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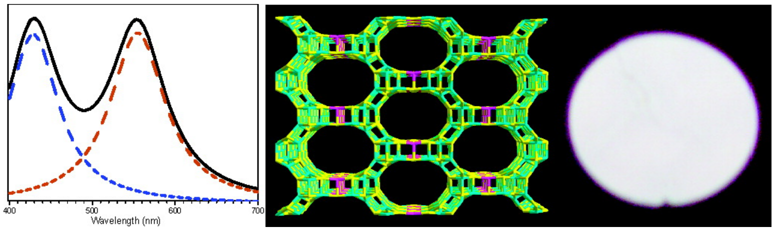

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Direct White Light Phosphor: A Porous Zinc Gallophosphate with Tunable Yellow-to-White Luminescence

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Microporous metal phosphates and silicates have a wide range of applications,[1,2] from catalysis, gas separation/sorption, and ion exchange to recently developed low-*k* materials[3,4] or zeolite-dye microlasers.[5] Photoluminescence is one of the newly discovered properties which may be potentially applicable as inorganic phosphor, an important part of lighting and display technology.[6,7] The mainstream of current lighting technology includes the employment of UV-LED with triple-wavelength RGB phosphors or blue LED with a YAG yellow phosphor to produce white light.[8] In the latter case, there is a serious demand for the exploitation of advanced yellow phosphors. At the present time, mixed luminescence from various sources has always been the route to white light, without other possibilities being advocated. Single host lattice intrinsically that emits white light through photoluminescence has not yet been perceived.

Compared with those inorganic materials added with dye or metal activators,[9,10] photoluminescence intrinsic to microporous metal phosphates was recently emphasized by Feng in 2001.[11] Thereafter, an extra-large pore-containing structure with significant photoluminescence property was reported.[12] As a continuing goal in searching for new microporous materials, with the strategy of employing the large 4,4′-trimethylenedipyridine (tmdp) amine as a template, we have successfully prepared another open framework material with extra-large channels as well as distinctive photoluminescence property. Herein, we report a new member in the system of zinc gallophosphate, NTHU-4. This unique host lattice has two analogues, NTHU-4Y and NTHU-4W, that individually emit yellow and white luminescence with exposure to 365 nm UV light (Figure 1).

Light-brown crystals of NTHU-4Y were obtained as a single phase product by reacting the mixture of tmdp, Ga_2O_3, $ZnCl_2$, oxalic acid, and H_3PO_4 with the molar ratio of 12.8:1:2:2.4:12 in water under a mild hydrothermal condition at 160 °C for 7 days. A tabular crystal of suitable size was selected for single-crystal X-ray diffraction analysis,[13] from which the chemical formula was determined to be $(H_2tmdp)_2[Zn_3Ga_6O(HPO_4)(PO_4)_8]\cdot 5H_2O$. EPMA data confirmed the Zn:Ga ratio to be 1:2, and the results of EA confirmed the organic content. When shined with a UV light at 365 nm, the pallet made of NTHU-4Y powder gave yellow fluorescence (the left photo in Figure 1). However, it would emit white light after heated at 280 °C for 4 h. Thereafter, with the same mixture, but by replacing half of the water with ethylene glycol, deep-brown crystals of NTHU-4W emitting white light (the right photo in Figure 1) were thus obtained. The chemical composition and structure of NTHU-4W are the same as those of NTHU-4Y, except the magnitude of disorderliness in the structure (vide infra) is different. The structures of two NTHU-4 analogues can be sustainable to 280 °C for days, but their luminescence properties would gradually disintegrate after prolonged heating.

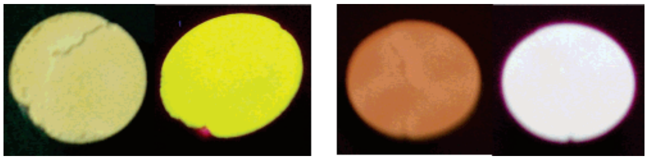

Figure 1. Luminescence property of NTHU-4: (left) the light-brown pallet of NTHU-4Y emits yellow light, and (right) the deep-brown pallet of NTHU-4W emits white light as the results of exposure to a 365 nm UV beam.

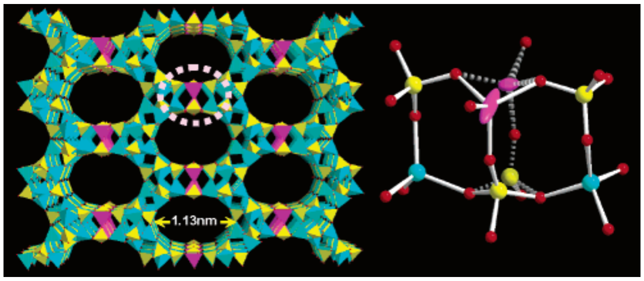

Figure 2. The structure of NTHU-4: (left) viewed along the *c*-axis showing the extra-large channels with oval-shaped aperture. In the plot, tetrahedra in cyan for ordered MO_4 (M = Zn/Ga), in purple for disordered GaO_4, and in yellow for phosphate groups; (right) ball-and-stick drawing of the disordered part of the framework (corresponding to the dotted circle to the left). The dotted bonds denote a set of disordered sites for GaO_4 and HPO_4 groups in an up-and-down manner along the channel direction.

The structure of NTHU-4 is built up with unique tetrahedra of two GaO_4 and three MO_4 (M denotes mixed Zn and Ga) corner-shared with PO_4 or HPO_4 to generate a unique three-dimensional network containing extra-large channels with an aperture consisting of 14-membered rings along the *c*-axis direction (Figure 2). Another set of channels with 10R apertures can be located along the *b*-axis direction. A unique type of cage, $[14^2.10^2.6^6.4^{10}]$, composed of 44 tetrahedra with a maximum free-diameter of 1.54 nm, can be located at the channel intersections wherein protonated tmdp molecules are residing. The large H_2tmdp^{2+} cations, which are disordered within the cages, could be ion-exchanged by Li^+ ions.[14] The structure of NTHU-4 is expected to be porous since 44% of the unit cell is estimated as void space,[15] and the size of 14R channels (1.13 nm in free diameter) is comparable with those of the 24R channels, for example, 1.21 nm in the zincophosphate ND-1[16] and 1.05 nm in the gallophosphate NTHU-1.[17]

NTHU-4 has been considered as the first 14R channel-containing transition-metal gallium phosphates to date.[18,19] Besides, it has the intriguing feature that one-ninth of its framework tetrahedra are in positional disorder,[20] distinctive from previously reported nanoporous phosphate-based materials with rather rigid frameworks. As depicted in Figure 2, on the rims of 14R channels are there the disordered sites, wherein two terminal tetrahedra, MO_4 and HPO_4, are disordered in an up-and-down manner along the channel. In this respect, the two analogues of NTHU-4 have strictly the same

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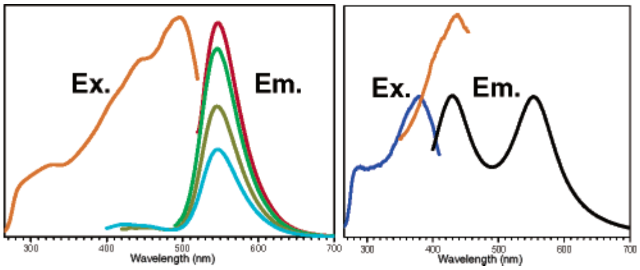

Figure 3. Excitation and emission spectra of NTHU-4: (left) NTHU-4Y invariably emits at 550 nm with excitation by 365 (cyan), 400 (brown), 465 (green), and 500 nm (red); (right) NTHU-4W emits tunable white-to-yellow luminescence with the blue emission peaked at 433 nm. Nearly perfect white light would result by excitation at 390 nm.

structure, except a small difference in the disordered MO_4 (e.g., larger thermal ellipsoids and greater displacement of M centers in NTHU-4Y than in NTHU-4W).[20]

As shown in Figure 3, NTHU-4Y can be excited by light with a broad wavelength ranging from 280 to 520 nm, while invariably emitting yellow luminescence at 550 nm, dissimilar to all precedent metal phosphates or silicate lattices, which typically emit UV or blue light. For NTHU-4W, the same light-excitation range would result in tunable yellow-to-white luminescence, that is, purely single emission in yellow when ex. > 420 nm and noticeably dual emissions in blue and yellow when ex. < 420 nm, due to the enhancement of blue emission at 433 nm (refer to Figure 3). The intensity of individual blue and yellow emission would be equal when the light excitation was tuned to 390 nm, which results in nearly perfect white light.[21] It is surprisingly substantial that the bare lattice of NTHU-4 emits in yellow without any extrinsic activator's presence. Emission influence from the organic templates was not seemingly obvious since replacing most of the H_2dmdp^{2+} ions with Li^+ did not change the absorption and emission spectra.[14] The colors of NTHU-4 crystals mainly come from the template tmdp molecule which gives no fluorescence by itself.

Combining the evidence that heating NTHU-4Y would turn NTHU-4Y from a yellow into white phosphor and that the structure of the white light emitter (NTHU-4W) is less disordered than that of the yellow one (NTHU-4Y), we are informed that the disorderliness of the NTHU-4 lattice may induce defect sites, thus causing the yellow emission in both analogues. From ESR measurements, we observed signals likely from reduced zinc ions. To NTHU-4Y, the heat-treatment tends to heal defect sites and reduces the magnitude of disorderliness, thus presumably converting itself into NTHU-4W. This process revives the blue emission that typically occurs to rigid inorganic phosphate or silicate lattices. As proposed in Figure 4, the absorbed energies via the more disordered NTHU-4Y lattice would be virtually transformed into a yellow emission line, while those via the less disordered NTHU-4W lattice are only partially transformed into yellow with the rest transformed into blue emission. The overall balance between these two emissions results in the white fluorescence of NTHU-4W.

NTHU-4Y is the first phosphate-based intrinsic yellow phosphor observed that can be irreversibly transformed into a white phosphor simply by heat-treatment. On the other hand, NTHU-4W, synthesized in the EG-H_2O solvent system and with luminescence tunable from yellow to both blue and yellow, is the first intrinsic white phosphor that has ever been discovered. Although the real mechanism that accounts for the unusual yellow-to-white photoluminescence is speculative, it no doubt pertains to the disordered nature of the NTHU-4 framework. This remarkable lattice may unfold new applications for nanoporous metal phosphates and, most importantly, may initiate a new class of advanced inorganic phosphors.

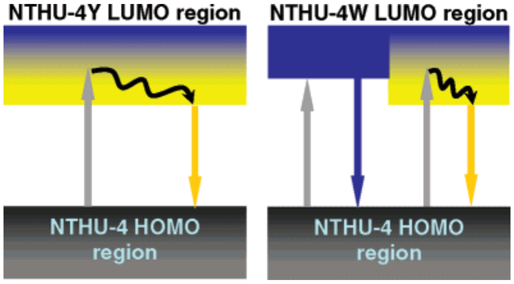

Figure 4. Proposed schematic diagrams showing the absorption and emission between the HOMO region of lone pairs of oxygen atoms and the LUMO region of the framework in NTHU-4.

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Supporting Information Available: X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for NTHU-4: $Zn_3Ga_6P_9O_{42}N_4C_{26}H_{45}$, monoclinic, space group $C2/c$, $Z = 4$, $M_r = 1978.82$, and $a = 30.746(2)$ Å, $b = 13.585(1)$ Å, $c = 14.329(1)$ Å, $\beta = 109.851(2)°$, $V = 5629(1)$ Å^3, $R1 = 0.0530$ for NTHU-4W; and $a = 30.748(6)$ Å, $b = 13.534(3)$ Å, $c = 14.310(3)$ Å, $\beta = 109.733(5)°$, $V = 5605(2)$ Å^3, $R1 = 0.0588$ for NTHU-4Y.
(14) Powders of NTHU-4Y were stirred with 5 M $LiNO_3$ in warm water (70 °C) for 12 h, and the product was filtered and washed with deionized water. Nearly 70% of H_2tmdp^{2+} ions were exchanged with Li^+, and the resulting Li@NTHU-4Y was characterized to contain nine more lattice waters than NTHU-4Y and its PL spectra remained the same as before.
(15) The calculation was performed by a PLATON analysis: Spek, L. *Acta Crystallogr., Sect A* **1990**, *46*, C34.
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(20) In both NTHU-4Y and NTHU-4W, one of the two gallium sites, Ga(5), showed static disorder with thermal parameters 4 times larger and a displacement between disordered sites 1.5 times larger in NTHU-4Y than in NTHU-4W. Moreover, among the five P sites, four are ordered PO_4 and one is disordered HPO_4.
(21) On a calculated CIE diagram, the chromaticity coordination of (0.29, 0.34) was reached by using the excitation at 390 nm.

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