Photoluminescence of open-framework phosphates and germanates

Pingyun Feng

Department of Chemistry, University of California, Riverside, CA 92521, USA.
E-mail: pingyun.feng@ucr.edu

Upon excitation by long wavelength UV radiation, strong room temperature luminescence is observed in a family of metal-activator-free zeolite-type materials; the luminescent output from the large cage UCSB-8Mg structure is independent of temperature from 298 K until at least 77 K.

The development of less-expensive and non-toxic luminescent materials for lighting and display technology represents a research area that could have significant commercial impact. In particular, efficient phosphors that could convert low energy UV radiation (340 to 400 nm) into visible light may lead to the replacement of toxic mercury widely used in fluorescent lamps. So far, the synthetic design of inorganic phosphors usually involves the doping of crystalline host lattices with metal activators that can be either expensive or toxic.[1]

Open-framework materials have been known for several decades and have undergone an explosive growth since the discovery of zeolite-type aluminophosphates.[2] Previous efforts to generate luminescent materials using crystalline porous materials were either by incorporating organic dyes or by doping with metal activators.[3] For example, laser action was observed when organic laser dye molecules, pyridine 2 {1-ethyl-4-[4-(*p*-dimethylaminophenyl)-1,3-butadienyl]pyridinium perchlorate}, were inserted into the pores of AlPO$_4$-5 crystals.[4] To our knowledge, dye-free or metal-activator-free open-framework phosphates or germanates that display luminescent properties have not been reported. Furthermore, no open-framework materials were previously known to display both fluorescence and phosphorescence. Here, a class of efficient luminescent crystalline open-framework materials that do not contain metal activators are described.† Some of these phosphors can display visually observable green afterglow with a lifetime up to 15 s.

One particularly interesting example is UCSB-8Mg (Fig. 1 and Table 1).[5] UCSB-8Mg is built from stacking of large cages, each of which has as many as 64 tetrahedral atoms (*i.e.* Mg, Al, P) and 128 oxygen atoms. Clear, transparent square plates of UCSB-8Mg can be synthesized by the low temperature hydrothermal synthesis. When illuminated with a long wavelength UV lamp (365 nm), the sample displays a strong bluish color. Surprisingly, the luminescent output from UCSB-8Mg is

independent of temperature until at least 77 K, suggesting that there might be no thermal non-radiative decay, even at room temperature. The lack of thermal non-radiative decay, could lead to a reasonably high quantum efficiency for UCSB-8Mg. The method of using the temperature dependence of the light output of a luminescent material to estimate the quantum efficiency was described earlier.[6] For open-framework materials, in addition to the possible intensity increase at lower temperatures, the luminescence bands also show a noticeable blue-shift (Fig. 2).

Another example is UCSB-10Mg (Table 1) with large cages and a framework topology closely related to that of faujasite.[5] Excited at 340 nm, the room temperature luminescence of UCSB-10Mg gives an emission band at $\lambda_{max} = 402$ nm (Fig. 1). The fit to a biexponential equation gives $\tau = 7.2$ ns and 2.0 ns. The strong luminescence of UCSB-10Mg is persistent even at
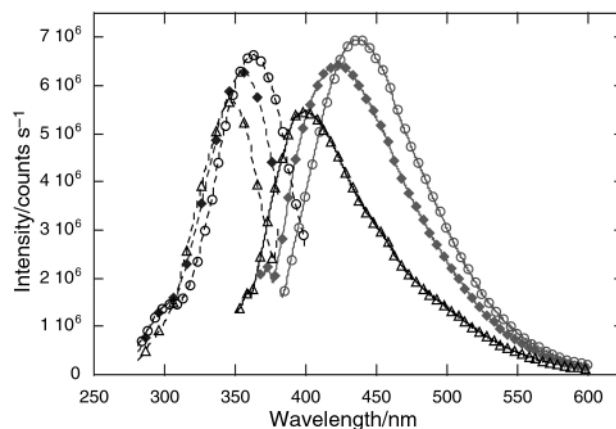

Fig. 1 The excitation (dashed curves) and emission spectra (solid curves) for selected open-framework materials. ($\triangle$): UCSB-10Mg; ($\blacklozenge$): UCSB-7AlGe; ($\bigcirc$): UCSB-8Mg. Intensity data for UCSB-10Mg and UCSB-8Mg are multiplied by 5 and 3, respectively. Fluorescent spectra were measured on a SPEX Fluorolog-3 Tau3 system equipped with a 450 W xenon lamp and double monochromators on both excitation and emission sides. Data were collected with a step size of 1 Å and an integration time of 1 s per step.

Table 1 Photoluminescent properties of selected open-framework materials

Name	Framework composition	Guest type[a]	Structure type[b]	Emission λ_{max}/nm
UCSB-10Mg	MgAlP$_2$O$_8$	R4710	SBT	402
UCSB-10Zn	ZnAlP$_2$O$_8$	R4710	SBT	407
UCSB-6Mg	MgAlP$_2$O$_8$	R17	SBS	410
UCSB-6Zn	ZnAlP$_2$O$_8$	R17	SBS	408
UCSB-8Mg	MgAlP$_2$O$_8$	R19	SBE	436
UCSB-10ZnGa	ZnGaP$_2$O$_8$	R4710	SBT	415
UCSB-7AlGe	Al$_{1-x}$Ge$_{1+x}$O$_4$	R33	UCSB-7	421
UCSB-7GaGe	Ga$_{1-x}$Ge$_{1+x}$O$_4$	R1	UCSB-7	396
UCSB-7K	GaGeO$_4$	K$^+$, H$_2$O	UCSB-7	Zero emission
ZnGaP-SOD	ZnGa$_2$P$_3$O$_{12}$	(CH$_3$)$_4$N$^+$	SOD	Zero emission

[a] R4710 = 1,13-diamino-4,7,10-trioxatridecane; R17 = 1,7-diaminoheptane; R19 = 1,9-diaminononane; R33 = 3,3′-diamino-*N*-methyldipropylamine; R1 = *N*-(2-aminoethyl)-1,3-propanediamine. [b] The three-letter codes are assigned by the Structure Commission of the International Zeolite Association (http://www.iza-structure.org/).
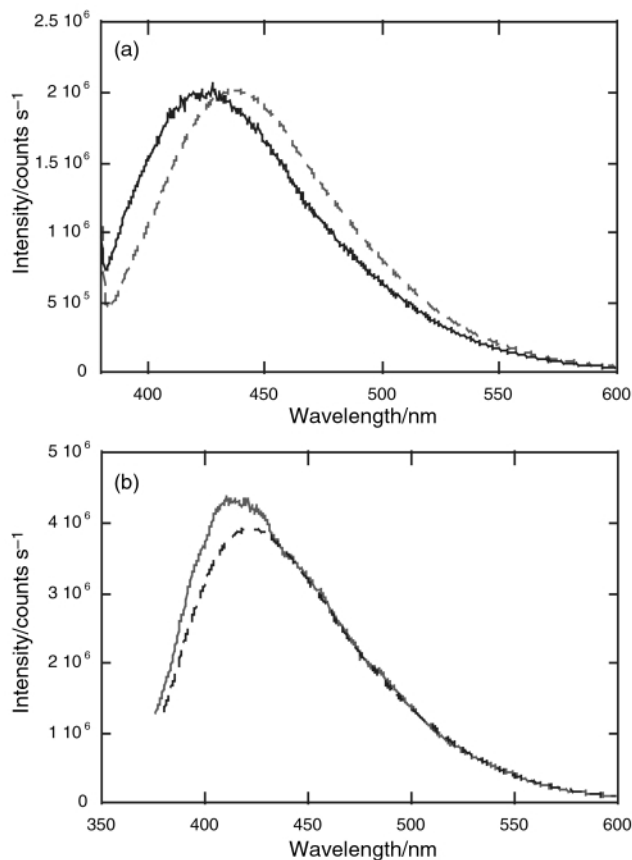
Fig. 2 The emission spectra at room temperature (dashed curves) and at liquid nitrogen temperature (solid curves). (a) UCSB-8Mg (excited at 360 nm); (b) UCSB-7AlGe (excited at 355 nm). Low temperature spectra were collected with the sample tube immersed in a quartz liquid nitrogen Dewar.

high temperatures, *e.g.* 200 °C, below or at which crystalline microporous materials are usually synthesized. Whether the observed photoluminescent phenomena can be used in a screening method for the rapid detection of crystalline open-framework materials represents an interesting question for further studies. In our synthesis, we have frequently found it convenient to detect crystalline open-framework phases with a UV lamp even in the presence of a large amount of amorphous phases because amorphous gel phases are generally not photoluminescent.

Other open-framework materials with efficient luminescence include UCSB-7GaGe and UCSB-7AlGe (Table 1) that are amine-templated gallo- or aluminogermanates with two sets of continuous helical channels separated by a gyroid minimal surface.[7–9] Strong bluish luminescence has also been observed for other open-framework materials with different guest amines, framework compositions and topologies (Table 1). The compositional diversity is advantageous because less expensive and more environmentally benign starting materials may be selected for the synthesis of phosphors reported here and it also offers opportunities for the fine tuning of emission wavelength and bandwidth.

The luminescent mechanism for these open framework materials is not unambiguously known at this stage. For insulating solids without metal activators, the luminescence is often attributed to the presence of various kinds of lattice defects such as oxygen vacancies. Such a defect mechanism is also possible for materials reported here. However, it is also observed that some closely related open-framework materials do not exhibit any photoluminescence. For example, gallogermanate UCSB-7 can be synthesized with either alkali metal cations or different organic amines. Fluorescence measurements show that purely inorganic UCSB-7 structures[7] (those templated with either K or Na cations) do not exhibit luminescence at all while those directed by protonated amine molecules show visible photoluminescence. In addition, it is noteworthy that open-framework materials templated by TMA (TMA = $N(CH_3)_4^+$) such as $(TMA)ZnGa_2X_3O_{12}$ (X = P or As) sodalites[10] do not have any observable photoluminescence when measured on a spectrofluorometer. These preliminary results suggest that the luminescence may also be related to the highly negatively charged inorganic framework and the presence of protonated guest amine molecules.

Considering the great variety of open-framework materials,[11] it is anticipated that additional novel properties will be discovered in the future, which might make it possible to use open framework materials for applications beyond traditional catalytic or adsorptive areas. The interesting luminescent phenomenon observed in open-framework oxides suggests that the investigation of non-oxide open-frameworks such as sulfides, selenides, halides, cyanides *etc.* might be desirable in order to achieve a broader range of emission spectral characteristics.

Notes and references

† The following is a typical synthesis procedure, using UCSB-10Mg as an example. Slurry A was prepared by adding aluminium isopropoxide (1.40 g, 98%, Aldrich) and H_3PO_4 (1.43 g, 85 wt% in water) into ethylene glycol (7.52 g). The mixture was stirred for 1 week. Solution B was prepared by mixing 1.19 g magnesium hydrogenphosphate trihydrate (99%, Aldrich) with H_2O (7.16 g) and H_3PO_4 (0.84 g, 85 wt% in water) and was stirred for 1 h. To the mixture of A and B, 3.01 g of 1,13-diamino-4,7,10-trioxatridecane was slowly added with stirring. The final pH of the mixture was 8.12. The mixture was stirred for 5 h at room temperature, transferred into a 23 mL autoclave, and heated in an oven at 170 °C for 4 days. The product was filtered off, washed with distilled H_2O and ethanol, and further purified by repeated sonication of the sample in deionised water and decanting off the cloudy solution. Hexagonal-shaped clear crystals were obtained.

1 G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer-Verlag, New York, 1994.
2 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan and E. M. Flanigen, *J. Am. Chem. Soc.*, 1982, **104**, 1146.
3 P. Behrens and G. D. Stucky, in *Comprehensive Supramolecular Chemistry*, ed. G. Albert and T. Bein, Elsevier, New York, 1996, vol. 7, pp. 721–772.
4 I. Braun, G. Ihlein, F. Laeri, J. U. Nockel, G. Schulz-Ekloff, F. Schuth, U. Vietze, O. Weiss and D. Wohrle, *Appl. Phys. B: Lasers Opt.*, 2000, **70**, 335.
5 X. Bu, P. Feng and G. D. Stucky, *Science*, 1997, **278**, 2080.
6 D. R. Vij, *Luminescence of Solids*, Plenum Press, New York, 1998.
7 T. E. Gier, X. Bu, P. Feng and G. D. Stucky, *Nature*, 1998, **395**, 154.
8 P. Feng, X. Bu and G. D. Stucky, *Nature*, 1997, **388**, 735.
9 X. Bu, P. Feng, T. E. Gier, D. Zhao and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120**, 13 389.
10 X. Bu, T. E. Gier, P. Feng and G. D. Stucky, *Microporous Mesoporous Mater.*, 1998, **20**, 371.
11 A. K. Cheetham, G. Ferey and T. Loiseau, *Angew. Chem., Int. Ed.*, 1999, **38**, 3268.