Mo $K\alpha$)	14.06 cm^{-1}	17.31 cm^{-1}
Scan type	ω-2θ	
Scan speed	16.0°/min	
No. of total reflections	4881	20104
No. of unique reflections	4874	19085
Refinement	Full-matrix least-squares on F	
No. of reflections ($I > 3.00\sigma(I)$)	3306	4112
No. variables	198	280
Reflection/Parameter ratio	16.70	14.18
Residuals: R, Rw	0.053, 0.058	0.050, 0.060
Goodness of fit indicator	0.875	1.402
$\Delta\rho_{max}$	3.15 $e^-/Å^3$	1.78 $e^-/Å^3$
$\Delta\rho_{min}$	–1.25 $e^-/Å^3$	–3.64 $e^-/Å^3$

Table 2 Positional, isotropic thermal parameters and BVS (Bond Valence Sum) for ZrPO-4

Atom	Position	*x*	*y*	*z*	B_{eq} (Å^2)	Occ.	BVS
Zr	2a	–0.08012(4)	0.4742(8)	0.22414(7)	0.862(6)	1	4.45
P(1)	2a	–0.0002(1)	0.475(1)	0.7504(2)	1.14(2)	1	4.87
P(2)	2a	–0.3684(9)	0.552(1)	0.179(2)	2.3(2)	0.5	4.96
P(3)	2a	–0.3662(6)	0.395(1)	0.181(1)	1.1(1)	0.5	4.79
O(1)	2a	–0.074(1)	0.165(2)	0.221(2)	1.8(2)	1	1.97
O(2)	2a	–0.0730(4)	0.469(3)	–0.0864(6)	1.81(9)	1	1.92
O(3)	2a	–0.076(1)	0.790(2)	0.230(2)	1.9(2)	1	1.93
O(4)	2a	–0.0800(4)	0.475(3)	0.5376(5)	1.56(6)	1	1.94
O(5)	2a	0.0859(3)	0.455(2)	0.2993(6)	1.2(1)	1	0.85
O(6)	2a	–0.2513(4)	0.470(3)	0.1459(8)	2.2(1)	1	2.89
O(7)	2a	–0.4516(4)	0.484(3)	–0.0145(8)	2.9(1)	1	2.28
O(8)	2a	–0.3886(5)	0.484(3)	0.3783(9)	3.3(1)	1	2.82
O(9)	2a	–0.378(2)	0.166(4)	0.211(5)	2.2(3)	0.5	1.30
O(10)	2a	–0.369(3)	0.790(4)	0.173(5)	2.9(4)	0.5	1.18
N(1)	2a	–0.269(1)	0.239(3)	0.718(3)	3.8(4)	0.5	–
N(2)	2a	–0.399(3)	0.207(5)	0.704(5)	4.9(7)	0.5	–
N(3)	2a	–0.2823(8)	0.867(2)	0.485(1)	2.6(2)	0.8	–
N(4)	2a	–0.404(4)	0.734(6)	0.699(5)	1.0(5)	0.2	–
C(1)	2a	–0.359(3)	0.061(8)	0.664(8)	3.8(8)	0.3	–
C(2)	2a	–0.310(2)	0.078(3)	0.807(3)	3.2(3)	0.7	–
C(3)	2a	–0.314(2)	0.870(3)	0.709(4)	5.5(5)	1	–

$B_{eq} = \frac{8}{3}\pi^2\left(U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}aa^*bb^*\cos\gamma+2U_{13}aa^*cc^*\cos\beta+2U_{23}bb^*cc^*\cos\alpha\right)$

Result and discussion

$[enH_2]Zr(OH)(PO_4)(HPO_4)$ (ZrPO-4)

This compound has a layered structure similar to that of γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ [2] as shown in Fig. 1. The crystal structure consists of macroanionic $[Zr(OH)(PO_4)(HPO_4)]^{2-}$ sheets separated by organic diprotonated ethylendiamine. The macroanionic sheet lying in the *bc* plane is built up by corner-sharing ZrO_6 octahedra and $P(1)O_4$ tetrahedra, and the hydrogen phosphate groups ($P(2)O_4$ and $P(3)O_4$ tetrahedra) are statistically distributed by corner-sharing at the apex oxygen atom O(6) in ZrO_6 octahedra. The apex oxygen atom O(5) opposite O(6) was not corner-shared by a phosphate group but bound to hydrogen atom. This alignment of the split model for hydrogen phosphates groups and formation of $ZrO_5(OH)$ octahedron are different from γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ [2] in which the corresponding hydrogen phosphate groups bridge the ZrO_6 octahedra and every oxygen atom of ZrO_6 octahedra is corner-shared by a phosphate group as shown in Fig. 2. Nonbridging of the hydrogen phosphate groups in our compound may be caused by nonaqueous solvothermal condition because both γ-$Zr(PO_4)(H_2PO_4)$ $2H_2O$ and $[enH_2]_{0.5}[Zr(PO_4)(HPO_4)]$ were prepared under solvothermal condition using water as a solvent. Nitrogen and carbon atoms except C(3) of the ethylene diamine molecule in the interlayer were statistically distributed, and the mean interatomic distances of N–C and C–C were 1.42 and 1.45 Å, respectively though short and long interatomic distances of N–C were observed.

The mean interatomic distance of Zr-O in ZrO_6 octahedra was 2.06 Å, which is compared with that in ZrPO-1 (2.06 Å) [7], $[enH_2]_{0.5}[Zr(PO_4)(HPO_4)]$ (2.07 Å) [5], and γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ (2.04 Å) [2]. The mean interatomic distance of P-O in the $P(1)O_4$ tetrahedron bridging ZrO_6 octahedra was 1.53 Å and that in the $P(2)O_4$ and $P(3)O_4$ tetrahedra was 1.53 and 1.55 Å, respectively. These values were in good agreement with that in ZrPO-1 (1.535 and 1.529 Å) [7], $[enH_2]_{0.5}[Zr(PO_4)(HPO_4)]$ (1.53 Å) [5], and γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ (1.55 and 1.56 Å) [2]. The values of the bond valence sum indicated that O(5) in ZrO_6 octahedron and O(10) in $P(2)O_4$ and O(9) in $P(3)O_4$ tetrahedra bound to hydrogen atom, and therefore this result is consistent with its chemical composition. Oxygen atom binding hydrogen atom is represented as bold letter in Tables 2 and 3 The bond valence sum of the terminal oxygen atoms, O(1)–O(4) was reasonable value (1.92–1.97), that of oxygen atoms (O(5), O(9), and O(10)) bound to hydrogen atom was low value (0.85–1.30) and that of

Table 3 Positional, isotropic thermal parameters and BVS(Bond Valence Sum) for ZrPO-5

Atom	Position	*x*	*y*	*z*	B_{eq} (Å^2)	BVS
Zr(1)	4e	0.14901(4)	0.2576(1)	0.79900(5)	1.23(2)	4.72
Zr(2)	4e	–0.40428(4)	0.0221(1)	0.89884(5)	1.28(2)	4.67
Zr(3)	4e	–0.12819(4)	–0.0416(1)	0.90077(5)	1.27(2)	4.67
P(1)	4e	0.0496(1)	0.2571(3)	0.5782(1)	1.30(4)	4.98
P(2)	4e	0.0120(1)	0.2447(3)	0.9150(1)	1.36(4)	4.98
P(3)	4e	–0.2589(1)	–0.2516(3)	0.9847(1)	1.36(4)	4.97
O(1)	4e	0.0589(3)	0.2904(9)	0.8510(4)	2.3(1)	1.97
O(2)	4e	–0.0425(3)	0.1046(8)	0.8732(4)	2.0(1)	1.89
O(3)	4e	–0.2147(3)	–0.1800(9)	0.9210(4)	2.4(1)	1.98
O(4)	4e	–0.0280(3)	0.4097(9)	0.9349(4)	2.6(1)	1.23
O(5)	4e	0.1545(3)	0.5223(7)	0.8068(3)	0.8(1)	0.84
O(6)	4e	–0.2794(4)	–0.4402(8)	0.9630(5)	2.9(2)	1.34
O(7)	4e	–0.3252(3)	–0.1324(8)	0.9779(4)	2.1(1)	1.87
O(8)	4e	0.1290(3)	–0.0017(7)	0.7891(4)	2.2(1)	0.86
O(9)	4e	0.0389(3)	0.0549(8)	0.5686(4)	2.6(1)	1.18
O(10)	4e	0.2375(3)	0.2420(9)	0.7506(4)	1.8(1)	0.85
O(11)	4e	0.0933(3)	0.2946(9)	0.6698(4)	2.7(2)	1.99
O(12)	4e	–0.1067(3)	–0.2207(7)	0.8144(3)	0.9(1)	0.83
O(13)	4e	–0.4766(3)	–0.1537(9)	0.9364(4)	2.2(1)	1.92
O(14)	4e	–0.1427(3)	0.1477(8)	0.9856(4)	2.2(1)	0.84
O(15)	4e	–0.1904(3)	0.0849(7)	0.7990(3)	1.0(1)	0.85
O(16)	4e	–0.4843(3)	0.1695(8)	0.8298(3)	1.3(1)	0.84
O(17)	4e	–0.4004(3)	–0.1219(7)	0.7940(3)	1.3(1)	0.92
O(18)	4e	–0.4094(3)	0.1736(9)	0.0114(4)	2.4(1)	1.89
O(19)	4e	0.2145(3)	0.232(1)	0.9206(4)	2.7(1)	1.99
O(20)	4e	–0.0585(3)	–0.1749(9)	0.9989(4)	2.5(1)	1.97
O(21)	4e	0.3313(3)	0.1889(8)	0.8775(3)	1.4(1)	0.94
N(1)	4e	–0.4074(4)	0.518(1)	0.8338(5)	2.3(2)	–
N(2)	4e	0.2528(4)	0.741(1)	0.9297(5)	2.2(2)	–
N(3)	4e	–0.1890(5)	–0.546(1)	0.8313(6)	3.3(2)	–
N(4)	4e	0.0458(4)	0.722(1)	0.8579(5)	2.7(2)	–
N(5)	4e	0.1235(4)	0.742(1)	0.6420(5)	2.7(2)	–

oxygen atoms (O(6), O(7), and O(8)) in $P(2)O_4$ and $P(3)O_4$ tetrahedra was somewhat high values (2.28–2.89) because of the overestimation of the split model.

The attempt of ion-exchange with alkaline ions or H^+ and intercalation with organic molecules such as amines for ZrPO-4 was unsuccessful, and therefore the interlayer space of ZrPO-4 was inactive unlike ZrPO-1 [12].

TG-DTA curves of this compound are shown in Fig. 3. The observed total mass loss (25.3%) agreed well with the value (26.6%) calculated from release of ethylene diamine and OH group. From high temperature X-ray diffraction patterns it was found that this compound held the crystal structure up to 300 °C and then became amorphous accompanying large mass loss caused by release of ethylene diamine and OH group. From the X-ray powder diffraction pattern the sample heated up to 1,000 °C was identified as ZrP_2O_7 [13]. Finally the amorphous phase crystallized to ZrP_2O_7 above 1,000 °C.

$(NH_4)_5[Zr_3(OH)_9(PO_4)_2(HPO_4)]$(ZrPO-5)

This phosphate had a three-dimensional structure build up by corner-sharing ZrO_6 octahedra and PO_4 tetrahedra and NH_4^+ ion is located in the tunnel as shown in Fig. 4. There were five crystallographic sites of NH_4^+ ions, and $N(1)H_4^+$, $N(3)H_4^+$, and $N(4)H_4^+$ ions were located in the tunnel formed by six ZrO_6 octahedra and six PO_4 tetrahedra and $N(2)H_4^+$ and $N(5)H_4^+$ ions in the tunnel formed by four ZrO_6 octahedra and four PO_4 tetrahedra. These tunnels were different

Table 4 Selected interatomic distances (Å) for ZrPO-4 and 5

ZrPO-4					
Zr–O(1)	2.04(1)	P(1)–O(1)	1.53(1)	P(2)–O(6)	1.59(1)
Zr–O(2)	2.063(4)	P(1)–O(2)	1.534(5)	P(2)–O(7)	1.52(1)
Zr–O(3)	2.08(1)	P(1)–O(3)	1.53(1)	P(2)–O(8)	1.45(1)
Zr–O(4)	2.061(3)	P(1)–O(4)	1.531(3)	P(2)–O(10)	1.57(3)
Zr–O(5)	1.998(4)	Ave.	1.53	Ave.	1.53
Zr–O(6)	2.057(4)				
Ave.	2.05	C(1)–C(3)	1.38(5)	N(1)–C(1)	1.60(5)
		C(2)–C(3)	1.51(3)	N(1)–C(2)	1.35(3)
P(3)–O(6)	1.56(1)	Ave.	1.45	N(2)–C(1)	1.14(6)
P(3)–O(7)	1.59(1)			N(2)–C(2)	1.43(4)
P(3)–O(8)	1.50(1)			N(3)–C(3)	1.60(3)
P(3)–O(9)	1.53(3)			N(4)–C(3)	1.42(5)
Ave.	1.55			Ave.	1.42
ZrPO-5					
Zr(1)–O(1)	2.069(1)	Zr(2)–O(7)	2.082(6)	Zr(3)–O(2)	2.093(6)
Zr(1)–O(5)	2.002(5)	Zr(2)–O(13)	2.088(7)	Zr(3)–O(3)	2.038(6)
Zr(1)–O(8)	1.993(6)	Zr(2)–O(16)	2.001(5)	Zr(3)–O(12)	2.006(5)
Zr(1)–O(10)	1.997(6)	Zr(2)–O(17)	1.969(5)	Zr(3)–O(14)	2.001(6)
Zr(1)–O(11)	2.069(5)	Zr(2)–O(18)	2.106(6)	Zr(3)–O(15)	1.998(5)
Zr(1)–O(19)	2.030(5)	Zr(2)–O(21)	1.960(6)	Zr(3)–O(20)	2.052(6)
Ave.	2.023	Ave.	2.034	Ave.	2.031
P(1)–O(9)	1.542(7)	P(2)–O(1)	1.515(7)	P(3)–O(3)	1.529(7)
P(1)–O(11)	1.509(6)	P(2)–O(2)	1.526(6)	P(3)–O(6)	1.495(7)
P(1)–O(13)	1.520(6)	P(2)–O(4)	1.527(7)	P(3)–O(7)	1.538(6)
P(1)–O(18)	1.520(7)	P(2)–O(20)	1.526(6)	P(3)–O(19)	1.533(6)
Ave.	1.522	Ave.	1.524	Ave.	1.524

from that of NASICON-type $(NH_4)Zr_2(PO_4)_3$ [14], which were built up by two ZrO_6 octahedra and two PO_4 tetrahedra.

The mean interatomic distances of Zr-O in three ZrO_6 octahedra were 2.026, 2.019, and 2.031 Å, which are somewhat shorter than in ZrPO-4 (2.06 Å) [7], $(NH_4)Zr_2(PO_4)_3$ (2.07 Å) [12], and γ-$Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ (2.04 Å) [2]. This comes from the fact that every ZrO_6 octahedron in ZrPO-5 is bound to three hydrogen atoms as mentioned later. The mean interatomic distances of P-O in three PO_4 tetrahedra were 1.523, 1.524, and 1.524 Å and these values were in good agreement with that in other zirconium phosphates as mentioned above. The values of the bond valence sum indicated that three oxygen atoms in every ZrO_6 octahedron and O(9) atom in $P(1)O_4$ tetrahedron bound to hydrogen atom, and therefore the number of hydrogen atoms from the bond valence sum is consistent with that from the charge neutrality derived by structural analysis.

TG-DTA curves of this compound are shown in Fig. 5. The observed total mass loss (28.3%) agreed well with the

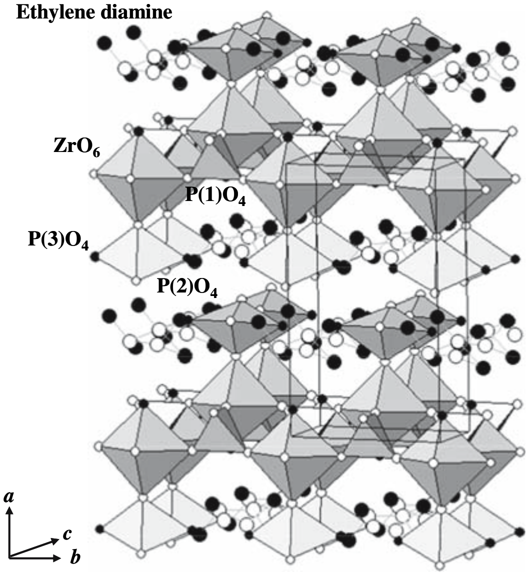

Fig. 1 Crystal structure of ZrPO-4. Oxygen atoms binding hydrogen atoms are represented by small solid circle

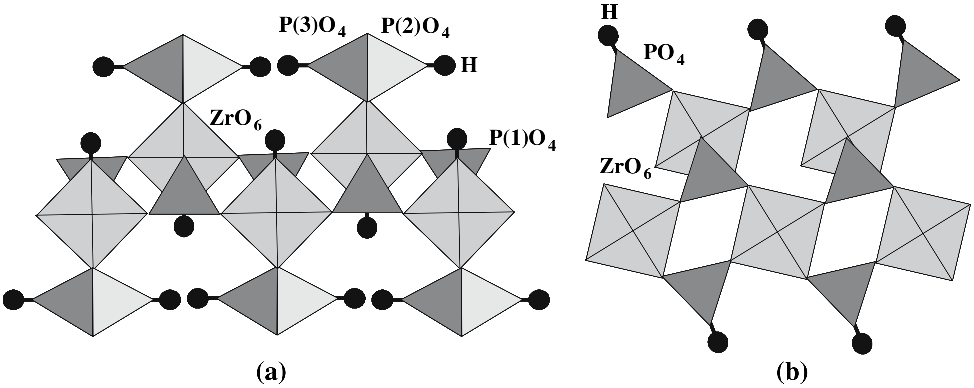

Fig. 2 Comparison of the crystal structure between ZrPO-4 (**a**) and γ-Zr(PO$_4$)(H$_2$PO$_4$)·2H$_2$O (**b**)

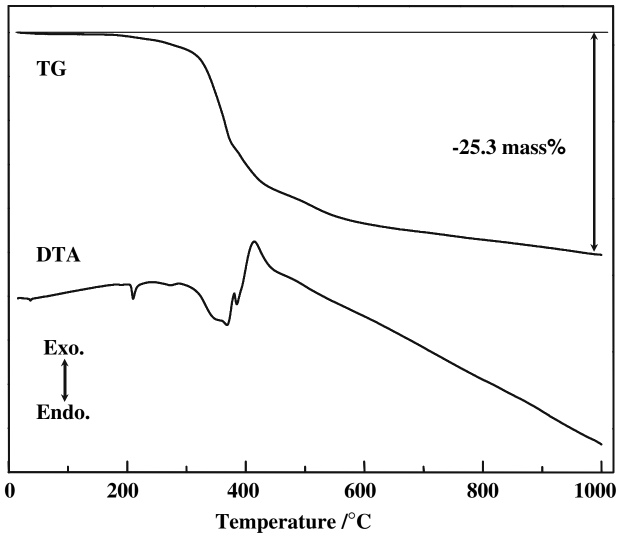

Fig. 3 TG-DTA curves of ZrPO-4

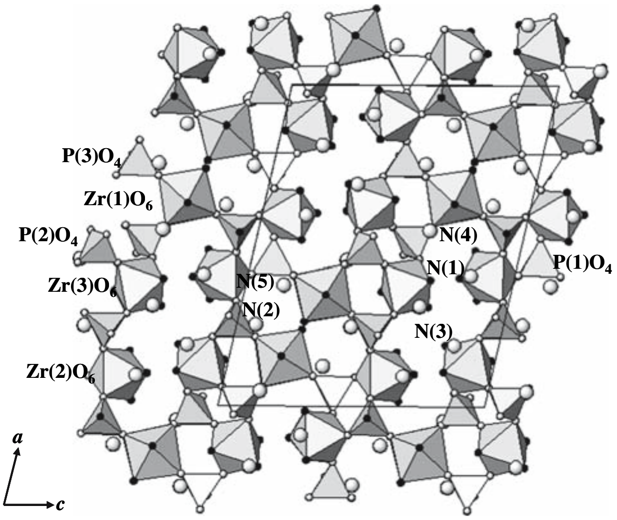

Fig. 4 Crystal structure of ZrPO-5. Oxygen atoms binding hydrogen atoms are represented by solid circle

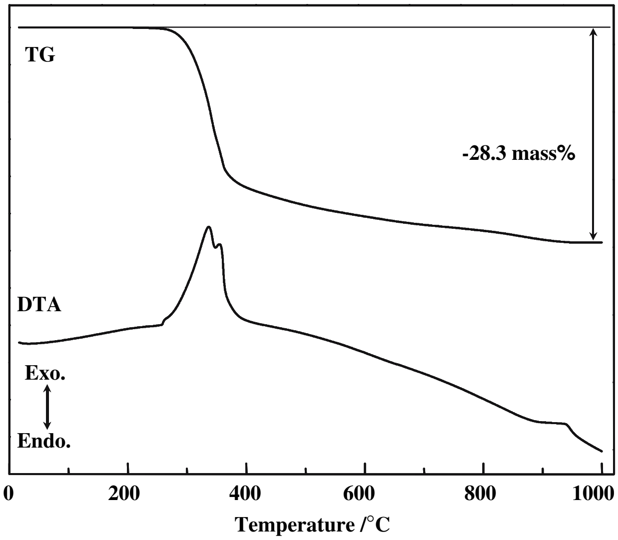

Fig. 5 TG-DTA curves of ZrPO-5

value (27.6%) calculated from release of ammonium ion and OH group. From high temperature X-ray diffraction patterns, it was found that this compound held the crystal structure up to 300 °C and then became amorphous by release of ammonium ion and OH group. From the X-ray powder diffraction pattern, the sample heated up to 1,000 °C was identified as $Zr_2P_2O_9$ [15]. The amorphous phase crystallized to $Zr_2P_2O_9$ at the endothermic peak of 940 °C.

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