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Syntheses and Characterizations of Transition-Metal-Substituted Aluminophosphate Molecular Sieves $|(C_3N_2H_5)_8|[M_8Al_{16}P_{24}O_{96}]$ (M = Co, Mn, Zn) with Zeotype LAU Topology

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Three transitional-metal-substituted aluminophosphate molecular sieves, $|(C_3N_2H_5)_8|[M_8Al_{16}P_{24}O_{96}]$ (denoted MAPO-LAU, M = Co, Mn, Zn), have been synthesized under solvothermal conditions in the presence of imidazole as the structure-directing agent. Their structures are determined by single-crystal X-ray diffraction and further characterized by powder X-ray diffraction, inductively coupled plasma, thermogravimetric, and diffuse reflectance spectroscopy (UV−vis) analyses. The structure of MAPO-LAU is based on the strict alternation of MO_4/AlO_4 tetrahedra and PO_4 tetrahedra through vertex oxygen atoms. Their frameworks are analogous to the zeotype LAU structure in which 33% of the aluminum sites are replaced by transitional-metal ions. The protonated imidazole cations resided in the 10-ring channels. These compounds show photoluminescent properties due to the existence of imidazole molecules in the structures. Magnetic measurements reveal that there is very weak antiferromagnetic interaction among the metal centers of MnAPO-LAU.

Introduction

Following the discovery of the aluminophosphate molecular sieves $AlPO_4$-*n* (*n* denotes the structure type) by Wilson et al. in 1982,[1] a large variety of open-framework aluminophosphates with different structure types have been synthesized by using organic templates or structure-directing agents (SDAs).[2] The structures of $AlPO_4$-*n* are made of the strict alternation of AlO_4 and PO_4 tetrahedra forming a neutral framework. The lattice Al and P atoms can also be partially replaced by silicon or other elements to generate heteroatom-containing aluminophosphate molecular sieves.[3,4] So far, among the 179 identified zeolite topological structures, 54 are based on aluminophosphates.

The isomorphic substitution of active transition metal ions, such as Ni(II), Pd(II), Mn(II), Fe(III), V(II), Co(II), and so forth, into the framework sites of $AlPO_4$-*n* has shown promising properties in catalysis, photoluminescence, magnetism, and so forth.[5−8] Significantly, transition-metal-substituted aluminophosphate molecular sieves open up a rich range of catalytic processes for selective oxidations as single-site solid catalysts in oxygen or air.[7] Strong room-temperature luminescence has been observed in a family of metal-substituted zeotype materials upon excitation by long-wavelength UV radiation, and the luminescent output from the large cage UCSB-8Mg structure is independent of the temperature from 298 K up to at least 77 K.[8] Recently, we have successfully synthesized novel chiral heteroatom-containing aluminophosphate molecular sieves MAPO-CJ40 (M = Co, Zn) with optical activity.[9]

In 1967, the aluminosilicate $|Ca_4^{2+}(H_2O)_{16}|[Al_8Si_{16}O_{48}]$ was first synthesized by Fischer and Bartl using the alkali ions as the SDAs.[10] Its structure has zeotype LAU topology with

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10.1021/ic801405e CCC: $40.75

Table 1. Crystal Data and Structural Refinement for MAPO-LAU (M = Co, Mn, Zn)[a]

compound	CoAPO-LAU	ZnAPO-LAU	MnAPO-LAU
empirical formula	$C_3H_5N_2Al_2CoO_{12}P_3$	$C_3H_5N_2Al_2ZnO_{12}P_3$	$C_3H_5N_2Al_2MnO_{12}P_3$
fw	465.88	472.32	462.32
temp	293(2) K	293(2) K	293(2) K
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst, space group	monoclinic, *C2/C*	monoclinic, *C2/C*	monoclinic, *C2/C*
unit cell dimensions			
a (Å)	14.718(3)	14.733(3)	14.877(9)
b (Å)	13.063(3	13.079(3)	13.063(3)
c (Å)	15.229(3)	15.210(3)	15.419(1)
α (deg)	90	90	90
β (deg)	110.92(3)	110.99(3)	110.74(5)
γ (deg)	90	90	90
V ($Å^3$)2734.9(9)	2736.4(9)	2802.5(6)	
Z, calcd density (Mg m^{-3})	8, 2.263	8, 2.293	8, 2.189
abs coeff (mm^{-1})	1.803	2.343	1.477
F(000)	1840	1864	1824
cryst size (mm^3)	0.23 × 0.12 × 0.08	0.20 × 0.20 × 0.10	0.20 × 0.20 × 0.08
θ range (deg) for data collection	3.12−27.47	3.12−27.48	2.14−27.04
limiting indices	$-16 \leq h \leq +19$ $-16 \leq k \leq +16$ $-19 \leq l \leq +18$	$-19 \leq h \leq +19$ $-16 \leq k \leq +16$ $-19 \leq l \leq +17$	$-13 \leq h \leq +18$ $-16 \leq k \leq +16$ $-19 \leq l \leq +16$
reflns collected/unique	13286/3118 [*R*(int) = 0.0682]	13131/3110 [*R*(int) = 0.0858]	8052/3043 [*R*(int) = 0.0367]
completeness to θ	27.47, 98.9%	27.48, 99.2%	27.04, 99.0%
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	3099/0/209	3110/0/209	3043/156/209
GOF on F^2	0.926	0.999	0.851
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0684$, $wR_2 = 0.1622$	$R_1 = 0.0678$, $wR_2 = 0.1833$	$R_1 = 0.0553$, $wR_2 = 0.1412$
R indices (all data)	$R_1 = 0.0956$, $wR_2 = 0.1797$	$R_1 = 0.1164$, $wR_2 = 0.2242$	$R_1 = 0.0885$, $wR_2 = 0.1664$
largest diff. peak and hole (*e* $Å^{-3}$)	0.894 and −0.808	0.922 and −1.072	0.594 and −0.539

[a] $R_1 = \sum(\Delta F/\sum(F_o))$; $wR_2 = (\sum[w(F_o^2 - F_c^2)])/\sum[w(F_o^2)^2]^{1/2}$, $w = 1/\sigma^2(F_o^2)$.

one-dimensional 10-ring channels. Since then, several gallophosphates and a Zn-substituted aluminoarsenate with the LAU zeotype had been prepared under hydrothermal conditions by using pyridine and imidazole as the SDAs.[11−13] However, the aluminophosphate-based LAU molecular sieves have not yet been prepared. In this work, we first present three transition-metal-substituted aluminophosphate molecular seives, $|(C_3N_2H_5)_8|[M_8Al_{16}P_{24}O_{96}]$ (denoted MAPO-LAU, M = Co, Mn, Zn), synthesized by using imidazole as the SDA in the solvothermal system. All of them possess the zeotype LAU structure, and the Me/Al ratio is up to 1/2. Their syntheses, structures, and photoluminescent and magnetic properties have been studied.

Experimental Details

Syntheses of MAPO-LAU (M = Co, Mn, Zn). The three compounds were prepared under solvothermal conditions. Typically, manganese chloride tetrahydrate (cobalt chloride hexahydrate or zinc nitrate hexahydrate) and aluminum triisopropoxide were first dispersed into triglycol with stirring for 2 h, followed by the addition of imidazole. The mixture was stirred for 1 h, and the orthophosphoric acid (85 wt %) was added dropwise to give a gel with an overall molar composition of MO/Al(*i*PrO)$_3$/H_3PO_4/imidazole/triglycol of 0.5:1.0:4.0:4.8:24.3. The gel was stirred until it was homogeneous and then was sealed in a 15-mL Teflon-lined stainless steel autoclave, and heated at 180 °C for 7 days. The final product containing large, light-pink single crystals for MnAPO-LAU (blue for CoAPO-LAU and colorless for ZnAPO-LAU) in the form of tetragonal prisms were separated by sonication, washed with distilled water, and dried in the air at room temperature.

Structure Determination. Three suitable single crystals with dimensions of 0.23 × 0.12 × 0.08 mm^3, 0.20 × 0.20 × 0.10 mm^3, and 0.20 × 0.20 × 0.08 mm^3 were selected for single-crystal X-ray diffraction analyses for CoAPO-LAU, ZnAPO-LAU, and MnAPO-LAU, respectively. Structural analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073Å). The data were collected at a temperature of 20 ± 2 °C. Data processing was accomplished with the SAINT processing program.[14] The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the SHELXTL97 crystallographic software package.[15] All Mn/Co/Zn, Al, P, and O atoms were easily located. For each metal site, the transitional metal and aluminum occupy the same site. An occupancy of M (M = Co, Mn, Zn) to Al of 0.33 to 0.67 was suggested by the inductively coupled plasma (ICP) analyses. The C and N atoms were subsequently located from the difference Fourier map. Protonation of the imidazole molecules was suggested by charge balance. All non-hydrogen atoms were refined anisotropically. Experimental details for crystal structure determinations of MAPO-LAU (M = Co, Mn, Zn) are listed in Table 1.

Characterizations. X-ray powder diffraction (XRD) data for the three compounds were collected on a Rigaku X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). Thermogravimetric analysis (TG) was performed on a Perkin-Elmer TGA7 unit in the air with a heating rate of 10 K min^{-1}. ICP analysis was carried out on a Perkin-Elmer Optima 3300 DV ICP instrument. Elemental analyses

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(11) Chippindale, A. M.; Walton, R. I. *Chem. Commun.* **1994**, 2453.

(12) Bond, A. D.; Chippindale, A.; Cowley, A. R.; Readman, J. E.; Powell, A. V. *Zeolites* **1997**, *19*, 326.

(13) Feng, P.; Zhang, T.; Bu, X. *J. Am. Chem. Soc.* **2001**, *123*, 8608.

(14) *SMART*; *SAINT*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.

(15) *SHELXTL*, version 5.1; Siemens Industrial Automation, Inc.: Madison, WI, 1997.

Table 2. Synthesis Conditions and Resulting Products

	gel composition (molar ratio)[a]				
sample code	MO	Al(*i*PrO)$_3$	H$_3$PO$_4$	imdazole	resulting product
1	0	1	4	4.8	layered AlPO[b]
2	0.1−0.5	1	4	4.8	layered AlPO and MAPO-LAU
3	0.5−1.0	1	4	4.8	MAPO-LAU
4	1.1−1.2	1	4	4.8	MAPO-LAU and dense phase
5	1.3−3	1	4	4.8	dense phase
6	0.5	1	4	1−4	dense phase and layered AlPO
7	0.5	1	4	4−6	MAPO-LAU
8	0.5	1	4	6−9	MAPO-LAU + dense phase
9	0.5	1	4	10−14	dense phase or amorphous phase

[a] Solvent: 24.3 triglycol; reaction temperature: 180 °C; reaction time: 7 days. [b] Layered AlPO: $[C_3N_2H_5]_2[Al_3P_4O_{16}H]$.[16]

Table 3. The Compositional Analysis Results for MAPO-LAU (M = Co, Mn, Zn)

	content (wt %)					
name	Al	M	P	C	N	H
MnAPO-LAU obsd	11.7	11.9	20.9	8.13	6.22	0.80
MnAPO-LAU calcd	11.66	11.88	20.09	7.78	6.05	1.08
CoAPO-LAU obsd	12.0	11.8	20.3	8.04	6.21	1.16
CoAPO-LAU calcd	11.56	12.63	19.91	7.71	6.00	1.07
ZnAPO-LAU obsd	11.00	13.6	19.7	7.87	6.17	0.95
ZnAPO-LAU calcd	11.42	13.74	19.66	7.61	5.92	1.06

were conducted on a Perkin-Elmer 2400 elemental analyzer. Diffuse reflectance spectroscopy (UV−vis) was performed on a Perkin-Elmer UV/vis instrument.

The luminescent properties were measured on a Perkin-Elmer LS55 spectrometer. The slit width for both excitation and emission measurements was 5 nm. The powdered sample was placed in the quartz cell for the photoluminescent measurement.

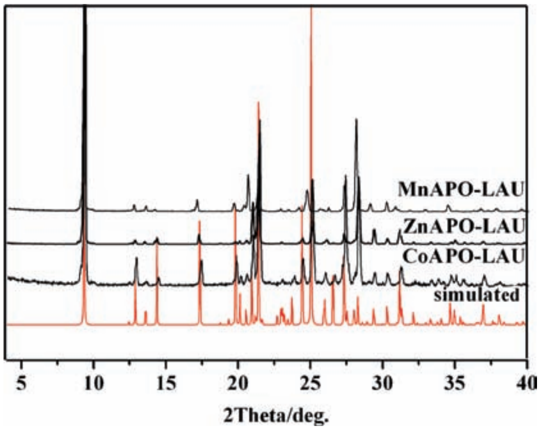

Figure 1. Experimental powder X-ray diffraction patterns of MAPO-LAU (M = Co, Mn, Zn) and the simulated one based on the crystal structure of CoAPO-LAU.

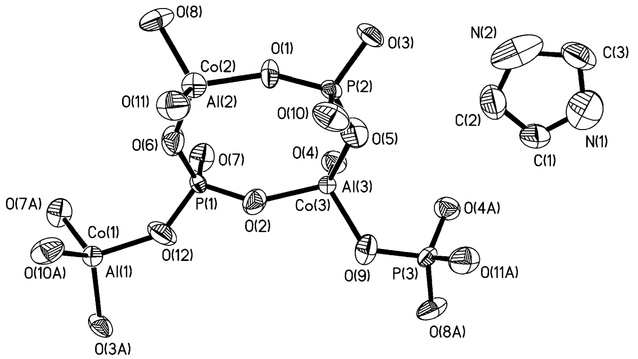

Figure 2. Thermal ellipsoids given at 50% probability, showing the atomic labeling scheme of CoAPO-LAU.

Temperature-dependent magnetic susceptibility data were recorded on a Quantum-Design MPMSXL SQUID magnetometer. Samples were loaded into gelatin capsules at room temperature, and the data were collected over the range 4−300 K, both after cooling the sample in a zero applied field and after cooling in the measured field under an applied field of 1 kOe.

Results and Discussion

Syntheses and Characterizations of MAPO-LAU (M = Co, Mn, Zn). Pure phases of MAPO-LAU (M = Co, Mn, Zn) could be prepared in the reaction system of MO/Al(*i*PrO)$_3$/H$_3$PO$_4$/imidazole/triglycol with a molar ratio of (0.5−1):1.0:4.0:4.8:24.3 at 180 °C for 7 days. It was found that many factors influenced the syntheses of MAPO-LAU, as shown in Table 2. For example, in the synthesis of CoAPO-LAU, when the molar ratio of Co/Al in the reaction mixture was lower than 0.5, it always produced a mixture of CoAPO-LAU and a layered aluminophosphate $[C_3N_2H_5]_2[Al_3P_4O_{16}H]$;[16] if this value was higher than 1.3, a dense phase was formed. ICP analysis shows that the M/Al ratio remains 1:2 in the products, which is independent of the amount of transition metal ions added in the initial reaction gel. It was noted that, without the presence of transitional metal ions in the above synthetic system, the resulting product was layered aluminophosphate $[C_3N_2H_5]_2[Al_3P_4O_{16}H]$.[16] The type of solvent also affects the crystallization of MAPO-LAU. When ethylene glycol, water, or 2-butanol was used as the solvent, while keeping other conditions unchanged, no MAPO-LAU (M = Co, Mn, Zn) was formed. While a mixture of water and triglycol, or tetraethylene glycol, was used as the solvent, target product MAPO-LAU could be produced.

MAPO-LAU could only be prepared by using imidazole as the SDA in our synthetic system. According to the Database of AlPO Synthesis,[17] only two layered alumino-

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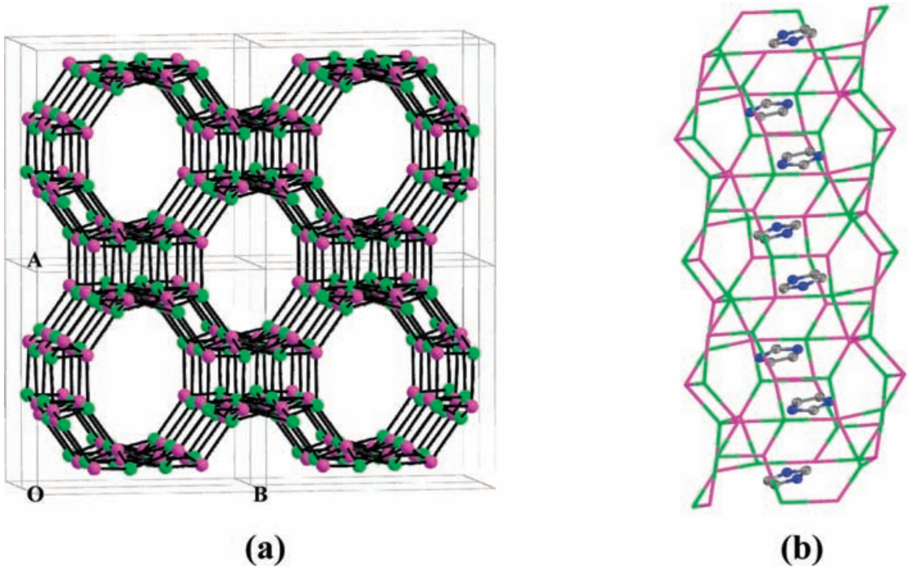
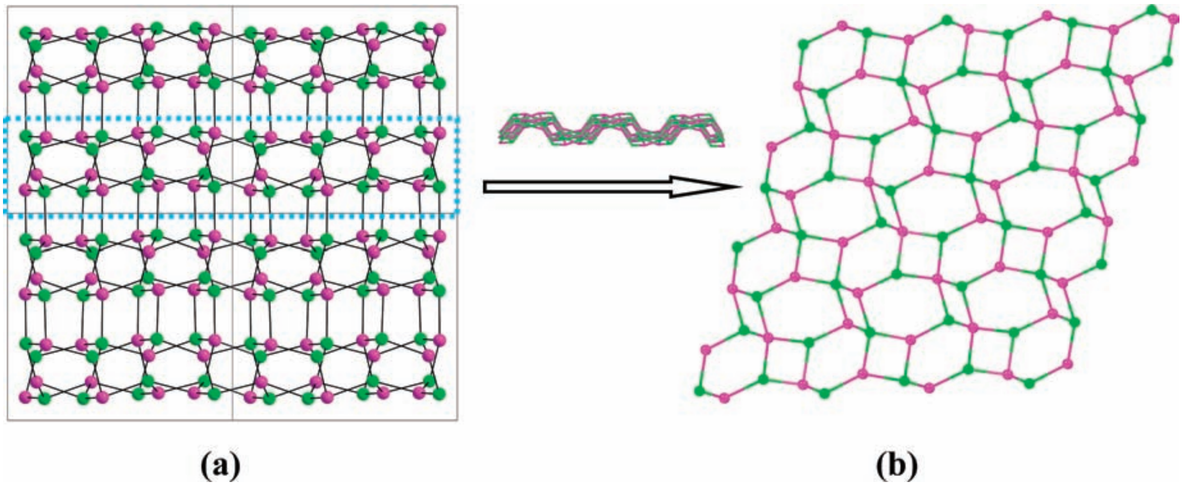
(16) Yu, J.; Terasaki, O.; Williams, I. D.; Qiu, S.; Xu, R. *Supramol. Sci.* **1998**, *5*, 297.



(a) (b)

Figure 3. (a) Framework of CoAPO-LAU viewed along the [001] direction showing the 10-ring channel. (b) Imidazole molecules residing in the 10-ring channel.



(a) (b)

Figure 4. (a) Framework of CoAPO-LAU viewed along the [100] direction. (b) 2D sheet with 4- and 6-rings parallel to the *ac* plane.

phosphate compounds, $[N_2C_3H_5]_2[Al_3P_4O_{16}H]$[16] and $[N_2C_3H_5][AlP_2O_8H_2(OH_2)_2]$,[18] have been prepared by using the imidazole as the SDAs. So far, very few aromatic molecules serve as the structure-directing agents in the M−Al−P−O system. MAPO-LAU is the first three-dimensional aluminophosphate prepared in the presence of imidazole as the SDAs.

It should be noted that pure aluminophosphate AlPO-LAU could not be prepared in the absence of transitional metal ions. This implies that the incorporation of transitional atoms might be necessary for stabilizing the LAU framework.

Figure 1 shows the experimental XRD patterns for MAPO-LAU (M = Co, Mn, Zn) and the simulated pattern based on the crystal structure of CoAPO-LAU, which are in good agreement with each other, suggesting that they are isostructural and that the phases of the as-synthesized products are pure.

The compositional analysis results for MAPO-LAU (M = Co, Mn, Zn) by ICP and elemental analyses, as presented in Table 3, give a ratio of (M + Al)/P of 1, and a ratio of M/Al of 1:2. Different from neutral framework aluminophosphate molecular sieves, most transition-metal-substituted aluminophosphates possess anionic frameworks that need protonated template cations to balance the negative charges of the frameworks. For a given structure with specific composition and charge density, only when the charge density of the organic cations is close to that of the framework can the templating effect of organic cations take place.[19] For MAPO-LAU, the framework charge density of 0.17 (defined as framework charge/framework T number) matches well with the charge density of protonated imidazole cations of 0.2 (defined as template charge/template non-H number).

The TG analysis in Figure S1 of the Supporting Information shows a total weight loss of 16.65, 15.98, and 16.90 wt % from 300−950 °C for CoAPO-LAU, MnAPO-LAU, and

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(17) Li, Y.; Yu, J. H.; Xu, R. R. http://mezeopor.jlu.edu.cn/alpo/ and http://crystals.ethz.ch:9006/AlPO/ (accessed Oct. 2008).

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(19) Li, J.; Yu, J.; Xu, R. *Microporous Mesoporous Mater.* **2007**, *101*, 406.

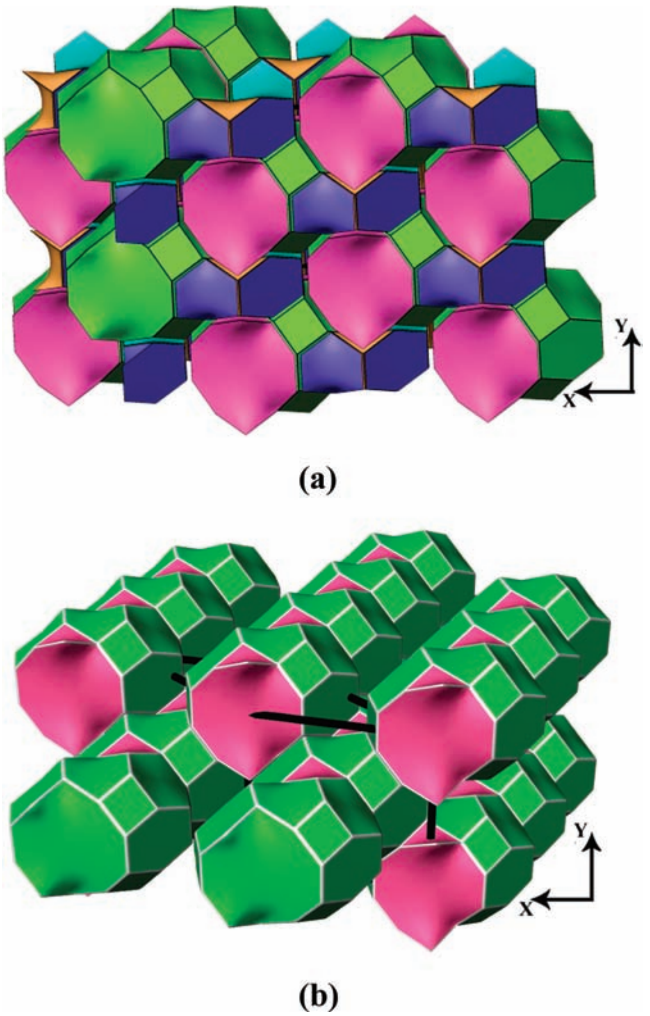

Figure 5. (a) Structural features of MAPO-LAU displayed by tiles: the face symbols for green, pink, dark blue, yellow, and light blue tiles are [$4^6.6^8.10^2$], [$4^2.10^2$], [6^3], [$4^2.6^2$], and [$4^2.6^4$], respectively. (b) The 10-ring channel of MAPO-LAU displayed by tiles: the green for [$4^6.6^8.10^2$] and the pink for [$4^2.10^2$].

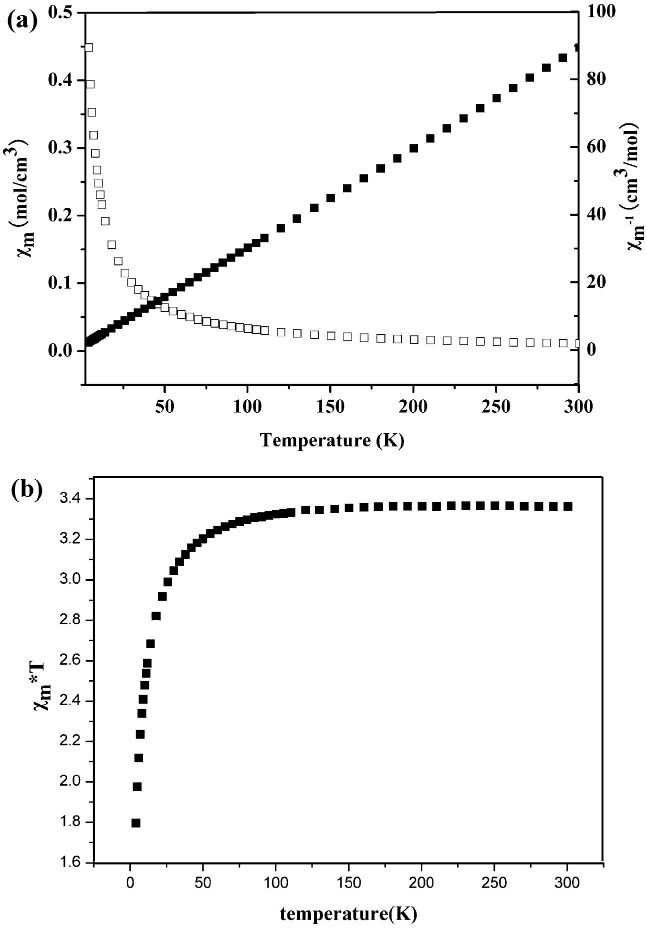

Figure 6. The plots of (a) χ_m and $1/\chi_m$ vs T and (b) $\chi_m T$ vs T for MnAPO-LAU.

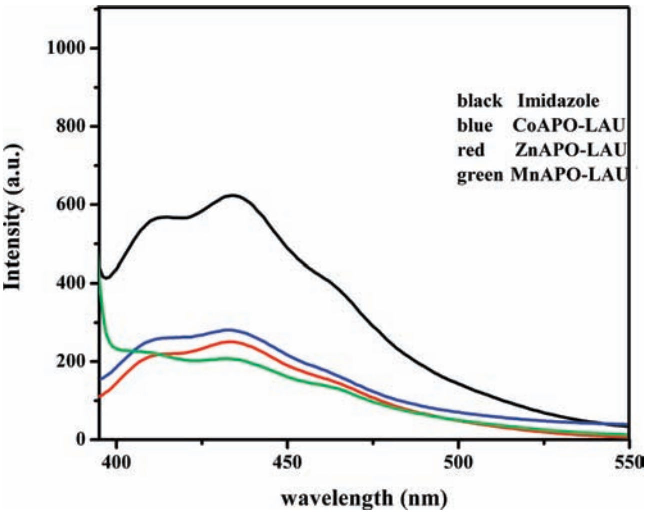

Figure 7. Room-temperature emission spectra of MAPO-LAU (M = Co, Mn, Zn) and imidazole molecules (λ_{ex}=377 nm).

ZnAPO-LAU, respectively. This corresponds to the release of the imidazole template (calcd. 14.78, 14.90, and 14.59 wt % for CoAPO-LAU, MnAPO-LAU, and ZnAPO-LAU, respectively). XRD studies show that the structures of MAPO-LAU are stable at 550 °C and collapse above 600 °C.

The valence state and the coordination of Co ions in CoAPO-LAU are confirmed by diffuse reflectance spectroscopy (UV−vis; Supporting Information, Figure S2). The peaks at 540, 580, and 625 nm are characteristic for tetrahedrally coordinated Co^{II} ions, which are in agreement with those observed in the other cobaltaluminophosphates.[20]

Crystal Structures of MAPO-LAU (M = Co, Mn, Zn). Single-crystal XRD analyses show that the MAPO-LAU (M = Co, Mn, Zn) compounds are analogous to zeotype LAU, and all of them crystallize in the space group *C*2/*c* (No. 15). The framework is constructed from the strict alternation of metal-centered (Al/M) tetrahedra and PO_4 tetrahedra. Figure 2 shows the thermal ellipsoids of CoAPO-LAU. In each asymmetric unit, there are six independent crystallographic positions: three crystallographically independent P atoms and three distinct metal sites that are shared by the Al and Co atoms with occupancies of 0.67 and 0.33, respectively, according to the ICP analysis. The average bond distance of P−O$_{av}$ is 1.514(9) Å. The average Co/Al−O$_{av}$ bond length of 1.789(2) Å lies between the Co−O and Al−O

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[20] Verberckmoes, A. A.; Uytterhoeven, M. G.; Schoonheydt, R. A. *Zeolites* **1997**, *19*, 180.

bond lengths, in agreement with those observed in the other cobaltaluminophosphates.[21]

The asymmetric units of ZnAPO-LAU and MnAPO-LAU are similar to that of CoAPO-LAU, in which the Co atom is replaced by Mn and Zn atoms, respectively. The average bond distances of P−O_{av} and M−O_{av} are 1.519(7) Å and 1.786(9) Å for ZnAPO-LAU and 1.512(4) Å and 1.798(3) for MnAPO-LAU, respectively. Crystal data and structural refinement for MAPO-LAU (M = Co, Mn, Zn) are shown in Table 1. The selected bond lengths and angles of MAPO-LAU (M = Co, Mn, Zn) are listed in the Supporting Information, Tables S1−S3, respectively.

The linkages of MO_4/AlO_4 (M = Co, Mn, Zn) and PO_4 tetrahedra through vertex oxygen atoms form the anionic open framework with a formula of $[M_8Al_{16}P_{24}O_{96}]^{8-}$. MAPO-LAU (M = Co, Mn, Zn) has a zeotype LAU structure. It contains one-dimensional 10-ring channels along the [001] direction (Figure 3a). The protonated imidazole molecules reside in the 10-ring channels to balance the charge of the framework (Figure 3b). The 10-ring opening is circumscribed by five metal atoms and five P atoms. Figure 4a shows the framework viewed along the [100] direction. The framework of MAPO-LAU can be described by the 2D undulated sheets with 4- and 6-rings connected by bridging oxygen atoms (Figure 4b). Such undulated 2D sheets are linked together, forming the 3-D open framework with 10-ring pores running in the direction parallel to the 2D nets.

The framework of MAPO-LAU can also be described as a three-periodic net with higher symmetry. The intrinsic symmetry of this underlying net, as determined by the Systre software,[22] is *C*2/*m* with three different T sites. The vertex symbols for the three T sites in the net of MAPO-LAU are $4\cdot4\cdot6\cdot6_2\cdot6\cdot10_4$, $4\cdot4\cdot6\cdot6_2\cdot6\cdot10_2$, and $4\cdot4\cdot6\cdot6_3\cdot6\cdot6_3$. This three-periodic net is carried by a unique natural tiling with a transitivity of (3 7 9 5).[23] There are five different tiles in this tiling with the face symbols $[6^3]$, $[4^2.6^2]$, $[4^2.10^2]$, $[4^2.6^4]$, and $[4^6.6^8.10^2]$ (Figure 5a). The signature of this tiling is $2[6^3]+[4^2.6^2]+[4^2.10^2]+[4^2.6^4]+[4^6.6^8.10^2]$. As shown in Figure 5b, the 10-ring channel running along the [001] direction is clearly defined by the linear arrangement of tiles of $[4^2.10^2]$ and $[4^6.6^8.10^2]$.

Magnetic Property. The temperature dependences of the magnetic susceptibilities of MnAPO-LAU were recorded at an applied magnetic field of 1000 Oe over a temperature range of 4−300 K. Figure 6a and b show the plots of χ_m and $1/\chi_m$ versus *T* and of $\chi_m T$ versus *T* of the compound, respectively. The susceptibility obeys the Curie−Weiss rule $[\chi_m = C/(T - \theta)]$ over a wide range of temperatures (4−300 K). The effective magnetic moment per Mn^{2+} calculated from the derived Curie constant is 5.21 μ_B. The negative Weiss constant, $\theta = -1.49$ K, implies weak antiferromagnetic interaction between Mn^{2+} ions in the framework.

Luminescent Property. The photoluminescent spectra of MAPO-LAU and imidazole molecules were measured in the solid state at room temperature (Figure 7). The emission spectra of MAPO-LAU and imidazole molecules both exhibit two peaks at 411 and 434 nm excited at a wavelength of 379 nm. The emissions of MAPO-LAU are due to the presence of the imidazole molecules in the structures. It is noted that the emission intensity of MnAPO-LAU is weaker than those of CoAPO-LAU and ZnAPO-LAU.

Conclusions

Three transition-metal-substituted aluminophosphate molecular sieves, MAPO-LAU (M = Co, Mn, Zn), with the zeotype LAU structures, have been synthesized solvothermally in the presence of imidazole as the SDA. The alternating connection of MO_4/AlO_4 and PO_4 terahedra forms the 3-D open frameworks of MAPO-LAU (M = Co, Mn, Zn), in which 33.3% of the aluminum sites are replaced by transitional-metal ions. This substitution is determined by the host−guest charge-density matching. MnAPO-LAU shows weak antiferromagnetic interaction between Mn^{2+} ions in the framework. All of the MAPO-LAU compounds show photoluminescent properties due to the existence of imidazole molecules in the frameworks. The transition-metal-substituted aluminophosphate molecular sieves are promising materials in optics and magnetism, as well as in catalysis as important single-site solid catalysts.

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Supporting Information Available: Crystallographic data (CIF), the TG curve of MAPO-LAU (Me = Co, Mn, Zn), the diffuse reflectance spectroscopy (UV−vis) for CoAPO-LAU, selected bond lengths (Å) and angles (deg) for MAPO-LAU (Me = Co, Mn, Zn). These materials are available free of charge via the Internet at http://pubs.acs.org.

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