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Unequivocal Heteroatom Insertion into a 24-Ring Channel Gallophosphate and Its Photoluminescence

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Five different transition metal elements have been successfully inserted into a unique 24-ring (24R) channel structure, NTHU-1, which is the first neutral framework gallophosphate displaying visible photoluminescence without added metal activators. Incorporation of heteroatoms into the intraframework sites has intricately tuned luminescence properties and made subtle changes in channel size as well as imposed magnetism to NTHU-1. The resultant phases, designated as NTHU-1M with M = Cr, Mn, Fe, Co, CrCo, and Zn, were respectively characterized by X-ray diffraction, thermal analyses, photoluminescence, UV−vis spectra, and/or magnetic studies. Our reaction conditions enabled the formation of large crystals with higher quality and a more definite degree of incorporation, which allowed unambiguous elucidation of the location, population, and environment of each of the heteroatoms in one 24R channel structure from single crystals, than ever reported before. In addition, the successful insertion of Cr produced unprecedented Cr and Ga mixed-metal phosphates with different optical properties from Cr-doped aluminophosphates or zeolites. Two distinct metal sites in different geometries were observed in NTHU-1, where the tetrahedral site was occupied by divalent heteroatoms and the octahedral site by the trivalent. The two distinct sites could even be occupied simultaneously, resulting in a unique CrCo dual insertion. Factors concerning the incorporation and the influence of heteroatoms on the luminescence property are discussed.

Introduction

Open-framework phosphates of aluminum and gallium as well as transition metals are an important class of microporous materials[1−4] owing to their rich structural chemistry, interesting properties, and wide applications ranging from traditional adsorptive and catalytic areas to modern low-*k* materials and zeolite-dye microlasers.[5−10] Photoluminescence (PL) is one of the newly discovered properties for lighting-element-free open-framework phosphates,[11−14] which are in contrast to other porous materials designed as phosphors with added dye or metal activators.[15,16] The luminescent mechanism of open-framework materials without metal activator elements has not been unambiguously understood. So far, all of these intrinsic phosphors are observed to possess extra-large-channel structures, protonated organic templates, and negatively charged frameworks. Would pore or channel sizes be effective in their luminescence property? Will any neutral frameworks emit luminescence? What is the influence of incorporated heteroatoms on the luminescence of the host or vice versa? Studies on more open-framework phosphates capable of emitting luminescence are needed to resolve these questions.

We have been searching in the field of crystalline metal phosphates and silicates for new topologies,[17−21] novel properties, and especially the extreme in pore size, which can widen the range of current applications.[12,13] Among the phosphate-based materials, the largest channel size which has been observed is 24-ring (24R), but only discovered in ND-1,[22] VSB-1,[23] VSB-5,[24] and NTHU-1.[17] The former three phosphates are with transition metals, and the latter one is with the main group metal instead. Compared with other

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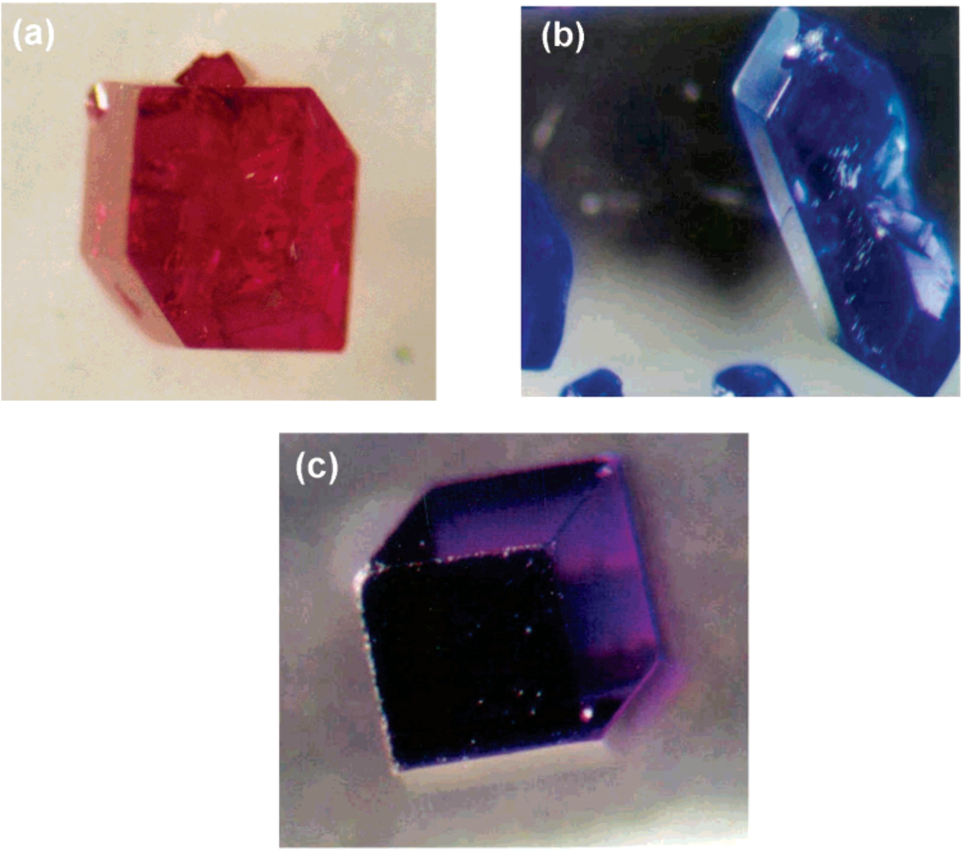

Figure 1. Optical micrographs of good quality and large-sized crystals of NTHU-1M: (a) ruby-red NTHU-1Cr, (b) navy-blue NTHU-1Co, and (c) violet NTHU-1CrCo.

luminant metal phosphates with anionic frameworks, we discovered that NTHU-1, simply bearing a neutral framework, was able to emit blue light with exposure to 254 and 360 nm UV light, respectively, and its light emission efficiency could be further improved by conventional thermal annealing. Moreover, we were able to incorporate five different transition metals (Cr, Mn, Fe, Co, and Zn), respectively, and one combination (CrCo) into the same framework to create six new derivatives, namely, NTHU-1M where M = Cr, Mn, Fe, Co, CrCo, and Zn. Among them, NTHU-1Cr is the most remarkable as Cr has been noted for its difficult framework incorporation.[5,25−27] It is for the first time that a series of heteroatoms, with differences in ionic radii, ionic charge, and affinity to the formation of certain geometric coordinations with phosphate oxygen, can be successfully inserted into one luminescent gigantic pore framework. The exact location, occupancy, and environment for each incorporated heteroatom are unambiguously elucidated from single-crystal data. This structural information is highly valuable to rationalize the activity of molecular sieves and to find a correlation between optimum catalytic activity and the structure of the active sites. Herein, we report the solvothermal synthesis, structural characterization, and thermal and magnetic properties of six NTHU-1M compounds. The PL spectra for both NTHU-1 and NTHU-1M were measured and compared with those of existing luminescent microporous phosphates. How each incorporated heteroatom influences the luminescent property is also discussed.

Experimental Section

Synthesis and Compositional Characterization. Chemicals of reagent grade were used as received. Solvothermal reactions were carried out at 180 °C for 3 days in a Teflon lined acid digestion bomb, followed by slow cooling at 6 °C h^{-1} to room temperature of an internal volume of 23 mL. A single-phase product consisting of transparent colorless crystals of NTHU-1 was obtained from a mixture of diethylenetriamine (dien), Ga_2O_3, H_3PO_4 (aq, 85%), and ethylene glycol (EG) in a molar ratio of 4.6:0.5:6:220.[28] To synthesize heteroatom incorporated NTHU-1M, the reagents $Cr(NO_3)_3{\cdot}9H_2O$, $MnCl_2{\cdot}4H_2O$, $FeCl_2{\cdot}4H_2O$, $CoCl_2{\cdot}6H_2O$, and $ZnCl_2$ were used as the sources for M. To achieve maximum incorporations, a sufficient amount of each metal salt was directly added into the reaction mixture used for preparing NTHU-1 but with partial substitution of Ga_2O_3 reactant (the optimal molar ratio for M and Ga was 2:5). As the ratio was increasingly approaching to 1:1, the reaction could result in either known structures for Mn and Zn (e.g., $(H_3dien)[Mn(H_2O)_2Ga(PO_4)_2]_3$ and $(H_3dien)[Zn_3Ga(PO_4)_4]{\cdot}H_2O$)[18] or amorphous phases for Cr, Fe, and Co. These reactions respectively produced crystals of ruby-red NTHU-1Cr (Figure 1a), colorless NTHU-1Mn, light-yellow NTHU-1Fe, navy-blue NTHU-1Co (Figure 1b), and colorless NTHU-1Zn. These

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(28) The ratios are the optimum condition for preparing NTHU-1, which are slightly different from those previously reported in ref 17. The reaction mixture included exactly 0.50 mL of dien, 95 mg of Ga_2O_3, 0.40 mL of H_3PO_4 (85%), 6.0 mL of EG, and 6.0 mL of water.

Table 1. Summary of Crystal Colors, Contents of Heteroatoms, Densities, Cell Dimensions, and Channel Sizes for NTHU-1M

		heteroatom content[a]					cell dimensions			
compound	crystal color	SXRD[b]	EPMA	ICP	SQUID	density d (g·cm^{-3})	a (Å)	c (Å)	V (Å^3)	ring size (Å)
NTHU-1	colorless	0	0	0	0	2.124	23.781(1)	13.466(1)	6595.2(8)	10.279
NTHU-1Cr	ruby-red	0.10	0.13	0.10	0.09	2.048	23.716(3)	13.447(2)	6549.9(17)	10.202
NTHU-1Mn	colorless	0.15	0.14	0.14	0.14	2.037	23.664(1)	13.569(1)	6580.0(8)	10.147
NTHU-1Fe	pale-yellow	0.20	0.20	0.20	0.23	2.033	23.697(1)	13.544(1)	6586.2(7)	10.200
NTHU-1Co	navy-blue	0.10	0.10	0.07	0.11	2.042	23.740(2)	13.485(1)	6581.8(9)	10.242
NTHU-1CrCo	purple	0.10, 0.10	0.13, 0.14	0.09, 0.10	0.21[c]	2.033	23.742(1)	13.489(1)	6584.8(4)	10.237
NTHU-1Zn	colorless	0.20	0.23	0.21	NA	2.042	23.690(1)	13.548(1)	6584.8(6)	10.112

[a] The content of each heteroatom is shown in a molar ratio at each site; refer to the text for details. [b] Results are obtained from single-crystal structure refinements. [c] This is the total amount of Cr and Co derived from magnetic susceptibility data.

Table 2. Bond Lengths (Å) of the Metal−Oxygen Polyhedra in NTHU-1 and NTHU-1M

	NTHU-1	NTHU-1Cr	NTHU-1Mn	NTHU-1Fe	NTHU-1Co	NTHU-1CrCo	NTHU-1Zn
Ga(1)−O(2)	1.826(2)	1.822(3)	1.869(4)	1.856(4)	1.834(3)	1.837(3)	1.863(3)
Ga(1)−O(3)	1.833(2)	1.828(3)	1.877(4)	1.857(4)	1.841(3)	1.841(3)	1.865(3)
Ga(1)−O(5)	1.838(2)	1.836(3)	1.869(3)	1.855(4)	1.842(2)	1.842(2)	1.860(3)
Ga(1)−O(6)	1.840(2)	1.843(3)	1.889(4)	1.875(4)	1.851(3)	1.853(3)	1.877(3)
Ga(1)−O$_{ave}$	1.834(2)	1.832(3)	1.876(4)	1.861(4)	1.842(3)	1.843(3)	1.866(3)
Ga(2)−O(1)	1.950(2)	1.944(3)	1.955(3)	1.953(4)	1.952(3)	1.948(3)	1.953(3)
Ga(2)−O(7)	1.999(2)	1.998(3)	1.999(3)	1.999(4)	2.002(2)	1.998(3)	1.999(3)
Ga(2)−O(8)	1.896 (2)	1.895(3)	1.892(3)	1.899(4)	1.898(3)	1.903(3)	1.895(3)
Ga(2)−N(1)	2.065(3)	2.062(4)	2.072(5)	2.066(6)	2.071(4)	2.071(4)	2.076(5)
Ga(2)−N(2)	2.065(3)	2.052(4)	2.073(4)	2.081(5)	2.065(3)	2.067(4)	2.071(4)
Ga(2)−N(3)	2.066(3)	2.061(4)	2.056(4)	2.056(5)	2.062(3)	2.068(4)	2.059(4)
Ga(2)−(O,N)$_{ave}$	2.007(3)	2.002(4)	2.008(5)	2.009(6)	2.008(4)	2.009(4)	2.009(5)

crystals were all sufficiently large for single-crystal structure analysis (vide infra). Each reaction product also contained a small amount of unidentified white powder which could be easily removed with the aid of an ultrasonic vibrator. The locations of Cr in NTHU-1Cr and Co in NTHU-1Co were found to locate on different gallium sites. Thus, we wondered if these two metals could be simultaneously inserted into the same lattice. We then conducted another synthesis by including both $Cr(NO_3)_3\cdot 9H_2O$ and $CoCl_2$ with the molar ratio 1:1 in the reaction mixture. It resulted in purple-colored crystals (Figure 1c), indicating a dual incorporation was successively achieved. All measurements in this study were performed on samples with individual purity preliminarily checked by powder X-ray diffraction (XRD) measurements. For each of the six NTHU-1M compounds, the molar ratios for M and Ga were first obtained from the refinements of single-crystal data. The M and Ga ratios were further corroborated by electron probe microanalysis (EPMA), inductively coupled plasma (ICP)−atomic emission spectroscopic data), and results from magnetic susceptibility studies (Table 1).

Single-Crystal Structure Analysis. Six different crystals of NTHU-1M with suitable sizes were selected for indexing and intensity data collection. Diffraction measurements, data processing, and reduction were all performed on a Bruker Smart-CCD system. Empirical absorption corrections were applied by using the SADABS program.[29] On the basis of the systematic absences and statistics of intensity distribution, the same space group, $R\bar{3}$, was determined for all six derivatives. Structure refinements had started with the atomic coordinates of NTHU-1. The location of each transition metal ion was carefully diagnosed from abnormalities in thermal parameters, bond lengths, and the bond-valence sum of each Ga site. We observed that the divalent Mn^{2+}, Co^{2+}, Fe^{2+}, or Zn^{2+} ions occupied the tetrahedral Ga(1) center, while the trivalent Cr^{3+} ion settled at the octahedral Ga(2) center. Subsequent refinements on the metal occupancies, with the sum of M and Ga being constrained to 1.00, had resulted in a value approximate to the results obtained from EPMA, ICP, and magnetic moment calculations. For structure factor calculations, the final occupancy for each transition metal was then fixed at an averaged value of these four approaches. Two water oxygen sites, O(9) and O(10), both with half occupancy, were located in all six NTHU-1M. The H atoms, except those of water molecules, could be located directly on difference Fourier maps. The final cycles of refinement, including the atomic coordinates and anisotropic thermal parameters for all non-H atoms and fixed atomic coordinates and isotropic thermal parameters for H atoms, converged at R1 = 3.91% for NTHU-1Cr, 4.29% for NTHU-1Mn, 4.32% for NTHU-1Fe, 3.24% for NTHU-1Co, 4.22% for NTHU-1CrCo, and 3.88% for NTHU-1Zn. The chemical formulas so determined were $[Cr_{0.1}Ga_{1.9}(dien)(PO_4)_2]\cdot H_2O$ for NTHU-1Cr and $[M^{II}_x(GaPO_4)_{2-x}(dien)(HPO_4)_x]\cdot H_2O$ for NTHU-1M (where $x = 0.10$ for M = Co, $x = 0.15$ for M = Mn, and $x = 0.20$ for M = Fe and Zn). Cell dimensions and contents of heteroatoms are listed in Table 1, and selected bond distances are listed in Table 2.

Thermogravimetric Analysis and Magnetic Study. Thermal analyses, using a Seiko TG 300 analyzer, were performed on powder samples under flowing N_2 with a heating rate of 10 °C min^{-1}. A two-step weight loss for all six NTHU-1M was observed, that is, from 30 to about 120 °C for the dehydration of lattice water and from about 280 for 450 °C for the removal of the dien molecule. The residue obtained after further heating to 1000 °C contained $GaPO_4$ (JCPDS no. 16-0185) as a major phase. Powder samples (100 mg each), except that of NTHU-1Zn, were used to collect variable temperature magnetic susceptibility $\chi(T)$ data from 2 to 300 K in a magnetic field of 0.5 T using a Quantum Design SQUID magnetometer. The measured susceptibility data were corrected for core diamagnetism.[30]

PL and UV−Visible Spectra. Solid-state PL and UV−visible studies were respectively performed on powder samples (240 mg each) at room temperature. PL spectra were measured on a HITACHI F-4500 FL spectrophotometer equipped with a Xe lamp (150 W) as the excitation light source. The excitation slit widths were set at 2.5 mm, and the emission slit widths were set at 1.0

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(29) *SAINT+ programs*, Version 6.02; Bruker Analytical X-ray Systems: Madison, WI, 1999.

(30) Selwood, P. W. *Magnetochemistry*; Interscience: New York, 1956.

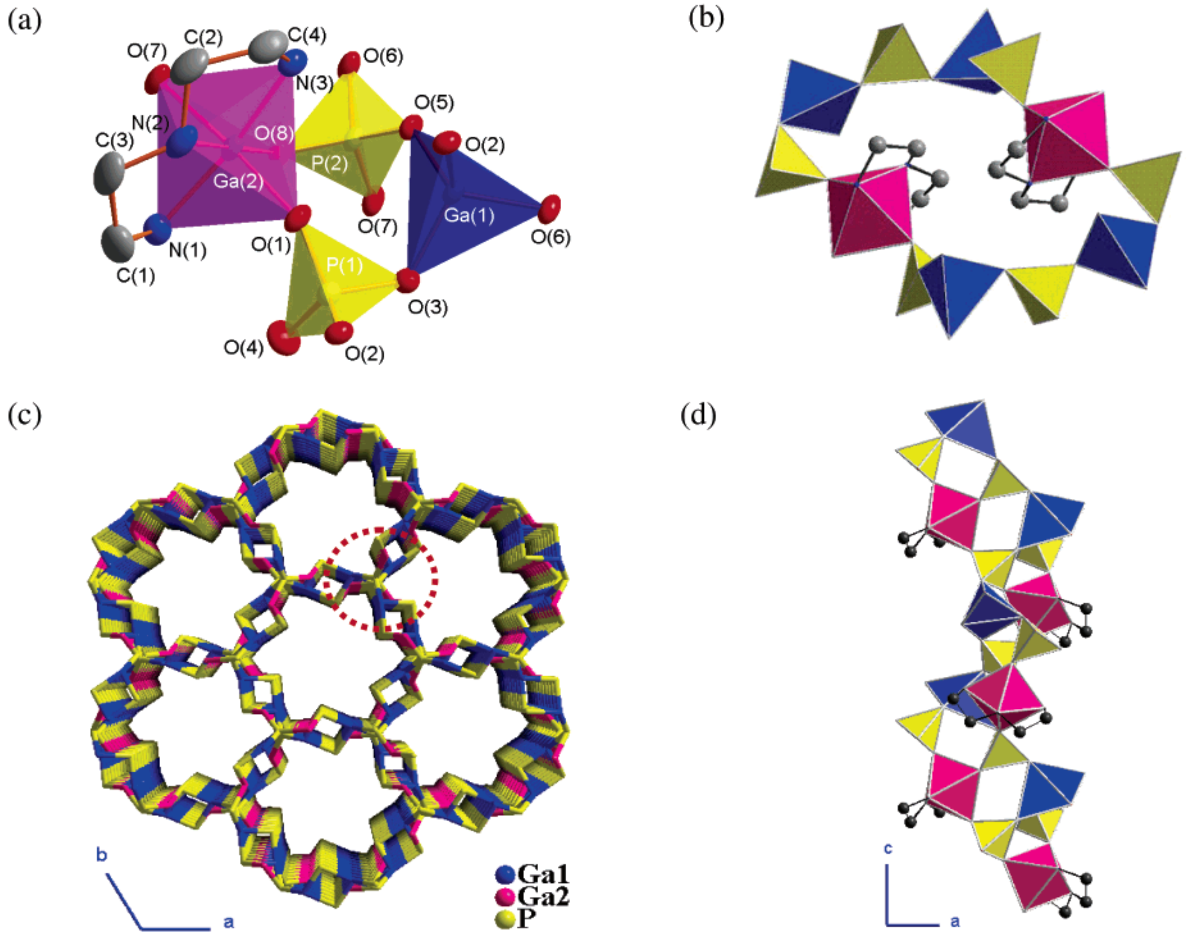

Figure 2. Structure of NTHU-1 showing (a) the 4R primary building unit, (b) lateral 12R window, (c) neutral framework with 24R channels surrounded by the pinwheel-like spiral columns (in the red circle); (d) a view of the spiral column parallel to the *b* axis. In these representations, Ga(1)O_4 tetrahedra are blue, Ga(2)N_3O_3 octahedra are red, and PO_4 tetrahedra are yellow. The tridentate ligand diens in a, b, and d are ball-and-stick models.

mm. The UV−vis spectra were measured on a Hitachi U-3310 spectrophotometer equipped with an integrating sphere attachment and against a $BaSO_4$ plate as the standard.

Results and Discussion

Structure Description and PL. The structure of NTHU-1 has a unique architecture with three types of ring components, 4-ring (4R), 12-ring (12R), and 24R (Figure 2). It is the largest crystalline pore GaPOs known to date. The three-dimensional framework is built up with 4R units, each of which is formed of three unique tetrahedra (Ga(1)O_4, P(1)-O_4, and P(2)O_4) and one octahedron (Ga(2)N_3O_3). These 4R units are connected through Ga(2) and P(2) polyhedra into a pinwheel-like spiral column extending parallel to the *c* axis. The spiral columns are further linked through Ga(1) and P(1) tetrahedra along *a* and *b* to create gigantic channels, which exhibit puckered 24R windows formed by the edges of 12Ga-(1) and 6P(1) and 6P(2) tetrahedra in the *ab* plane. Each channel also contains six lateral 12R windows delimited by two Ga(2) octahedra and 10 tetrahedra of 4Ga(1), 2P(1) and 4P(2). Within the uni-dimensional 24R channels are merely water molecules, which can be reversibly removed and restored.[31]

The transparent colorless crystals of NTHU-1 can emit blue bands (peaked at 450 nm) under $\lambda_{ex} = 254$ and 360 nm. The emission and excitation spectra are shown in Figure 3. According to a literature survey, dye-free or metal-activator-free open-framework phosphates that can display a PL property are limited in number. The only reported examples include UCSB-*n* (n = 6, 7, 8, and 10)[11] and NTHU-*n* (n = 2, 3, and 4),[12−14] which are all capable of giving blue fluorescence in the range from 390 to 480 nm. Besides indefinite lattice defects, their luminescence mechanisms were considered to be closely related to the anionic charge of frameworks and the presence of protonated amine templates. In contrast to previous observations, NTHU-1 possesses merely a neutral framework and a noncharged ligand amine and yet still displayed luminescence. What would be potential luminescence centers here? Looking into the inorganic constituents of NTHU-1, gallium is the only element belonging to the presently known luminescence centers in solid-state spectroscopy.[32] But, Ga is required to be in the monovalent state to be active. So far we have not obtained solid evidence to conclude that Ga^+ is present in NTHU-1. As to the organic constituent, we made PL

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(31) The number of lattice water molecules is less in NTHU-1M than in NTHU-1. All water molecules could be removed by heating powder samples at 180 °C for 5 h without collapsing the structure. Such a thermal treatment improved the efficiency of luminescence emission of NTHU-1. Upon PL measurements, the water content was fully restored from humidity.

(32) Gaft, M. Reisfeld, R.; Panczer, G. *Modern Luminescence Spectroscopy of Minerals and Materials*; Springer-Verlag: Berlin, Heidelberg, 2005.

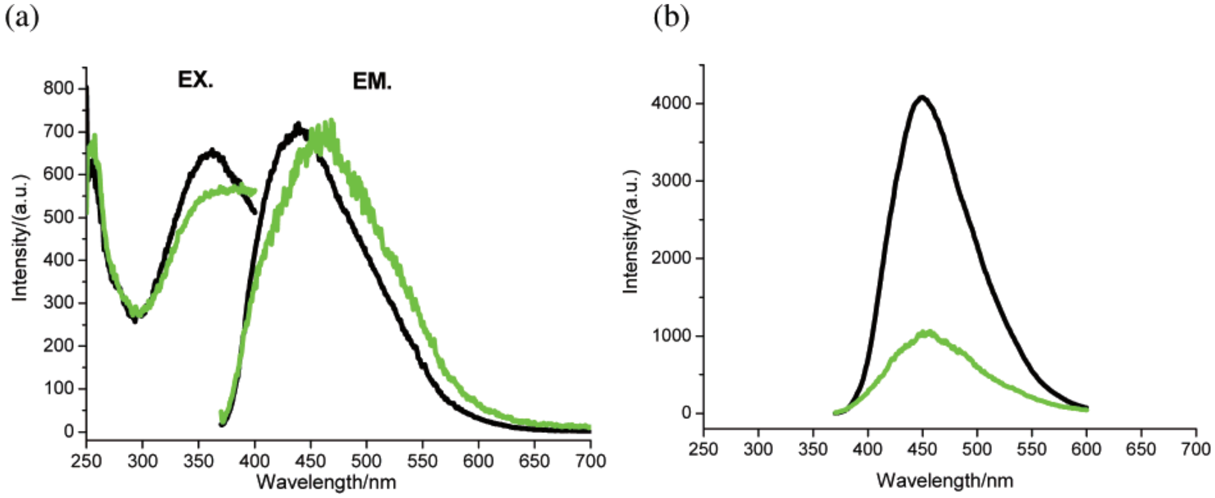

Figure 3. Emission and excitation spectra of NTHU-1 measured before heat treatment (left) and after heat treatment (right). Emission curves in green were under $\lambda_{ex} = 254$ nm, and the ones in black were under $\lambda_{ex} = 360$ nm.

measurements on the ligand dien itself, which gave a weak blue band at 425 nm under $\lambda_{ex} = 360$ nm only. No emission from dien was observed under $\lambda_{ex} = 254$ nm or other wavelengths. These findings suggested the blue band being originated from two different emission centers, one connected with the ligand dien (on Ga(2), sensible to the longer wavelength), and the other connected with unknown centers (or unconfirmed Ga^+, sensible to the shorter wavelength). It is interesting to note that the emission intensity from a heat-treatment sample[31] of NTHU-1 was significantly enhanced (Figure 3b), which indicated that, regardless of their origins, the total number of active luminescence centers in NTHU-1 could be promoted via thermal annealing.

Location of Cr in NTHU-1Cr and NTHU-1CrCo. The question of whether the trivalent chromium can be incorporated into the framework or can only occupy an extraframework site has remained open for years because of the difficulty in incorporating a sensible amount of Cr or preparing usable crystalline samples.[5] The crystals of NTHU-1Cr and NTHU-1CrCo prepared in the study were all of good quality and in large sizes (1−3 mm, refer to Figure 1). In both crystals, Cr occupied the octahedral Ga(2) center with the molar ratio for Cr and Ga being 1:9. UV−vis spectra revealed two broad absorption bands (peaked at 395 and 528 nm, refer to Figure 4) corresponding to the characteristic emission of Cr^{3+} in the octahedral coordination. No Cr was detected in the tetrahedral Ga(1) site. Bond lengths in the $Ga(2)O_3N_3$ octahedron were barely affected upon Cr insertion (Table 2), because both six-coordinated Cr^{3+} and Ga^{3+} ions have similar crystal radii (0.755 vs 0.76 Å).[33] It is worth noting that, in contrast to the green color used to observed in Cr^{3+}-incorporated aluminophosphate zeolites, NTHU-1Cr is ruby-red instead. Surrounded by three N from one dien molecule and three O from phosphate groups, it is in a sufficiently strong crystal field that Cr^{3+} ions lean toward the red color as they do toward ruby. In the case of dual incorporation where Cr and Co separately settled in octahedron Ga(2) and tetrahedron Ga(1) (vide infra), the crystals exhibited purple color (Figure 1c), a consequence of blue from tetrahedral Co^{2+} and red from octahedral Cr^{3+}.

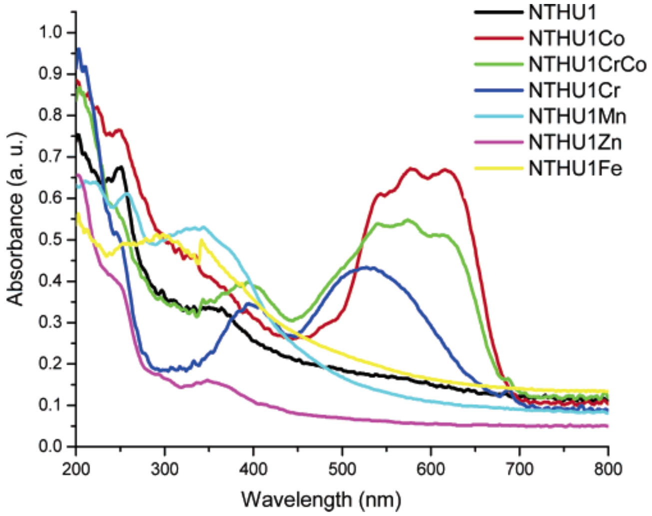

Figure 4. Solid-state UV−vis spectra of NTHU-1 and NTHU-1M measured at room temperature.

Distribution of Divalent Metals in NTHU-1M. Respective sites determined for divalent Mn^{2+}, Fe^{2+}, Co^{2+}, and Zn^{2+} ions were exclusively in the tetrahedral Ga(1) center.[34] In UV−vis spectra three characteristic bands (maxima at 541, 578, and 617 nm) belonging to the tetrahedral Co^{2+} center (which rendered blue color to the incorporated) were observed. The degree of incorporation was the least for Co, medium for Mn (in NTHU-1Mn), and the most for Fe and Zn (Table 1). According to Shannon,[33] the effective crystal radii of tetrahedral Mn^{2+}, Fe^{2+}, Co^{2+}, and Zn^{2+} ions (respectively 0.80, 0.77, 0.72, and 0.74 Å) are all significantly larger than that of tetrahedral Ga^{3+} (0.61 Å). Hence, the insertion of these ions in the Ga(1) site led to an obvious change in the bond lengths of Ga(1)−O. As shown in Table 2, the averaged length of Ga(1)−O increased the most (0.043 Å) by Mn incorporation and the least (0.008 Å) by Co

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(33) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751.

(34) Such divalent ions were found to occupy five-coordinated instead of tetrahedral Ga sites in other GaPOs. See Mrak, M.; Tusar, N. N.; Ristic, A.; Arcon, I.; Thibault-Starzyk, F.; Kaucic, V. *Microporous Mesoporous Mater.* **2002**, *56*, 257.

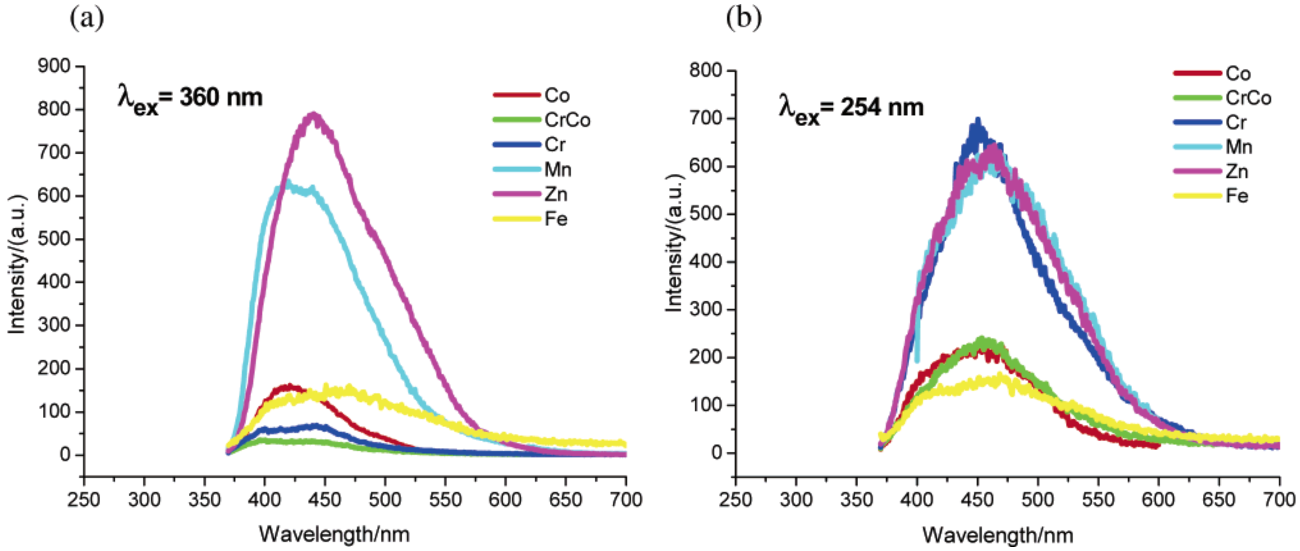

Figure 5. Emission spectra of NTHU-1M showing the influence of each incorporated heteroatom on the intensity.

incorporation. No evidence supported the occupation of aliovalent ions at the octahedral Ga(2) site. The bonds associated with Ga(2) thus remained intact before and after heteroatom incorporation.

Heteroatom Effects on Structure and Properties. Incorporation of heteroatoms through solvothermal reactions has produced high-quality homogeneous crystals of NTHU-1M, which is contradictory to the poor crystalline powders or amorphous phases used to obtain from isomorphous substitutions in aluminophosphates. One common feature of NTHU-1M is in that their crystals tended to grow large with an average size up to millimeters. For example, blue chunky crystals with a dimension up to 10 mm could be readily picked in the reaction product of NTHU-1Co. Lighter in atomic weight and larger in ionic radii as compared with Ga, the heteroatoms led to six NTHU-1 analogues with densities consistently lowered (up to −4.28% in NTHU-1CrCo); their channel apertures were reduced, from 10.28 Å in NTHU-1 to 10.11 Å in NTHU-1Zn, owing to a moderate tuning from the expansion in $Ga(1)O_4$ (caused by partial occupation of larger divalent ions). Another common feature among all NTHU-1M is their compositions being stoichiometric without forming a solid solution. Indeed, with Ga and heteroatoms differing in size by more than 30% (32.8% in the case of Mn^{2+}), solid solutions would not be expected to form; with those differing by 15−20%, solid solutions would not form until high temperatures.[35] The fixed amount of heteroatoms was as well-supported by magnetic susceptibility data (Figure S4). The incorporation of heteroatoms had the parent diamagnetic NTHU-1 convert into paramagnetic NTHU-1M (except M = Zn).

Among the five heteroatoms, Cr and Mn are well-known luminescence activator elements, Fe and Co are quenchers, and Zn belongs to the class of host lattice elements.[36] Surprisingly, neither Cr^{3+} nor Mn^{2+} were observed to emit characteristic lines in the PL spectra, indicating that NTHU-1 was not a suitable host lattice for both Cr and Mn; that is, Ga(2) and Ga(1) were not emitting sites for them. Furthermore, the blue band after Cr's incorporation was consistent in its intensity under $\lambda_{ex} = 254$ nm but drastically suppressed under $\lambda_{ex} = 360$ nm (Figure 5). In the previous section, we had pointed out that the ligand dien as an activator contributes to the luminescence under 360 nm. We assume this phenomenon might be caused by the poisoning of Cr^{3+} in the Ga(2) site, making its ligand dien nonluminescent. However, the incorporation of Zn and Mn, under either 254 or 360 mm, exercises no influence on NTHU-1's emission, while Fe and Co incorporated as quenchers eliminate the emission as expected (Figure 5).

Conclusion

The study presents an unprecedented finding on the luminescent property of the 24R-channel containing gallophosphate, NTHU-1, and a successful incorporation of a series of transition metal ions, with differences in ionic radii, ionic charges, and preference for certain coordination, into its framework. On the basis of the strategy of solvothermal synthesis we were able to prepare high-quality homogeneous crystals of NTHU-1M which allowed unambiguous determination of each individual heteroatom in its structure. In terms of the structure, NTHU-1 has a great capacity for both aliovalent and homovalent incorporation, including the most difficultly incorporated Cr^{3+} ion (into an octahedral environment). It is the exactitude in the location and the variety of heteroatoms that enabled us to elucidate the potential nature of luminescence in the neutral NTHU-1 framework. On the other hand, it was surprising to discover that added Cr^{3+} or Mn^{2+} ions, well-known activators, did not endow NTHU-1 with their characteristic luminescence. This finding can be important toward a better understanding of these metal activators' influence on the luminescence of microporous materials.

This study suggested the origin of emission is not related to the charges of both the framework and the amine. According to our observation and related studies, all activator-free phosphates that can be luminescent possess extra-

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large channels as the common feature, and the luminescence mechanism is definitely related to various kinds of lattice defects. In these microporous materials, we speculate that the defects are closely related to the rigidity of host lattices, that is, extra-large channels apt to be accompanied by a less rigid lattice; thus, we can ascribe this to NTHU-1 luminance. The synergistic effect of extra-large channels in lattice defects should not be overlooked. Studies on more examples are unquestionably crucial to underlie the potential mechanisms residing in the luminescence. Investigation in this direction is underway.

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Supporting Information Available: Crystallographic data (CIF) for NTHU-1 and NTHU-1M (M = Cr, Mn, Fe, Co, CrCo, and Zn); TGA curves, PL spectra, powder XRD patterns, and magnetic susceptibility data for NTHU-1Cr, NTHU-1Mn, NTHU-1Fe, NTHU-1Co, and NTHU-1CrCo (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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