White Phosphors from a Silicate-Carboxylate Sol-Gel Precursor That Lack Metal Activator Ions

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Highly emissive (with an external quantum yield exceeding 35 percent at a 365-nanometer excitation wavelength) broadband phosphors can be synthesized from a tetraalkoxysilane sol-gel precursor and a variety of organic carboxylic acids. The air-stable phosphors were synthesized at low temperatures (less than 300°C) and displayed broad visible photoluminescence spectra that appeared white to the eye. Water-soluble phosphors can be prepared by the substitution of 3-aminopropyltriethoxysilane for tetraalkoxysilane in the synthesis. These materials are the most efficient extrinsic phosphors that do not contain activator metal ions.

Stable, highly emissive, white phosphors are important for display and lighting technologies. The majority of commercially available lamp phosphors require excitation by short ultraviolet (UV) light for operation, a requirement that has led to the almost universal use of a mercury vapor plasma in fluorescent lighting products (*1*). The development of new materials that convert long-wavelength UV light (340 to 400 nm) into visible light could help replace the mercury currently used in fluorescent lights with a less toxic alternative and lead to higher net conversion efficiencies (*2*). In addition, the emissive centers used in fluorescent lamp or cathodoluminescent display phosphors are typically expensive or environmentally toxic metals such as silver, cadmium, germanium, or rare earth elements (*1, 3*). In this report, we present a new class of stable, efficient, and environmentally "friendly" photoluminescent silicate materials prepared from an alkoxysilane and a carboxylic acid through a sol-gel route.

The sol-gel technique has been used to prepare silicate glasses with a wide range of unusual properties (*4–13*). The sol-gel synthesis of silica proceeds by aqueous hydrolysis of a tetraalkoxysilane (*14*). When the alcohol and water by-products are removed, a rigid porous silicate network remains. If special care is taken to prevent cracking during the drying and densification stages, high-quality optical components can be produced. Chemical species can be added before gelation to impart distinctive characteristics to the resultant gels or glasses. For example, the addition of laser dyes provides luminescent materials that have been used as laser cavities (*13, 15*), the use of an asymmetric silicate precursor can generate nonlinear optical materials (*15, 16*), and the incorporation of enzymes or molecular catalysts has been shown to yield catalytically active silicates (*17*).

The reaction of tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) with a variety of organic carboxylic acids (Table 1) at room temperature produced a gel at times ranging from a few minutes to a few days (*18*). Thermal treatment (in air) between 200° and 500°C produced a white or yellowish solid material that underwent photoluminescence (PL). Ultraviolet excitation (with a filtered 365-nm mercury arc lamp) of the sample derived from the reaction of formic acid with TMOS resulted in intense white PL with an emission maximum between 450 and 600 nm, depending on the preparation conditions (Fig. 1). The absorption edge of the material was shifted to the red relative to that of pure SiO_2 (Fig. 2). The external PL quantum yield of this material (measured with 365-nm excitation) ranged from 0.20 to 0.45 (*19*). The PL lifetime (337-nm pulsed N_2 laser excitation) was <10 ns (our instrumental resolution) for all of the materials studied. Elemental analysis of the formic acid and TMOS sol-gels that were heated to 275°, 450°, and 800°C yielded carbon contents of 0.31, 0.13, and 0.07% by weight, respectively.

When heated above 650°C, the transparent glassy formic acid–TMOS material turned an opaque brown-black color. Raman spectra of this black glass displayed broad peaks at 1340 and 1590 cm^{-1}, which suggested the formation of a graphitic carbon phase in the sol-gel (*20, 21*). The physical appearance and Raman spectra were similar to those reported for silicon oxycarbide, which can form during the pyrolysis of carbon-containing siloxane polymers (*22, 23*). The black glass still displayed the short-lived (<10 ns) PL and also a bright phosphorescence (PP) tail with a

Table 1. Carboxylic acids used to make PL silicates. Most acids were used as neat liquids; solid acids were dissolved in a minimum of anhydrous methanol. Reactions were carried out under a N_2 atmosphere by means of an excess acid; heat treatments were performed in air. Spectra were measured with 365-nm excitation; vs, very strong; s, strong; m, medium; w, weak.

Organic acid	Silicate source	Conditions	Luminescence intensity
Formic	TMOS and TEOS	1°C min^{-1} to 250°C, 3 hours	PL vs, no PP, clear yellow glass
		1°C min^{-1} to 425°C, 4 hours	PL vs, PP m, clear amber glass
		2°C min^{-1} to 800°C, 1 hour	PL s, PP s, opaque black glass
	$SiCl_4$	110°C, 1 hour	PL s, no PP, white powder
	APTES	70°C, 1 day	PL vs, pale yellow glass
Lactic	TMOS	450°C, 3 hours	PL m, clear colorless glass
	APTES	70°C, 2 days	PL vs, clear orange glass
Acetic	TMOS	1°C min^{-1} to 425°C, 4 hours	PL w, PP s, clear colorless glass
	APTES	70°C, 2 days	PL s, deep orange glass
Trifluoroacetic	TMOS	1°C min^{-1} to 425° C, 4 hours	PL m, PP w, tan opaque solid
	APTES	70°C, 2 days	PL m, deep red glass
Cyclopropanoic	TMOS	1°C min^{-1} to 225°C, 5 hours	PL m, no PP, brown solid
	$SiCl_4$	25°C, 1 day	PL s, no PP, white powder
Malonic	TMOS	5°C min^{-1} to 225°C, 4 hours	PL w, no PP, white powder
Citric	TMOS	2°C min^{-1} to 425°C, 4 hours	PL vs, PP w, yellow glass
Tartaric	TMOS	2°C min^{-1} to 325°C, 2 hours	PL s, no PP, yellow glass
Glyoxylic	TMOS	2°C min^{-1} to 425°C, 4 hours	PL s, no PP, opaque orange solid
Oxalic	TMOS	2°C min^{-1} to 425°C, 4 hours	PL s, no PP, white powder

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lifetime of several seconds at room temperature. The PL and PP spectra (Fig. 3) were highly structured, and the spacing between the most prominent features was about 1330 cm^{-1}. The separation between the peaks decreased when ^{13}C-labeled formic acid was used in the synthesis, which indicates that the luminescence mechanism involves vibronic coupling to one or more carbon atoms derived from formic acid. A similar experiment with deuterated formic acid did not result in a detectable spectral shift.

The reaction between 3-aminopropyltriethoxysilane (APTES) and carboxylic acids yielded a clear water-soluble material that can be drawn into fibers from a melt or cast into thick films or monolithic structures without shrinking or cracking. The optical absorption and PL properties of the APTES-derived glasses (Figs. 1 and 2) were similar to those of the TMOS- and TEOS-derived glasses; the steady-state emission spectra were broad, and they peaked between 390 and 450 nm. The emission lifetimes were <10 ns. Unlike the TMOS and TEOS materials, the APTES material decomposed when it was heated above 200°C.

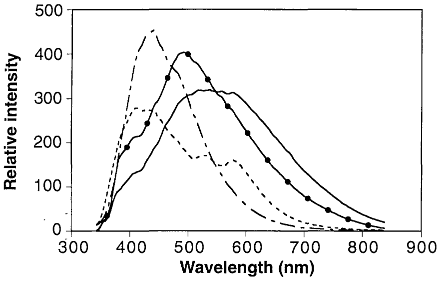


Fig. 1. PL spectra (337-nm excitation at 298 K) of representative carboxysilicate phosphors prepared from formic acid and TMOS (solid curve), citric acid and TMOS (dotted curve), formic acid and APTES (dashed-dotted curve), and lactic acid and APTES (solid curve with circles). All spectra are corrected for the spectral response of the monochromator (Acton Research Corp. Model 150) and the detector (Princeton Instruments, Model CCD-1152 EUV, liquid N_2 cooled charge-coupled device, UV-enhanced). Spectra were obtained on different days, so the relative intensities are not directly comparable.

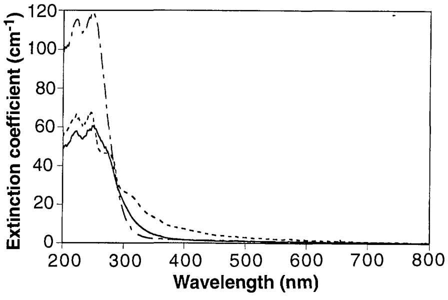


Fig. 2. Absorption spectra of thin films of silicate materials synthesized from formic acid and TMOS (annealed at 300°C for 2 hours) (solid curve) and lactic acid and APTES (cast from an aqueous solution and dried at 100°C for 2 days) (dotted curve). An absorption spectrum of optical-quality SiO_2 glass (Fisher Scientific) is included for comparison (dashed-dotted curve).

The Fourier transform infrared (FTIR) spectra of the TEOS- or TMOS-derived phosphors (Fig. 4, bottom curve) are similar to the spectrum of pure amorphous SiO_2; strong bands associated with Si–O stretching and bending vibrations are apparent at 1090, 800, and 470 cm^{-1}. However, additional weak absorptions in the 3000- to 2700-cm^{-1} and the 1700- to 1400-cm^{-1} regions indicate the presence of hydrocarbon and carbonyl impurities. A sharp band at 2341 cm^{-1} is assigned to the asymmetric stretching vibration of CO_2. This peak is seen in almost all TEOS–carboxylic acid or TMOS–carboxylic acid sol-gels that have been heated over 400°C and probably arises from thermal decomposition of the carboxylic acid and any residual alkoxy groups. The lack of rotational fine structure in the 2341-cm^{-1} band indicates that the CO_2 molecule is immobilized in the silicate lattice.

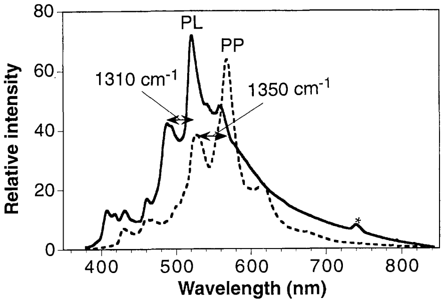


Fig. 3. PL (solid curve) and PP (×10) (dashed curve) spectra (337-nm excitation at 298 K) of a carboxysilicate prepared from formic acid and TMOS. The sample was slowly heated (1°C min^{-1}) to 800°C, where it was held for 2 hours. The prominent peak spacings correspond to a vibrational stretching frequency at ground state of ≈1330 cm^{-1}. Both spectra are corrected for the spectral response of the monochromator and the detector system. The PP spectrum was obtained 10 ms after excitation with a pulsed (2 ns, 337-nm N_2) laser. The feature marked with an asterisk is a grating artifact.

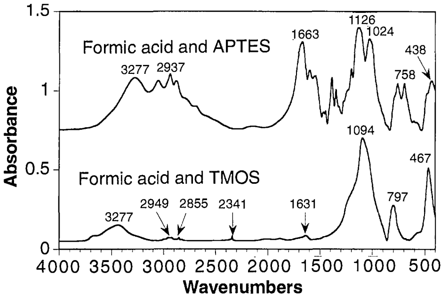


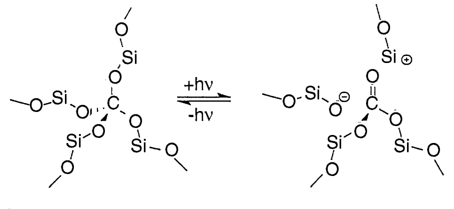
Fig. 4. Transmission FTIR spectra (KBr disk) of silicate materials synthesized from APTES and formic acid (top curve) TMOS and formic acid (bottom curve). The top curve has been offset by 0.75 absorbance units for clarity.

Despite the small amount of carbon (<0.5%) present in these glasses, the observed luminescence is almost certainly related to its incorporation into the glass. The retention of organics (typically unhydrolyzed alkoxy groups) in sol-gel–derived glasses can lead to discoloration and poor light transmission and is generally considered to be a disadvantage of this route over other methods for producing optical-quality SiO_2 (*24*). In the present work, however, it is thought that the trapped carboxylic acid leads to luminescent defect centers that are responsible for the bright PL. Weak PL from carbon-doped silicon and carbonized silica gels has been reported previously (*25–30*), but the source of the emission has not been positively identified. Plasma-deposited amorphous carbon and diamond-like carbon films can also produce materials that exhibit room-temperature PL (*31–33*).

In general, the materials synthesized from TMOS or TEOS form hard, brittle glasses or powders. For example, with formic acid and TMOS, the reaction produces silica according to Eq. 1 (*34*)

$$2HC(O)OH + (CH_3O)_4Si \rightarrow SiO_2 + 2CH_3OH + 2HC(O)OCH_3 \quad (1)$$

Equation 1 is anhydrous and hence it eliminates methyl formate rather than water to form the Si–O–Si bonds. However, under anhydrous conditions, a substantial amount of formic acid may be retained in the gel as a silyl formate species. When heated, this formate may decompose to create a C substitutional defect for Si, which is assumed to be the luminescent species in the lattice (Scheme 1).



Scheme 1

A similar carbon species has been assumed to be responsible for the blue emission of oxidized porous silicon (*35*), aluminum oxides (*36*), and oxidized silicon carbides (*37*).

The PL material in the water-soluble luminescent material generated from APTES is probably different from the luminescent species in the TEOS- and TMOS-based silicates. The APTES-derived materials do not require heating over 100°C to be luminescent, and the FTIR spectra display strong absorption bands characteristic of amide (1663 cm^{-1}), ammonium (3277 cm^{-1} and 2500 to 2000 cm^{-1}), and aliphatic (2950 to 2850 cm^{-1}) functionalities (Fig. 4, top curve). The Si–O asymmetric stretching bands (1126 and 1024 cm^{-1}) are characteristic of long-chain linear siloxanes (*38*). The PL quantum yield of the APTES–formic acid material (measured with 365-nm excitation) is 0.15 ± 0.03 in a dilute aqueous solution (*39*) and 0.35 ± 0.1 in the solid state.

The reaction of alkoxysilanes with organic acids is not new and has been used to prepare both $\mathrm{SiO_2}$ glasses and molecular silicate complexes (*40, 41*). There are also reports of PL materials generated from the reaction of alkoxysilanes with photoluminescent organic acids (*42, 43*). Even more widely studied are the sol-gel reactions of organofunctional alkoxysilanes that give molecular solids with properties intermediate between organic polymers and inorganic ceramics (*44–47*). It is therefore surprising that the efficient PL of silicate sol-gels made from carboxylic acids has not previously been reported.

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The Late Neogene $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ Record of Lowland Himalayan Rivers

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Fossil shells and paleosol carbonate from ancestral Himalayan river deposits provide a $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ record of lowland Himalayan river water during the late Neogene. Reconstructed $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ river values increased sharply in the late Miocene, probably marking the beginning of exhumation of high-$^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ metalimestones, more in the central than in the western Himalayas. These results imply that the marine $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ record may not be a proxy for silicate weathering or consumption of atmospheric $\mathrm{CO_2}$ resulting from that weathering.

Large volumes of sediment were eroded and weathered as the Himalayas were uplifted starting ~60 to 50 million years ago (Ma). Weathering of these sediments—and specifically of silicate minerals—would have consumed significant quantities of atmospheric $\mathrm{CO_2}$ (*1*), perhaps sufficient to cool global climate. Several records, including the $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio of the ocean, have been used as proxies for the extent of silicate weathering during this and other major uplift events. Starting ~40 Ma, there is a marked increase in the slope of the marine $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ curve, which is thought to reflect the onset of significant weathering of high-$^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ minerals in the Himalayas (*2, 3*). Himalayan rivers, mainly the Ganges and Brahmaputra systems, are able to increase the marine $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio because of their high $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ (>0.720) ratios and high Sr concentrations, which is the reverse of the usual relation in rivers (*3*). Edmond (*3*) suggested that this reversal is caused by Himalayan metamorphism, which redistributed Sr with a high $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio from Rb-rich silicate phases to more weatherable silicates such as Ca-feldspar. Others have argued that the weathering of carbonate rocks accounted for the major ion chemistry of many large Himalayan rivers (*4*) and that the source of high $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratios may be metamorphically altered carbonate minerals (*5*).

Siwalik Group paleosols and fossils provide an archive for studying the impact of weathering reactions on lowland river composition during the late Neogene. The Si-

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