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Two New Four-Connected Zeolite-like Magnesium Aluminophosphates with Intersecting 8-Ring Channels

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Two new Mg-containing aluminophosphates JU94 and JU95 (|$C_4H_{12}N_2$|[$Mg_2Al_6(PO_4)_8(H_2O)_4$]) have been hydrothermally synthesized in the same reaction system of MgO-Al_2O_3-P_2O_5-piperazine-H_2O. Both of their structures are constructed by the connection of AlO_4/$MgO_4(H_2O)_2$ polyhedra and PO_4 tetrahedra, forming two-dimensional intersecting 8-ring channels. Their frameworks exhibit distinct 4-connected zeolite-like topologies, as well as different dehydration behaviours during the calcinations. Their structure correlation has been discussed through the different linkage modes of $Mg_2Al_3P_5O_{30}$ building units. This work will provide insight into the synthesis and design of the novel MAPO (M=metal) molecular sieves.

Introduction

Zeolites are strictly defined as those built up from TO_4 tetrahedra, which are widely used in catalysis, adsorption, and ion-exchange.[1-3] Aluminophosphate molecular sieves, designated $AlPO_4$-*n*, have become the second major family of zeolite materials since their first discover by Wilson and co-workers in 1982.[4-6] The typical structure of $AlPO_4$-*n* is constructed by the strict alternation of AlO_4 and PO_4 tetrahedra to form the three-dimensional (3D) crystalline neutral framework with ordered nanopores. The incorporation of metal heteroatoms into the frameworks of $AlPO_4$-*n* to replace the Al sites will generate MAPO molecular sieves (M = metal heteroatom except Al) with Brönsted or Lewis acid sites, which have extensive applications in catalysis, ion-exchange, photoluminescence, magnetism, and so forth.[7-9] Notably, some MAPOs with well-separated active centres can be used as single-site solid catalysts in many catalytic processes. Such examples include MAlPO-18 (AEI, M = Co^{2+}, Mg^{2+}, Zn^{2+}, Mn^{2+}),[10,11] Co^{3+}AlPO-34 (CHA)[12] and $M^{2+}M^{3+}$APO-36 (ATS, M^{2+}=Co^{2+}, Mg^{2+}, M^{3+}= Co^{3+}, Mn^{3+}),[13] etc.

Nowadays, a large variety of MAPO molecular sieves with various openings of 8-, 10-, 12-, 14-, 18- and 20-rings have been synthesized. Up to now, among all the 218 known zeolite topological types, more than 60 belong to this category.[14,15] It is noted that the existence of metal heteroatoms not only affects the property, but also stabilizes the structure of the resulting MAPOs. Besides the traditional $AlPO_4$-*n* analogues, many MAPO molecular sieves with new zeolite topology have been synthesized, including UCSB-6 (SBS),[16] MAPO-CJ40 (JRY),[17] MAPO-CJ62 (JSW),[18] MAPO-CJ69 (JSN),[19] MAPO-57 (AFV),[20] MAPO-59 (AVL),[20] and so on. These compounds could not be synthesized in the pure AlPO system, highlighting the important role of heteroatoms in stabilizing the framework of these MAPOs. The reason is that the M-O-P angles may vary in a wider range of 120-150° compared to the typical Al-O-P angles closed to 145°, the replacement of flexible MO_4 tetrahedra to rigid AlO_4 tetrahedra can release the stress and stabilize the resulting structure. Hence, the incorporation of heteroatom into the frameworks is an efficient strategy to synthesize novel zeolite structures.[21-23]

In recent years, our research focuses on the synthesis of MAPO molecular sieves with novel zeolite topology, new property and tunable framework compositions. For this purpose, the selection of heteroatom and the organic template, and the careful regulation of the reaction gel are very important. As successful examples, ACO-zeotype FeAPO-CJ66[24] and LEV-zeotype MgAPO-CJ67[25] with variable M/Al ratios have been synthesized by adjusting the type and the amount of organic template based on the host-guest charge balance. Magnesium aluminophosphate JU92 and its derivatives with novel zeolite structure and photoluminescence have been synthesized by using *n*-methylpiperazine as the template.[26] In this work, we present two new Mg-containing microporous aluminophosphates JU94 and JU95, which exhibit four-connected (connected four neighbour T atoms through O atoms, T=Al, P, Si, etc.) zeolite-like topology with intersecting 8-ring channels. Interestingly, these two compounds are synthesized in the similar reaction system just with slightly different gel compositions. They possess the same framework composition of $[Mg_2Al_6(PO_4)_8(H_2O)_4]^{2-}$, the same organic template and the same coordination modes of Mg, Al and P atoms, but with distinct framework structures. The syntheses and structures of as-synthesized and calcined samples, as well as their structural correlation have been discussed.

Experimental Section

Materials and Syntheses

The reagents and solvents employed in the synthesis were commercially available and used as received without further purification. JU94 and JU95 were synthesized under hydrothermal conditions in the same reaction system of MgO-Al_2O_3-P_2O_5-piperazine (PZ)-H_2O. Typically, pseudoboehmite (Al_2O_3, 62%, Shandong aluminium industry) and magnesium acetate ($Mg(CH_3COO)_2 \cdot 4H_2O$, Tianjin Fuchen Chemical Reagents Factory) were dispersed in a solution of orthophosphoric acid (85 wt%, Beijing Chemical Industry Group Co. LTD) in water under vigorous stirring at room temperature. Then, PZ ($C_4H_{10}N_2$, Aldrich) was added into this mixture. After stirring for one hour, a homogeneous gel with an overall molar composition of $1.0Al_2O_3$: 0.67MgO: $2.91P_2O_5$: 1.70PZ: $224H_2O$ (for JU94) or $1.0Al_2O_3$: 0.67MgO: $2.62P_2O_5$: 2.63PZ: $224H_2O$ (for JU95) was formed, which was heated under autogenous pressure at 180 °C in a 15 mL Polytetrafluoroetylene-lined stainless steel autoclave for 3 days. The colorless crystals were washed in distilled water and dried at room temperature overnight. The final products containing main phase of JU94 mixed with an unknown phase, and the pure phase of JU95 were obtained. Pure crystals of JU94 were picked up from the mixture for further characterization.

For the study of thermal stability, the as-synthesized JU94 and JU95 were placed into a normal furnace and heated from RT to 400 °C (for JU94) or to 300 °C (for JU95) at a temperature ramp rate of 1 °C min^{-1} in air and a 4 h isothermal hold at the respective temperature. The calcined samples were denoted as JU94-400 and JU95-300, respectively.

Characterizations

Powder X-ray diffraction (PXRD) data were collected on a Rigaku D/max-2550 diffractometer with Cu K*α* radiation (λ = 1.5418 Å). Field-emission scanning electron microscopy (JEOL JSM-6700F) was used to study the crystal morphology by using conventional sample preparation and imaging techniques. Thermogravimetric analysis (TGA) was carried out on a TA Q500 analyzer in air with a heating rate of 10 °C min^{-1} from RT to 800 °C. Inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300DV spectrometer. Elemental analysis was conducted on a Perkin-Elmer 2400 elemental analyzer. Compositional analyses of JU94 and JU95: Mg, 4.23; Al, 14.22; P, 22.05; C, 4.10; H, 1.79; N, 2.40; and Mg, 4.20; Al, 14.20; P, 22.03; C, 4.47; H, 2.03; N, 2.63, respectively. Anal. Calcd. for JU94 and JU95: Mg, 4.25; Al, 14.34; P, 21.95; C, 4.25; H, 1.77; N, 2.48

Structural Determination

Suitable single crystals of JU94, JU94-400, JU95 and JU95-300 with dimensions of 0.21 × 0.15 × 0.14 mm^3, 0.20 × 0.12 × 0.10 mm^3, 0.10 × 0.10 × 0.10 mm^3, and 0.30 × 0.20 × 0.05 mm^3, respectively, were selected for single-crystal X-ray diffraction analyses. The intensity data were collected on a Bruker SMART APEX Π CCD diffractometer by oscillation scans using graphite-monochromated Mo K*α* radiation (λ = 0.71073 Å) at temperature of 23 ± 2 °C. Cell refinement and data reduction were accomplished with the SAINT processing program.[27] The structures were solved in the space group $P2_1/c$ (for JU94 and JU94-400) and $P2_1/n$ (for JU95 and JU95-300), respectively, by direct methods and refined by full matrix least-squares technique with the SHELXTL crystallographic software package.[28] The heaviest atoms of Al, Mg, P and O could be unambiguously located, and the C and N atoms were subsequently located in the difference Fourier maps. The H atoms in their structures were not added. All non-hydrogen atoms were refined anisotropically. The structure details are given in Table S1† and Table S2†, and the selected bond distances and bond angles are listed in the Table S3† and Table S4†. CCDC 1007280 (JU94), 1007281 (JU94-400), 1007282 (JU95) and 1007283 (JU95-300) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and discussion

Syntheses and Characterizations

JU94 and JU95 are hydrothermally synthesized by using piperazine (PZ) as the template in the same reaction system of Al_2O_3-MgO-P_2O_5-PZ-H_2O at 180 °C for 3 days. Interestingly, the slight changes of the amount of H_3PO_4 and piperazine in the synthesis produce two different phases of JU94 and JU95. Their crystal morphologies are different (Fig. S1†). The as-synthesized JU94 is thin rod-like crystals aggregated with an unknown phase with irregular block-like crystals, while JU95 is thick conical crystals. Study shows that the pH value of the reaction mixture is crucial for the synthesis of these two compounds. The lower pH value (pH = 1.5) favours the formation of JU94, while higher pH value (pH = 5.0) induces the formation of JU95. As the pH < 1.0, a dense phase of aluminophosphate is formed. When the pH > 7, a layered magnetism aluminophosphate is obtained, whose structure is analogous to $|C_4H_{12}N_2|[Al_2P_2O_8(OH)_2]$ (AlPO-CJ9).[29] In addition, the existance of Mg heteroatoms is also very important for the synthesis of JU94 and JU95. Neither of them can be synthesized in the pure AlPO system, or in the presence of other divalent metal except Mg, such as Co, Zn, Ni, etc in above synthetic system.

The PXRD study further verifies that the as-synthesized JU95 samples are pure phase and JU94 samples are mixed with another phase (Fig. S2†). The compositional analyses of JU94 (selected pure crystals) and JU95 give rise to the Mg/Al ratios of 1/3 and the (Mg+Al)/P ratios of 1/1. These results are in good agreement with the empirical formula $|C_4H_{12}N_2|[Mg_2Al_6(PO_4)_8(H_2O)_4]$ given by single-crystal structure analyses. The thermogravimetric (TG) curves of JU94 and JU95 are shown in Fig. S3†. Two continuous weight losses of 12.8 wt% are observed for JU94 from room temperature to 800 °C, which is attributed to the removal of coordinated water (cal. 6.4 wt%) and the decomposition of organic amines (cal. 7.8 wt%). As for JU95, the observed weight losses from room temperature to 800 °C is 14.6 %, which is due to the removal of physical adsorbed water (around 100 °C), coordinated water and organic amines (cal. 14.2 wt%). Obviously, the weight losses of JU94 and JU95 are slightly lower than the calculated value, which maybe because some carbogenic species are still occluded in the calcined samples after calcinations. This phenomenon is similar to that of previously reported JU92.[26]

Structure of JU94

Single-crystal structure analysis reveals that JU94 crystallizes in the monoclinic space group $P2_1/c$ (No. 14). The structure of JU94 consists of the $[Mg_2Al_6(PO_4)_8(H_2O)_4]^{2-}$ anionic framework with the Mg/Al ratio of 1/3, and the diprotonated piperazine cations to compensate the negative charge of the framework. As shown in Fig. S4a†, its asymmetric unit contains one crystallographically distinct Mg site, three crystallographically distinct Al sites and four crystallographically distinct P sites. All of the Al and P atoms are tetrahedrally coordinated to oxygen atoms. The Mg atom is six coordinated to four framework oxygen atoms and two water molecules. The Al-O and P-O bond distances are in the range of 1.716(2)–1.746(2) Å and 1.486(2)–1.545(2) Å, respectively. They are reasonable for microporous aluminophosphates. Mg-O_f (O_f: framework O atom) bond lengths vary from 2.032(3) to 2.076(3) Å, and two terminal Mg-O_w bond distances are 2.085(3) and 2.232(3) Å.

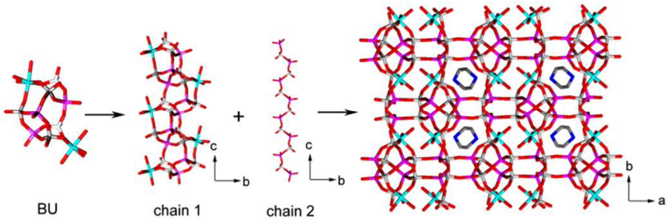

Fig. 1 Open-framework structure of JU94 constructed by the characteristic BUs of $Mg_2Al_3P_5O_{30}$. Diprotonated PZ cations are located in the channels.

The inorganic framework of JU94 is constructed by the strict alternation of AlO_4/MgO_6 polyhedra and PO_4 tetrahedra. As shown in Fig.1, such structure is featured by a characteristic $Mg_2Al_3P_5O_{30}$ building unit (BU), which is formed by four PO_4 tetrahedra, four AlO_4 tetrahedra and one $MgO_4(H_2O)_2$ octahedron. The face-sharing connection of the BUs generates a complex chain along the [001] direction (denoted chain 1). In addition, the alternative connection of AlO_4 and PO_4 tetrahedra forms a single zigzag chain along the [001] direction (denoted chain 2). Thus, the 3D skeleton of JU94 can be viewed as the construction of these two kinds of chains alternately along the [100] and [010] directions. The structure contains two-dimensional (2D) intersecting 8-ring channels along the [001] and [100] directions. The pore sizes of 8-ring openings are 5.4 × 2.5 Å and 5.8 × 2.0 Å (O···O distances) along the [001] direction and 4.4 × 2.5 Å (O···O distances) along the [100] direction. Different from some reported MAPOs with undistinguished Al and heteroatom M sites, Mg atoms occupy the distinct site in the framework of JU94, and distribute along the wall of 8-ring channels.

JU94 exhibits a new four-connected zeolite-like structure. The highest symmetry of its framework is $P2_1/c$, which contains eight types of T sites as determined by the Systre software.[30] The vertex symbols for the eight T sites are $4.4.4.6.6.6_3$, $4.6_2.4.8_2.6_3.6_4$, $4.6.6.6.6_4.8_5$, $4.4.4.8_4.6.8_4$, $4.4.4.8_3.6_2.8_4$, $4.6.6.8_2.6.8_4$, $4.6.6.8_2.6.8_7$ and $4.6.4.6.6_2.8_7$. This three-periodic net is carried by a unique natural tiling with a transitivity of (8 16 20 11).[31] There are six different tiles with the face symbols of $[4.6^2]$, $[4.8^2]$, $[6.8^2]$, $[6^2.8^2]$, $[6.8^3]$ and $[4^2.6^4.8^4]$. The signature of this tiling is $8[4.6^2]+6[4.8^2]+2[6.8^2]+2[6^2.8^2]+2[6.8^3]+[4^2.6^4.8^4]$. The intersecting 8-ring channel system can be clearly seen in the tiling structure of JU94. As shown in Fig. 2, the 8-ring channel (A) running along the [100] direction is defined by the linear arrangement of tiles of $[4^2.6^4.8^4]$ and $[6.8^3]$. Two different 8-ring channels (B and C) running along the [001] direction are composed of the tiles of $[4^2.6^4.8^4]$, $[6.8^2]$ and $[4.8^2]$; and the tiles of $[4.8^2]$, $[6^2.8^2]$ and $[6.8^3]$, respectively. A novel cage $[4^2.6^4.8^4]$ is found in the structure of JU94, in which the diprotonated PZ cations are occluded to balance the negative charge of inorganic framework.

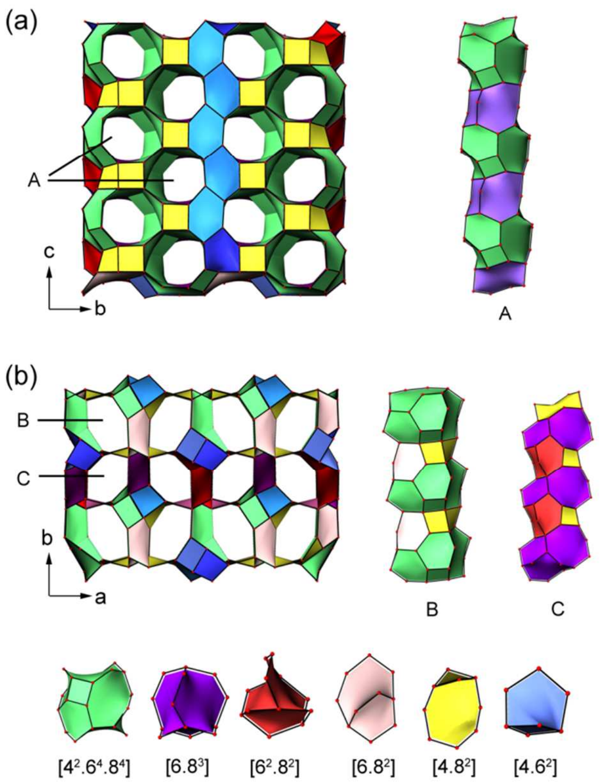

Fig. 2 Structural features of JU94 displayed by tiles, showing the 8-ring channels running along the (a) [100] and (b) [001] directions. The face symbols for green, purple, red, pink, yellow and blue tiles are $[4^2.6^4.8^4]$, $[6.8^3]$, $[6^2.8^2]$, $[6.8^2]$, $[4.8^2]$ and $[4.6^2]$, respectively.

Structure of JU95

JU95 crystallizes in the monoclinic space group $P2_1/n$ (No. 14). Its structure also contains the $[Mg_2Al_6(PO_4)_8(H_2O)_4]^{2-}$ anionic framework constructed by AlO_4 tetrahedra, MgO_6 polyhedra and PO_4 tetrahedra, and the diprotonated piperazine cations to achieve the charge balance. Each asymmetric unit of JU95 contains one crystallographically distinct Mg site, three crystallographically distinct Al sites and four crystallographically distinct P sites (Fig. S4b†). The coordination modes of Mg, Al and P atoms are the same as those found in JU94. The average Al-O and P-O bond distances are 1.727 and 1.517 Å, respectively. Mg-O_f bond lengths vary from 1.992(2) to 2.068(2) Å, and terminal Mg-O_w bond distances are 2.126(2) and 2.199(3) Å.

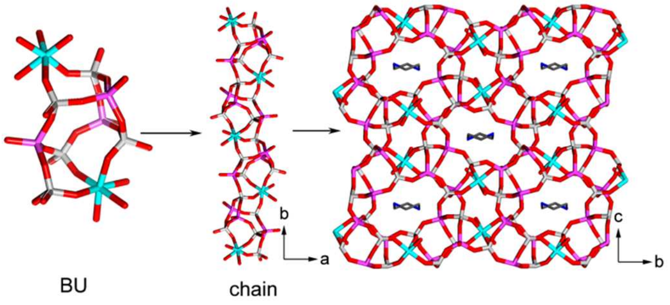

Fig. 3 Open-framework structure of JU95 constructed by the characteristic BUs of $Mg_2Al_3P_5O_{30}$. Diprotonated PZ cations are located in the channels.

The linkage of metal-centered MgO_6/AlO_4 polyhedra and PO_4 terahedra gives rise to the framework structure of JU95. It possesses 2D intersecting 8-ring channels with the openings of 6.0 × 2.1 Å and 5.5 × 1.8 Å (O···O distances) along the [100] direction, and 6.2 × 1.1 Å (O···O distances) along the [-101] direction. In such framework, Mg atoms also occupy the distinct site and distribute along the wall of 8-ring channels. JU95 contains the same BU of $Mg_2Al_3P_5O_{30}$ as that of JU94. Different from JU94, these BUs are edge-sharing connected to form 1D chains along the [010] direction, and then further linked by bridging O atoms to form the open framework of JU95 (Fig. 3). It should be noted that the topology structure of JU95 is analogous to the reported magnesium aluminophosphate JU92 synthesized by using methylpiperazine (NMP) as the template. However, some structure differences caused by organic templates can be found between them. First, the Mg atom of JU95 is in an octahedral geometry, while the Mg atom of JU92 is five/six coordinated due to the half occupancy of O(18) atom. Second, the free diameters of the 8-ring channels in these two compounds are different due to the different occluded organic species.

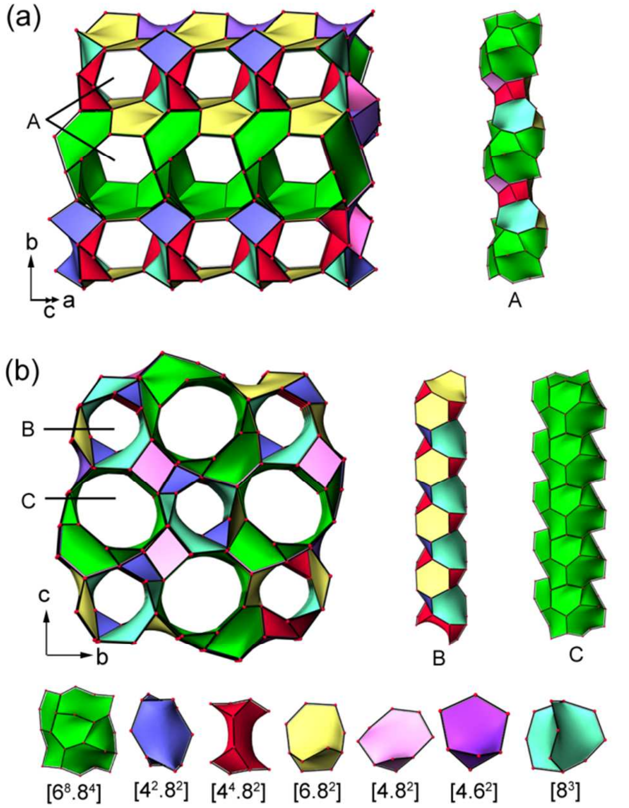

Fig. 4 Structural features of JU95 displayed by tiles, showing the 8-ring channels running along the (a) [-101] and (b) [100] directions. The face symbols for green, blue, red, yellow, pink, purple and cyan tiles are [$6^8.8^4$], [$4^2.8^2$], [$4^4.8^2$], [6.8^2], [4.8^2], [4.6^2] and [8^3], respectively.

As shown in Fig.4, the 4-connected framework of JU95 can also be described as a 3-periodic net with highest symmetry of $P2_1/c$. It is carried by a unique natural tiling with a transitivity of (8 16 18 11).[31] There are seven nonequivalent tiles in this tiling, which include [4.6^2], [4.8^2], [6.8^2], [8^3], [$4^2.8^2$], [$4^4.8^2$] and [$6^8.8^4$]. The signature of this tiling is $8[4.6^2]+2[4.8^2]+4[6.8^2]+2[8^3]+[4^2.8^2]+[4^4.8^2]+[6^8.8^4]$. The 8-ring channel (A) running along the [-101] direction is defined by the linear arrangement of tiles of [$6^8.8^4$], [4.8^2], [6.8^2], [8^3] and [$4^4.8^2$]. Two different 8-ring channels (B and C) running along the [100] direction are composed of the tiles of [6.8^2], [$4^4.8^2$], [8^3] and [4.8^2]; and the tiles of [$6^8.8^4$], respectively.

Structures of JU94-400 and JU95-300

Both of JU94 and JU95 possess 3D 4-connected zeolite-like frameworks, in which Mg atoms are in an octahedral geometry due to the coordination of two water molecules. Hence, the calcined samples of JU94 and JU95 are studied in order to obtain the zeotype structure with fully four coordinated framework.

PXRD study shows that the structures of JU94 and JU95 can be stable up to 500 °C. However, no adsorption capacity is found in them because the organic SDAs are occluded in the pores. The structures of JU94-400 and JU95-300 have been studied by single-crystal X-ray diffraction analyses. JU94-400 crystallizes in the monoclinic space group $P2_1/c$ (No. 14). As shown in Fig. S5a†, each asymmetric unit of JU94-400 contains one crystallographically distinct Mg site, three crystallographically distinct Al sites and four crystallographically distinct P sites. The Al and P atoms are in a tetrahedral geometry, while Mg atom is five-coordinated to four bridging O atoms and one water molecule. The average Al-O and P-O bond distances are 1.741 and 1.530 Å, respectively. Mg-O_f bond lengths vary from 1.971(7) to 2.060(7) Å, and terminal Mg-O_w bond distance is 2.098(8) Å.

JU95-300 crystallizes in the monoclinic space gourp $P2_1/n$ (No. 14). Each asymmetric unit of JU95-300 contains one crystallographically distinct Mg site, three crystallographically distinct Al sites and four crystallographically distinct P sites (Fig. S5b†). The Al, Mg and P atoms are all in a tetrahedral geometry. The average Al-O, P-O and Mg-O bond distances are 1.728, 1.520 and 1.935 Å, respectively.

The structures of JU94-400 and JU95-300 are analogous to that of JU94 and JU95, respectively, only difference is the removal of the coordination water molecules. As for JU95, the coordinated water molecules can be completely removed during the calcinations upon 300 °C, and its framework changes to a zeolite structure with 8-ring channels. Different from JU95, only one coordinated water molecule can be removed from JU94 after calcination upon 400 °C. Comparing the structures of JU94 and JU95, we find that their Mg-O_w bond distances are different. Among the coordinated water molecules, O(18) atom in JU94 has the shortest bond length with Mg atom, indicating its strongest interaction with the inorganic framework. Therefore, it is difficult to be removed from JU94 during the calcination, resulting in the 5-coordinated Mg atom existed in the framework.

Structure Relativity of JU94 and JU95

It is interesting to find that not only the synthesis conditions of JU94 and JU95 are very similar, but also their structures are closely related. They both exhibit 4-connected zeolite-like frameworks based on the connection of $MgO_4(H_2O)_2$ octahedra, AlO_4 tetrehedra and PO_4 terahedra, which contains 2D intersecting 8-ring channels. Particularly, their frameworks are both composed of a characteristic building unit $Mg_2Al_3P_5O_{30}$ comprised of four 4-rings and two 6-rings. Such BU has only been occured in JU92, but not found in other known zeolite structures. Fig. 5 shows that the different connections of such BUs result in distinct frameworks of JU94 and JU95. As for

JU94, the BUs are linked by face to face to form 1D chains along the [001] direction, which are further linked by the zigzag chains to form the open framework. In the structure of JU95, the BUs are edge-sharing connected to generate 1D chains along the [010] direction, such chains are linked to each other to form the open framework. We believe that more unknown zeolite structures can be designed by using different connection modes of the $Mg_2Al_3P_5O_{30}$ BUs, and the different linkages of the generated chains.

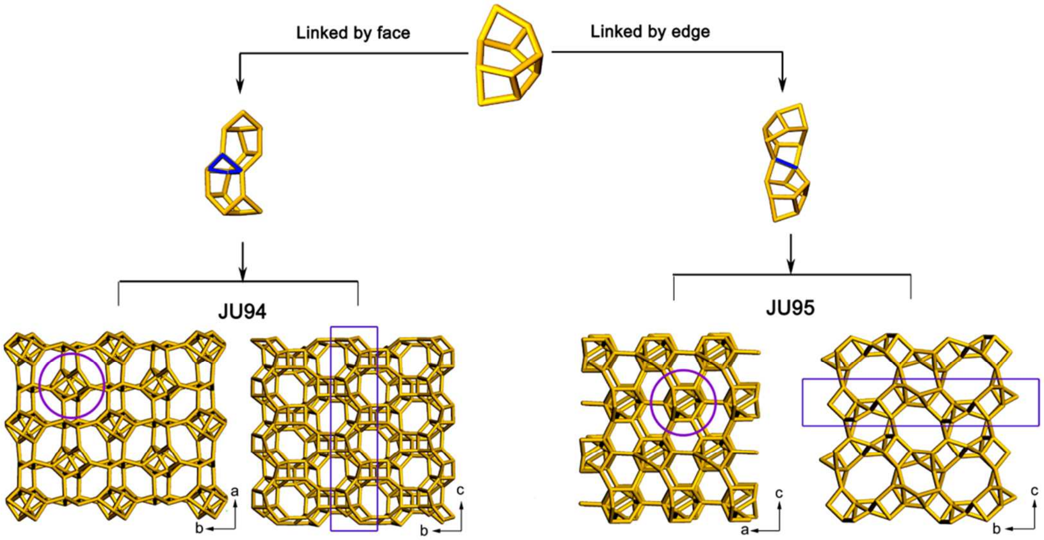

Fig. 5 Scheme showing the building process from BUs to related structures of JU94 and JU95.

Conclusions

Two new magnesium aluminophosphates, JU94 and JU95 with formula of $|C_4H_{12}N_2|[Mg_2Al_6(PO_4)_8(H_2O)_4]$, have been hydrothermally synthesized by using piperazine as the template in the similar reaction system. Several structural similarities can be found in these two compounds. They both exhibit 4-connected zeolite-like open frameworks, which are composed of the alternative connection of $AlO_4/MgO_4(H_2O)_2$ polyhedra and PO_4 tetrahedra. Their structures contain two-dimensional intersecting 8-ring channels, which are located by diprotonated piperazine cations. The $Mg_2Al_3P_5O_{30}$ building unit comprised of four 4-rings and two 6-rings is featured in their frameworks, while the different connections of such BUs result in distinct frameworks of JU94 and JU95. During the calcination, the coordinated water molecules can be completely or partly removed, giving rise to a zeolite structure of JU95-300 and an open framework of JU94-400 with 5-coordinated Mg atom. Their different dehydration behaviours have been elucidated based on their structures.

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Notes and references

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† Electronic Supplementary Information (ESI) available: [The crystallographic information files (CIF) of JU94, JU95, JU94-400 and JU95-300; Crystal data and structure refinement, and selected bond lengths and angles for JU94, JU95, JU94-400 and JU95-300; SEM images, TG curves and PXRD patterns of JU94 and JU95; thermal ellipsoids of JU94, JU95, JU94-400 and JU95-300]. See DOI: 10.1039/b000000x/

1 Y. Li and J. Yu, *Chem. Rev.,* 2014, **114**, 7268-7316.
2 Y. Li, J. Yu, R. Xu, C. Baerlocher and L. B. McCusker, *Angew. Chem. Int. Ed.,* 2008, **47**, 4401-4405.
3 Y. Li, J. Yu and R. Xu, *Angew. Chem. Int. Ed.,* 2013, **52**, 1673-1677.
4 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.,* 1982, **104**, 1146-1147.
5 J. Yu and R. Xu, *Acc. Chem. Res.,* 2003, **36**, 481-490.
6 J. Yu and R. Xu, *Chem. Soc. Rev.,* 2006, **35**, 593-604.
7 J. Li, J. Yu and R. Xu, *Proc. R. Soc. A.,* 2012, **468**, 1955-1967.
8 A. K. Cheetham, G. Férey and T. Loiseau, *Angew. Chem. Int. Ed.,* 1999, **38**, 3268-3292.
9 J. Yu and R. Xu, *Acc. Chem. Res.,* 2010, **43**, 1195-1204.
10 J. Chen and J. M. Thomas, *J. Chem. Soc., Chem. Commun.,* 1994, 603-604.
11 P. A. Barrett, R. H. Jones, J. M. Thomas, G. Sankar, I. J. Shannon and C. R. A. Catlow, *Chem. Commun.,* 1996, 2001-2002.
12 R. Raja, G. Sankar and J. M. Thomas, *Angew. Chem. Int. Edit.,* 2000, **39**, 2313-2316.
13 R. Raja, G. Sankar and J. M. Thomas, *J. Am. Chem. Soc.,* 2001, **123**, 8153-8154.
14 C. Baerlocher, L. B. McCusker and D. H. Olson, *Atlas of zeolite framework types. Elsevier Science:* Netherlands, 2007.
15 C. Baerlocher and L. B. McCusker, *Database of Zeolite Structures:* http://www.iza-structure.org/.
16 X. Bu, P. Feng and G. D. Stucky, *Science,* 1997, **278**, 2080-2085.
17 X. Song, Y. Li, L. Gan, Z. Wang, J. Yu and R. Xu, *Angew. Chem. Int. Edit.,* 2009, **48**, 314-317.
18 L. Shao, Y. Li, J. Yu and R. Xu, *Inorg. Chem.,* 2011, **51**, 225-229.

19 Z. Liu, X. Song, J. Li, Y. Li, J. Yu and R. Xu, *Inorg. Chem.,* 2012, **51**, 1969-1974.

20 R. W. Broach, N. Greenlay, P. Jakubczak, L. M. Knight, S. R. Miller, J. P. S. Mowat, J. Stanczyk and G. J. Lewis, *Micropor. Mesopor. Mat.,* 2014, **189**, 49-63.

21 Z. Wang, J. Yu and R. Xu, *Chem. Soc. Rev*., 2012, **41**, 1729-1741.

22 Y. Xu, Y. Li, Y. Han, X. Song and J. Yu, *Angew. Chem. Int. Ed.,* 2013, **52***,* 5501-5503.

23 Y. Han, Y. Li, J. Yu and R. Xu, *Angew. Chem. Int. Ed.,* 2011, **50**, 3003-3005.

24 Y. Wang, Y. Li, L. Wang, J. Zhang, Y. Yan, J. Li, J. Yu, J. Wang and R. Xu, *Inorg. Chem.,* 2011, **50,** 1820-1825.

25 Y. Wang, L. Shao, Y. Li, X. Li, J. Li, J. Yu and R. Xu, *Dalton T.,* 2012, **41**, 6855-6860.

26 Y. Wang, Y. Li, Y. Yan, J. Xu, B. Guan, Q. Wang, J. Li and J. Yu, *Chem. Commun.,* 2013, **49**, 9006-9008.

27 SAINT, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711-5373, USA, 2000.

28 SHELXTL, Bruker AXS Inc., 5465 East Cheryl Parkway, Madison, WI, 53711-5373, USA, 2000.

29 K. Wang, J. Yu, P. Miao, Y. Song, J. Li, Z. Shi and R. Xu, *J. Mater. Chem.,* 2001, **11**, 1898-1902.

30 O. Delgado-Friedrichs and M. O'Keeffe, *Acta Crystallogr. A,* 2003, **59**, 351-360.

31 V. A. Blatov, O. Delgado-Friedrichs, M. O'Keeffe and D. M. Proserpio, *Acta Crystallogr. A,* 2007, **63**, 418-425.

Graphical Abstract

Two New Four-Connected Zeolite-like Magnesium Aluminophosphates with Intersecting 8-Ring Channels

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JU94 and JU95 are synthesized in the same reaction system, but exhibit different zeolite-like frameworks containing 2D 8-ring channels.