Luminescent Properties of Sodium Salicylate Films Prepared by the Sol−Gel Method

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The preparation of sodium salicylate doped sol−gel films and their application as phosphor screens have been studied. The sol−gel process opens the possibility of homogeneously tailoring the overall thickness and chemical composition of such films. The adhesion of the sol−gel processed film to the substrate is noteworthy and, together with the rad-hard characteristics of the silica matrix, contributes to the durability of these films. With regard to the characteristics of the sodium salicylate doped sol−gel films as phosphor screens, the measured relative fluorescence efficiency is found to be among the highest ever reported without adverse affects on the fast response time (∼4 ns).

Of all known organic phosphors/luminophors, sodium salicylate (ss) has been the one most widely used as a fluorescent wavelength converter for vacuum ultraviolet (VUV) radiation from 30 to 350 nm.[1] Possible reasons to warrant its widespread use include its high relative fluorescent efficiency, which is almost constant over a wide incident radiation range, the good matching between its fluorescence spectrum and the spectral response (S − 11) of standard photomultipliers, and its other well-known and extensively studied properties (quantum efficiency, angular response, radiation hardness, etc.).[2−5] In addition, when compared with other organic phosphors such as diphenyl stilbene, tetraphenyl butadine, or *p*-terphenyl, ss shows higher stability in a vacuum.[2] On the other hand, in a study of standard phosphors (e.g., Y_2SiO_5:Ce, Y_2O_3:Eu, Y_2O_2S:Tb, $Y_3Al_5O_{12}$:Ce), only Y_2O_2S:Tb (=15 times higher) exhibited better response than ss in terms of luminescence efficiency. However, the luminescence lifetime of Y_2O_2S:Tb is long (∼1 ms), which presents a major drawback for applications where time resolution is critical.[4,5]

The classic preparation methods to obtain thin films from ss powder (paintbrush or spray, among others) result in a serious lack of thickness homogeneity as a consequence of the resultant surface roughness. Also, the adherence to a substrate and, as a consequence, the film durability are significantly poorer.[6−8] In an attempt to improve the behavior just mentioned, encapsulation of ss within a polymer matrix was explored as a new approach for depositing ss on a substrate.[9] Unfortunately, the response exhibited by the polymer−ss was substantially lower than that of the classically deposited ss powders over the entire UV spectral range. Furthermore, the principal disadvantage of polymer-encapsulated organic luminophors has been their vulnerability to damage by radiation.[9,10]

At this time, an encapsulation matrix that maintains the good efficiency behavior of ss as a VUV converter is still required in order to optimize the development of broad band single and array detectors for this wavelength range. Therefore, the most promising approach might be that of a fast, rad-hard hybrid system resulting from a combination based on the high radiation resistance characteristics of inorganic phosphors and the short fluorescence lifetime characteristics of organic ones. One such approach is the sol−gel process which provides a means of preparing inorganic oxide matrixes into which organic dyes capable of acting as luminescent materials can be incorporated.[10,11] The ability to incorporate organic additives within silica matrixes is one of the most important properties of the sol−gel process and is due to the fact than the process start at the solution stage and take place at room temperature.[12,13] In addition, silica can be considered as a rad-hard material,[10,11] thereby making it a very suitable matrix for hosting a scintillating organic dye. Of course, this package does not necessarily avoid the bulk radiation damage in ss in the soft-X-ray range.[5]

In this work, we propose the encapsulation of ss within a porous silica matrix by means of the sol−gel process. The sol−gel processing of ss-doped silica glasses provides a route for preparing thin films with tailored thickness, good transmission properties,[14] and excellent adherence

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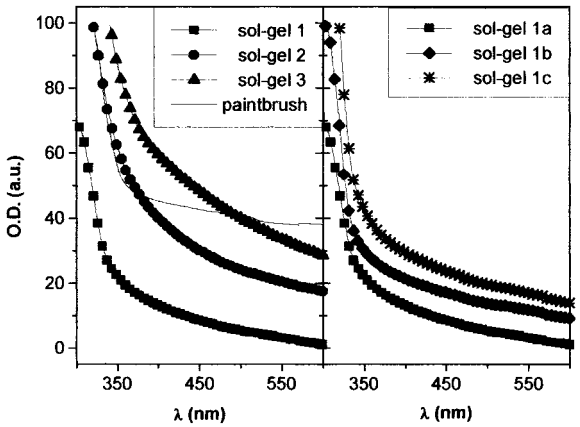

Figure 1. Absorption spectra of different sol−gel samples. Left: sol−gel 1, sol−gel 2, and sol−gel 3 with thickness of 17 μm and ss starting amounts of 0.2, 0.3, and 0.6 g, respectively. The absorption spectrum of a paintbrush sample ($\approx$1.2 mg/cm^2 and $\approx$8 μm) is also included for comparison. Right: sol−gel 1a, sol−gel 1b, and sol−gel 1c with ss starting concentrations of 0.2 g and thickness of 17, 29, and 44 μm, respectively.

to a substrate (lens, filter, etc.),[15] thereby further improving the characteristic durability of ss.

Sol−gel processed films were prepared by spin coating a solution of ss in methanol and glicidoxypropyltrimethoxysilane (GPTMS), the sol−gel precursor. Three starting ss concentrations were used: 0.2, 0.3, and 0.6 g. The GPTMS/ss solution was hydrolyzed with acid water (pH = 1, the water to monomer molar ratio was 2) while stirring vigorously. The resulting solution was then stirred overnight in order to attain the optimum viscosity for spin deposition. The solution was filtered (0.2 μm) prior to deposition. Films with thickness in range 15−45 μm were prepared on substrates by repeated layer depositions (up to three). Thicker films (up to 230 μm) were obtained by simple casting. Immediately after deposition, the films were heated at 50 °C in an oven for 6 h in order to promote the prompt gelation and drying of the host matrix. Films were prepared in parallel on glass substrates using paintbrush deposition of saturated ss in acetone/methanol (1/1 in volume) in order to compare both methods.[6] The thickness of the sol−gel samples was obtained from a Digimatic Outside Micrometer (Mitutoyo) by averaging 10 measurements for each sample.

A first glance at the absorption spectra of the different films revealed that the absorption band of ss is mostly overlapped by the characteristic cutoff of silica-based matrixes (Figure 1). Nevertheless, a significantly higher visible spectrum transmittance through the ss spin coated films is observed as compared to that through the paintbrush film (Figure 1). This was also true even when the thickness of the spin coated films was more than twice that of the paintbrush film (17 μm versus 8 μm, respectively). It is well-known that in the visible region transmission is limited mainly by interference phenomena and by light scattering due to dispersion centers.[16] The prompt gelation and drying of the sol−gel matrix control the growth of ss crystallites (Figure 2b) and keep their size well below that achieved with the paintbrush method, thereby improving the transparency (Figure 2a). In particular, the decrease in crystallite size attenuates both

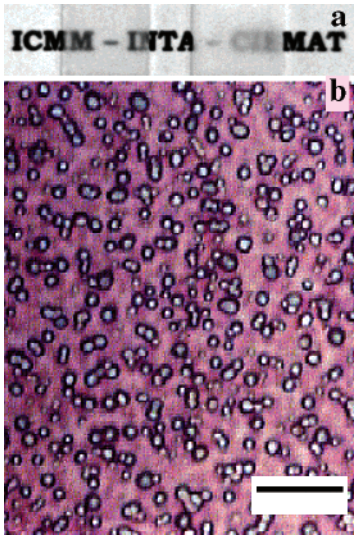

Figure 2. Picture of ss-doped sol−gel films with ss starting concentration of 0.6 g and with thickness of 44 μm (left) and 100 μm (right) (a) and optical microscopy image of ss crystallites of $\approx$2 μm diameter dispersed within the silica matrix (b). Bar is $\approx$10 μm.

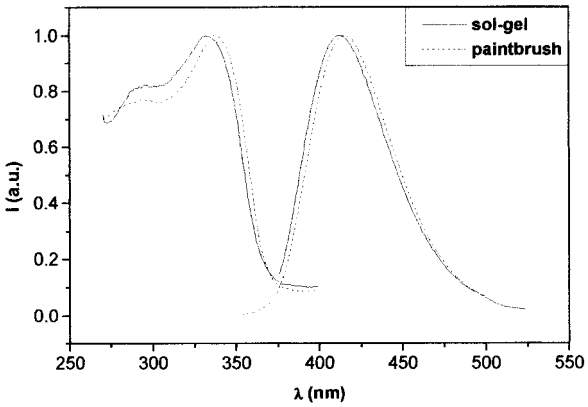

Figure 3. Fluorescence excitation (left) and emission (right) spectra of a paintbrush sample ($\approx$1.2 mg/cm^2, dotted line) and a sol−gel sample (17 μm, solid line).

the interference phenomena and the light-scattering processes. Also, the good dispersion of the ss crystals within the silica matrix shown in the picture (Figure 2b) should be noted. Nevertheless, the concentration of dispersing centers (i.e., ss crystallites) must also be taken into account when comparing the transmission spectra of the different samples. Typically, the thickness of paintbrush films is expressed in terms of milligrams of ss per centimeters square,[6] while the concentration of ss-doped sol−gel films is expressed in terms of film thickness. This is possible as the ss concentration is fixed by the highest ss solubility in the starting solution of the sol−gel process; i.e., 0.6 g of ss.

Notwithstanding the excellent properties outlined above, the goodness of a ss-doped sol−gel film must be judged by its capabilities as a phosphor, which are basically related to its fluorescence emission and expressed in terms of emission wavelength(s), time decay, and efficiency. Figure 3 shows the emission and excitation fluorescent spectra of the ss-doped sol−gel film, which is slightly blue shifted (~5 nm) compared to paintbrush deposited ss. Note, these measurements were made in reflection mode. Shifts in fluorescent spectra are typically ascribed to interactions that the organic molecule establishes with its surrounding environment, i.e., the porosity of the silica matrix.[17] In

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Table 1. Quantum Efficiency of ss Doped Sol−Gel Films

thickness (μm)[a]	17	71	229
quantum efficiency[b]	0.42	3.35	1.27

[a] Experimental error is within ±5 μm [b] Data are normalized to the maximum value reported for paintbrush samples.[3,4]

addition, the large Stokes shift (~78 nm) exhibited by both samples is noteworthy, this being most likely due to an intermolecular proton-transfer process characteristic of salicylate molecules.[18] Finally, the fluorescence lifetime (measured as described elsewhere[17]) of the ss-doped sol−gel films was ~4 ns. This value was independent of both concentration and film thickness and is a factor 2 (in the order of the lifetime) shorter than that reported for ss films deposited by classical methods.[4]

At this stage, the evaluation of the ss-doped sol−gel films as useful phosphors only requires a measurement of their fluorescence efficiency. Table 1 shows the relative fluorescence efficiency of several ss-doped sol−gel films. The outstanding result obtained is the times 3 higher maximum efficiency exhibited by our ss-doped sol−gel films as compared to the highest values obtained for ss paintbrush films (~1−2 mg/cm^2).[3,4] This places the ss-doped sol−gel films among the most efficient organic or inorganic phosphors ever reported (higher efficiencies have only been reported for Y_2O_2S:Tb, which also shows a very slow response time).[3,4,10]

In summary, and from the above results, the sol−gel process appears to be a most promising approach for deposition of ss-based phosphors encapsulated within an inorganic matrix, and it opens a pathway for the renewal of the technologies used to date for deposition of organic phosphors.

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