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ARTICLE

A New Magnesium-Containing Aluminophosphate with Zeolite-Like Structure

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A novel Mg-containing aluminophosphate $|C_4H_{12}N_2|[Mg_2Al_6(PO_4)_8(H_2O)_4]$ (JU96) has been hydrothermally synthesized by using piperazine as structure-directing agent. Its framework constructed by the connections of $AlO_4/MgO_4(H_2O)_2$ polyhedra and PO_4 tetrahedra exhibits a new 4-connected zeolite-like topology with intersecting 8-ring channels. Such framework contains unique $[4^4.6^6.8^6]$ cages that are occupied by diprotonated piperazine cations. Study shows the existance of Mg atoms and pH value of the reaction gel have the vital effect on the formation of JU96.

Introduction

Aluminophosphate molecular sieves, designated $AlPO_4$-*n*, are a class of three-dimensional (3D) microporous crystalline materials, whose structures are constructed by the strict alternation of AlO_4 and PO_4 tetrahedra forming a neutral open framework.[1,2] Since their first discovery in 1982, [3] more than 60 different zeotype AlPO-based molecular sieves and a large variety of open-framework aluminophosphates have been synthesized under hydrothermal or solvothermal conditions by using organic amines or quaternary ammonium cations as structure-directing agents (SDAs).[4-7] Such materials have important applications in the fields of catalysis, adsorption, and ion exchange.[5,8]

$AlPO_4$-*n* molecular sieves not only exhibits diverse pore structures, but also have rich framework compositions. The Al atoms in the framework can be partially replaced by other metal elements to form heteroatom-containing aluminophosphate molecular sieves (denoted as MAPO, M= metal heteroatom except Al).[9] Up to now, more than 13 kinds of metal heteroatoms can be incorporated into the frameworks of $AlPO_4$-*n* molecular sieves, giving rise to various MAPO molecular sieves with about 50 different zeolite topologies.[10, 11] The existence of metal heteroatoms offers the Brönsted acid sites to MAPO molecular sieves, which enables such materials excellent catalysis property. For example, some MAPOs including MAPO-18, MAPO-34 and MAPO-5 as single-site solid catalysts are widely applied in the selective oxidation and MTO reactions.[12, 13] On the other hand, the metal heteroatoms also play the stabilizing role on the resulting open framework, which provides a great opportunity to synthesize novel zeotype structures.[7,10,14] More than 20 kinds of MAPOs with distinct zeolite topology have been discovered, which have been not found in pure AlPO system yet. For examples, APC-1 (ACO, M=Co, Fe),[15, 16] MAPO-46 (AFS, M=Co, Mg, Mn, Ni, Zn),[17] UCSB-6 (SBS, M=Co, Zn, Mn, Mg), UCSB-8 (SBE, M= Co, Zn, Mn, Mg), UCSB-10 (SBT, M=Co, Zn, Mn),[18] MAPO-CJ40 (JRY, M= Co, Zn, Fe),[19] MAPO-CJ69 (JSN, M=Co, Zn),[20] MAPO-CJ62 (JSW, M=Co, Zn),[21] and so on.

Recently, more and more attentions have been focused on the synthesis of MAPO molecular sieves with novel zeolite topology, variable framework compositions, and distinctive properties.[22,23] This requires us to carefully regulate the synthetic system, particularly, the selection of heteroatoms and the organic SDAs. Our previous study shows that the type and the amount of organic SDAs in the synthesis can influence the M/Al ratios in the frameworks of MgAPO-CJ67[24] and FeAPO-CJ66[15] with LEV and ACO zeotype structures, respectively. By using n-methylpiperazine as the SDA, a magnesium aluminophosphate JU92 with novel JNT zeotype structure and luminescent property have been synthesized.[25]

In this work, we present a novel Mg-containing microporous aluminophosphate $|C_4H_{12}N_2|[Mg_2Al_6(PO_4)_8(H_2O)_4]$ (denoted as JU96). This compound was synthesized by using piperazine as SDA in the similar reaction system with our reported magnesium aluminophosphates JU94 and JU95 containing the

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Electronic Supplementary Information (ESI) available: The crystallographic information files (CIF) of JU96; bond lengths and angles for JU96; CCDC : 1432162. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

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basic unit, but with slightly different gel composition and distinct structures.[26] JU96 possesses a new zeolite-like framework structure with intersecting 8-ring channels and unique [$4^4.6^6.8^6$] cages. Its synthesis and structure and the structural comparison of JU94, JU95 and JU96 have been discussed.

Experimental section

Materials and synthesis

JU96 was synthesized under hydrothermal conditions by using piperazine (PZ) as the structure-directing agent (SDA). In a typical synthesis, magnesium acetate ($Mg(CH_3COO)_2{\cdot}4H_2O$, Tianjin Fuchen Chemical Reagents Factory) and pseudoboehmite (Al_2O_3, 62%, Shandong Aluminium Industry) were added into a solution of orthophosphoric acid (85 wt%, Beijing Chemical Industry Group Co. Ltd) and water with vigorous stirring, followed by the addition of PZ ($C_4H_{10}N_2$, Aldrich). After stirring for 1 hour, a homogeneous gel with an overall molar composition of $1.0Al_2O_3$: 0.67MgO: $2.62P_2O_5$: 1.36PZ: $224H_2O$ was formed, which was heated at 180 °C for 3 days in a 15 ML Teflon-lined stainless steel autoclave. The pure phase of JU96 was obtained by filtered off, washed with distilled water and then dried in the air at room temperature overnight.

Structure determination

Single crystals of JU96 with dimensions of 0.21 × 0.19 × 0.18 mm^3, respectively, were selected for single-crystal X-ray diffraction analyses. The data were performed on a Bruker AXS SMART APEX Ⅱ diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at the temperature of 23±2 °C. Data processing was accomplished with the SAINT processing program.[27] The structures were solved by direct methods and refined by full matrix least-squares technique with the SHELXTL software package.[28] The heaviest atoms of Al, Mg, P and O were easily located, and the C and N atoms were subsequently located from the difference Fourier maps. The H atoms in their structures were not added. All non-hydrogen atoms were refined anisotropically. Thermal ellipsoids of JU96 are given at 50% probability by using the SHELXTL software package. The structure details are given in Table S1.

Characterizations

Powder X-ray diffraction (PXRD) data was collected on a Rigaku D/max-2550 diffractometer with Cu Kα radiation (λ = 1.5418 Å, scan range from 4 to 40°, scan speed 0.5°/min, stride is 0.02°). 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. 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.

Table 1 Crystal data and structure refinement for JU96

compounds	JU96
empirical formula	$Mg_2Al_6P_8C_4H_{14}N_2O_{36.5}$
formula weight	1132.43
temperature	296(2) K
wavelength(Å)	0.71073
crystal system, space group	Monoclinic, $P2_1/c$
unit cell dimensions	
a (Å)	12.675(2)
b (Å)	14.423(3)
c (Å)	9.5745(17)
α(deg)	90
β(deg)	100.568(2)
γ(deg)	90
volume($Å^3$)	1720.7(5)
Z, calculated density(mg/m^3)	1, 2.186
absorption coefficient(mm^{-1})	0.728
F(000)	1132
crystal size(mm^3)	0.21 × 0.19 × 0.18
ϑ range(°) for data collection	1.63–28.37
limiting indices	$-10 \le h \le 16$, $-19 \le k \le 19$, $-12 \le l \le 12$
reflections collected/unique	12203/4269, [R(int) = 0.0319]
completeness to ϑ (%)	28.37, 99.5 %
absorption correction	Semi-empirical from equivalents
max and min transmission	0.8801and 0.8621
refinement method	Full-matrix least-squares on F^2
data/restraints/parameters	4269/0/269
goodness-of-fit on F^2	0.992
final R indices [$I > 2\sigma(I)$]	R_1 = 0.0487, wR_2 = 0.1287
R indices (all data)	R_1 = 0.0754, wR_2 = 0.1461
largest diff. peak and hole ($eÅ^{-3}$)	0.772 and -0.562

Results and discussion

Synthesis and characterization of JU96

JU96 has been synthesized by using piperazine as SDA under hydrothermal conditions. It is noted that other two magnesium aluminophosphates JU94 and JU95 can also be produced in such reaction system but with different gel compositions. In the synthesis, the pH value determined by the amounts of SDA and H_3PO_4 in the reaction gel influences the final product. For instance, $1.0Al_2O_3$: 0.67MgO: $2.62P_2O_5$: 1.36PZ: $224H_2O$ is the best gel proportion for synthesizing pure JU96. In such condition, the slight change of the amount of piperazine may produce magnesium aluminophosphate JU95. When the molar ratio of piperazine /Al_2O_3 in 1.36 this results in the formation of JU96, whereas if the ratio is 2.63 it leads to JU95 formation. When the molar ratio of piperazine /Al_2O_3 is between of 1.36 and 2.63, the mixture of JU95 and JU96 could be produced. As for JU94 and JU96, pH value of 1 favours the formation of JU96, higher pH value of 1.5-2 facilitates the formation of JU94. Furthermore, the content of Mg also plays an important role in the synthesis of JU96. Pure JU96 could be synthesized when the molar ratio of Mg/Al is 1:3, the increasing Mg/Al ratio results in the formation of a mixture of JU94 /JU96 or JU95 /JU96. However, JU96 could not be produced without Mg atoms or in the presence of other divalent metals including Co and Zn. In

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summary, compared with the synthetic conditions of JU94 and JU95, low pH value and low piperazine /Al_2O_3 ratio are better for the formation of pure JU96.

The powder X-ray diffraction pattern of JU96 is consistent with the simulated one based on the single-crystal structure of JU96, (Figure 1) indicating the pure phases of the as-synthesized samples. The structure of JU96 can stable up to 400°C suggested by the XRD analysis. ICP and elemental analyses show the contents of Mg, Al, P, C, H, N of JU96 are 4.18, 14.11, 21.60, 4.18, 1.92, 2.43 wt% (calcd: Mg, 4.20; Al, 14.05; P, 21.83; C, 4.18; H, 1.92; N, 2.44 wt%), giving the Mg/Al ratios of 1/3 and the (Mg+Al)/P ratios of 1/1. The 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 analysis.

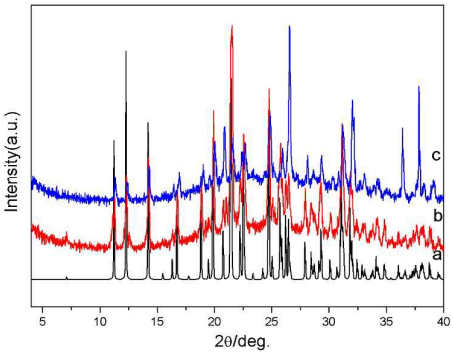

Figure 1 XRD patterns of (a) simulated JU96 based on the single-crystal structure, (b) synthesized JU96 and (c) calcined JU96 at 400°C.

TG curve in Figure 2 shows three continuous weight losses for JU96. The first weight loss of 1.5 wt% around 130°C is attributed to the removal of adsorption water in channels, the second weight loss of 6.4 wt% from 130 to 300 °C is due to the removal of coordinated water (calcd. 6.3 wt%), and the third weight loss of 4.6 wt% from 450 to 800°C is due to the decomposition of organic amines (cal. 7.6 wt%). This result indicates that the organic SDAs could not be completely removed, and some organic species may still occluded in the calcined sample after calcinations. This phenomenon also has been observed in JU94 and JU95.[25]

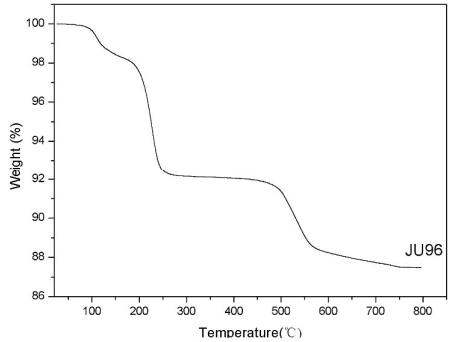

Figure 2. TG analysis of JU96.

Crystal structure of JU96

Single-crystal structure analysis shows that JU96 crystallizes in the monoclinic space group $P2_1/c$ (No.14).The structure of JU96 consists of the $[Mg_2Al_6(PO_4)_8]^{2-}$ anionic framework and the diprotonated piperazine cations to achieve the charge balance. Thermal ellipsoids of JU96 show in Figure 3. Its asymmetric unit contains eight crystallographically distinct framework positions: one Mg site, three Al sites and four P sites. All of the Al and P atoms are tetrahedrally coordinated. The Al-O and P-O bond distances are in the range of 1.715(2)–1.749(2) Å and 1.484(2)–1.545(2) Å, respectively. The Mg-O_f (O_f: framework O atom) bond lengths vary from 1.999(2) to 2.107(2) Å, and two terminal Mg-O_w bond distances are 2.100(2) and 2.237(3) Å.

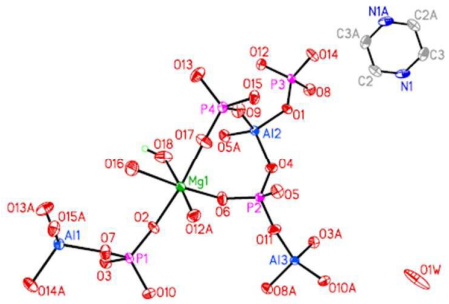

Figure 3 Thermal ellipsoids given at 50% probability, showing the atomic labelling scheme of JU96.

JU96 exhibits a new four-connected zeolite-like topological structure. Its open-framework is constructed by the connection of AlO_4 tetrahedra, MgO_6 octahedra and PO_4 tetrahedra, which possesses two-dimensional intersecting 8-ring channels. One 8-ring channel is running along the [100] direction (Figure 4a) with the free diameter of pore opening of 5.9 ×2.3Å (O···O distances). Two 8-ring channels are running along the [001] direction (Figure 4b) with different free diameter of 5.4 ×2.5 Å and 4.8 ×2.0 Å (O···O distances), respectively. Notably, a new cage $[4^4.6^6.8^6]$ is found in JU96, which has not been observed in the previously known zeolite structures. The diprotonated PZ cations are occluded in these $[4^4.6^6.8^6]$ cages, and interact with the inorganic framework through hydrogen bonds.

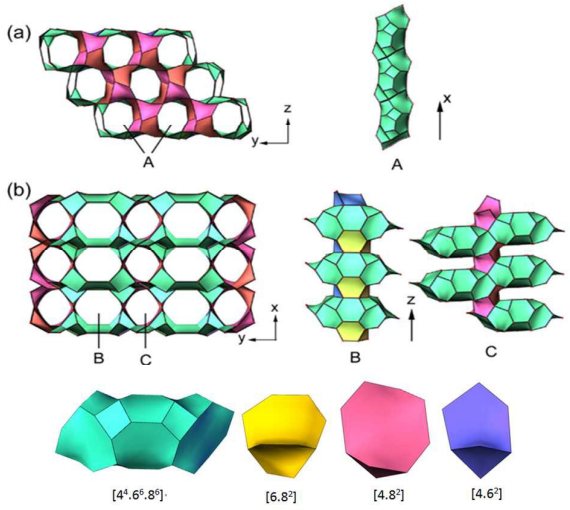

Figure 4. Topological structure of JU96 by tiles showing intersecting 8-ring channels along (a) [100] and (b) [001] directions.

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The 4-connected framework structure of JU96 can be described as a (4, 2)-connected three-periodic net. This three-periodic net is carried by a unique natural tiling with a transitivity of (8 16 19 10). Four different tiles are observed in this tiling, which include $[4.6^2]$, $[4.8^2]$, $[6.8^2]$, and $[4^4.6^6.8^6]$. The signature of this tiling is $8[4.6^2] + 4[4.8^2] + 6[6.8^2] + [4^4.6^6.8^6]$. The intersecting channel system of JU96 can also be viewed as construction by different tile. The 8-ring channel along [100] direction (Figure 4a) is defined by the linear arrangement of tiles of $[4^4.6^6.8^6]$ (channel A). Two 8-ring channels along [001] direction (Figure 4b) are composed by the tiles of $[4^4.6^6.8^6]$, $[6.8^2]$ and $[4.8^2]$ (channel B) and tiles of $[4^4.6^6.8^6]$ and $[6.8^2]$ (channel C), respectively.

Interestingly, the structures of JU96 and the reported JU94 and JU95[26] are all composed by the strict alternation of AlO_4/MgO_6 polyhedra and PO_4 tetrahedra, but their structures are quite different. Meanwhile, all of them possess the 2D interconnected 8-ring channels. However, their zeolitic frameworks are quite different. In details, the structures of JU94 and JU95 are constructed by a characteristic building unit $Mg_2Al_3P_5O_{30}$ comprised of four 4-rings and two 6-rings, but their connection modes are different. As shown in Figure 5, the structure of JU96 is featured by a 2D (4, 8)-net, such layers are connected by bridging O atoms to form the 3D framework. In the (4, 8)-net, two edge-sharing 4-rings composed by MgO_6, 3 PO_4 and 2 AlO_4 polyhedras can be found as a building unit (BU). The BUs are linked with each other through two PO_4 tetrahedra, giving rise to the 2D layers.

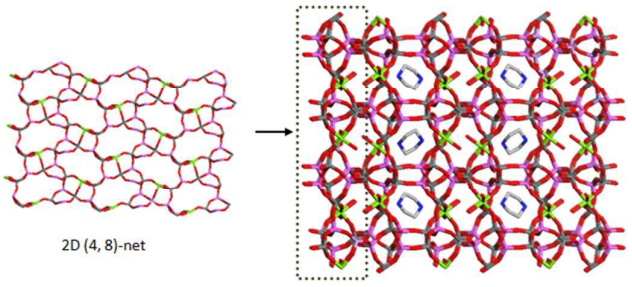

Figure 5. Open-framework structure of JU96 constructed by the 2D (4,8)-net.

Conclusions

A new magnesium aluminophosphate $|C_4H_{12}N_2|[Mg_2Al_6(PO_4)_8(H_2O)_4]$ (JU96) has been hydrothermal synthesized in presence of piperazine as the structure-directing agent. The connection of AlO_4 tetrahedra, $MgO_4(H_2O)_2$ octahedra and PO_4 tetrahedra forms the 3D open framework of JU96 with intersecting 8-ring channels along the [100] and [001] directions. Unique $[4^4.6^6.8^6]$ cages are observed in such 4-connected topology, which are occupied by diprotonated piperazine cations. Mg atoms are in octahedral geometry due to two coordination water molecules, which occupy the distinct site in the framework. The synthesis and structure comparison of JU94 and other known magnesium aluminophosphate JU95 and JU96 obtained in the same reaction system will provide more insight into the relationship of synthesis and structure, which makes it possible to synthesize more novel MAPO zeolitic materials.

Acknowledgements

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Graphical Abstract

A New Magnesium-Containing Aluminophosphate with Zeolite-Like Structure

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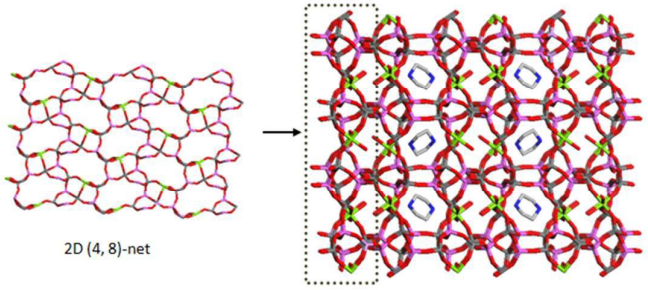
A novel Mg-containing aluminophosphate JU96 is presented, which exhibits a new 4-connected zeolite-like topology with intersecting 8-ring channels.



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