

A promising way to obtain large, luminescent and transparent thick films suitable for optical devices

Jérôme Deschamps,^{*ab} Audrey Potdevin,^{bc} Nathalie Caperaa,^{ab}
Geneviève Chadeyron,^{bc} Sandrine Therias^{bd} and Rachid Mahiou^{ab}

Received (in Montpellier, France) 13th November 2009, Accepted 19th November 2009

First published as an Advance Article on the web 22nd January 2010

DOI: 10.1039/b9nj00667b

This work focuses on the formation of large, luminescent and transparent thick films of polyvinylpyrrolidone (PVP) embedding phosphors. Characterization of these films was made using UV-Visible absorption spectroscopy and cw-selective excitation induced photoluminescence. Results presented here demonstrate the preparation polymer films incorporating luminescent materials in order to obtain large, transparent and thick surfaces of well-dispersed phosphors suitable for use in optical devices. This technique allows the preparation of self-standing, flexible and handy films that could be easily cut or shaped and then used for various purposes.

In the last few years, phosphor films have attracted much attention due to their potential applications in a large variety of optical devices; for instance, they are of great interest as radiation to visible light converters in medical imaging or as phosphors for white light generation in Hg-free lamps.^{1–3} Compared with luminescent powders used in conventional displays, phosphor films are known to exhibit superior thermal conductivity, higher degree of uniformity and better adhesion.³ Various methods can be used to fabricate thin films: chemical vapour deposition, ion beam sputtering, liquid phase epitaxy, sol–gel.⁴ Compared to other techniques, sol–gel allows the preparation of transparent thin films on simple and complex-shaped substrates from cheap precursors such as chlorides.⁵ However, due to the difficulty of obtaining thick coatings of good optical quality from metal alkoxides,^{5,6} such films cannot presently compete favourably with powder-based devices.

Generally, a film thickness greater than 100 nm by layer is achieved *via* several deposition cycles or by using viscous sols that can entail delamination or cracking. For example, the work of Menaa *et al.* shows films up to 150 μm in thickness, coated onto substrates *via* a multi-step spin-coating process. The cracking of their films is principally controlled by the spinning process and the sol viscosity.⁷

Recently, it has been reported that the use of chemical additives such as chelating agents or polymers, in particular polyvinylpyrrolidone (PVP) mixed with metal alkoxide precursor sol represents an effective way to produce thick crack-free films *via* non-repetitive deposition.^{6,8,9} They act as capping elements for the OH-groups of alkoxides, slowing or preventing the condensation step involved in the sol–gel mechanism. This feature leads to a significant reduction in the stress supported by the films during their densification.^{6,9,10}

Here we report the achievement of large, thick and transparent luminescent film from Tb^{3+} doped aluminate alkoxide sol and PVP. The sol employed is known to have interesting optical properties¹¹ and to be suitable for the elaboration of transparent luminescent films with waveguiding properties.¹² The polymer chosen was PVP because of several characteristics; among them, it is soluble in alcoholic solutions, it does not absorb in the visible range¹³ and can even enhance luminescence efficiency^{14,15} *via* an effective energy-transfer between PVP and luminescent centers.¹⁵ Moreover, the photochemical behaviour of PVP in the form of films has been characterized and can be considered as well-known.¹⁶

Contrary to previous studies on luminescent thick layers containing PVP,^{6,8,13} the films studied here were not elaborated on substrates. Indeed, thanks to an original and scarcely used deposition method,¹⁷ they were remarkably flexible, handy, robust and more importantly, free-standing. That is, to the best of our knowledge, the first time that free-standing, luminescent thick (19 μm) films are obtained in a single step procedure. Consequently, they seem combinable to a large variety of complex-shapes substrates as they can be manipulated, rolled and even cut very easily. They thus represent good candidates for many devices. Film quality has been assessed by UV-visible spectroscopy, whereas Tb^{3+} luminescence has been investigated upon UV-radiation. Results have been compared with a similar PVP film without embedded alkoxide.

PVP films, one incorporating mixed heterometallic alkoxides, *film A*, and one free of heterometallic alkoxides, *film B*, were prepared as described hereafter. After drying, *film A*, dimensions of 10 cm wide by 20 cm long, incorporating a proportion of 7% in mass of heterometallic alkoxides compared to PVP, was easily peeled off from the Teflon surface (see Experimental section). It was entirely crack-free. Its thickness was found to be 19 μm (± 2 μm) and its homogeneity in thickness was demonstrated by measuring

^a CNRS, UMR 6002, Laboratoire des Matériaux Inorganiques, F-63173, Aubière, France.

E-mail: Jerome.Deschamps@univ-bpclermont.fr;
Fax: +33 4 73 40 71 08; Tel: +33 4 73 40 75 99

^b Clermont Université, Université Blaise Pascal, BP 10448, F-63000, Clermont-Ferrand, France

^c Clermont Université, Ecole Nationale Supérieure Chimie de Clermont-Ferrand, Laboratoire des Matériaux Inorganiques, BP 10448, F-63000, Clermont-Ferrand, France

^d CNRS, UMR 6505, Laboratoire de Photochimie Moléculaire et Macromoléculaire, F-63173, Aubière, France

the thickness on different points of the film. Similarly, the thickness of *film B* was found to be $23\ \mu\text{m} \pm 2\ \mu\text{m}$. Thickness of those films is directly linked to the viscosity of the casted solutions, and therefore, depends on the PVP concentration. In the conditions we chose (see Experimental section) the thickness of *film B* is the upper limit of thickness that can be achieved as it is the more viscous (it contains only PVP). Then, it was expected that *film A* would be slightly thinner than *film B* as the corresponding sol is less viscous (addition of solution of heterometallic alkoxides to PVP solution). This means that the thickness of the film can be modulated by the viscosity, as has already been proved for other deposition techniques. In some other works, and in order to get better optical properties, only 50% of PVP is added to the sol-gel solution, resulting in cracked films. In our case, we used more than 90% of PVP to form crack-free films. On another hand, a compromise has to be found between the resistance of the film and its optical properties. Therefore, the determination of the optimal proportion between PVP/heterometallic alkoxides is currently under investigation. Transparency of the *film A* was evidenced by two means. First, it is visually colorless and transparent, as can be seen in Fig. 1. This is due to the well-known transparency properties of PVP¹⁸ and to the fact that heterometallic alkoxide particles are quite small (40 nm average), as has been previously reported for that type of intermediate sol-gel process.¹¹ It can be noticed that, in the picture, a frame was added to the film borders in order to distinguish them better. The second evidence of the transparency of *films A* and *B* is given by their UV-visible absorption spectra (Fig. 2), that show no absorption in the visible region. To be more specific, no absorption was observed from 800 to 350 nm for neither *film A*, nor *film B*. The absorbance centered at 303 nm in *film A* is due to the presence of terbium-oxygen bonding. This absorption is similar with absorption observed in the $\text{Tb}(\text{acac})_3$ cluster.¹⁹ The absorption before 250 nm, observed in *films A* and *B*, comes from the PVP.

A very interesting point of this single step procedure is that, in a reproducible way, large and homogeneous surfaces of well-dispersed functional charges can be obtained very easily and rapidly. In our case, we introduced rare-earth doped heterometallic alkoxides as charge in the PVP film, resulting in transparent luminescent thick film, emitting under irradiations ranging from VUV to blue. In Fig. 3, the Tb^{3+} characteristic green emission induced by UV excitation can be seen.

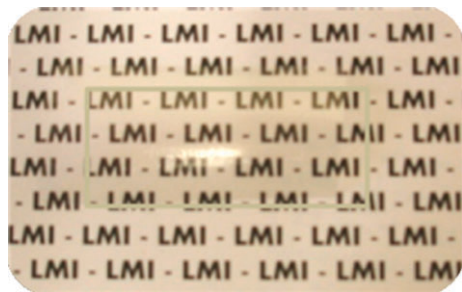


Fig. 1 Photograph showing large and transparent thick PVP film containing heterometallic alkoxides, 19 μm in thickness, prepared by Dr Blade technique.

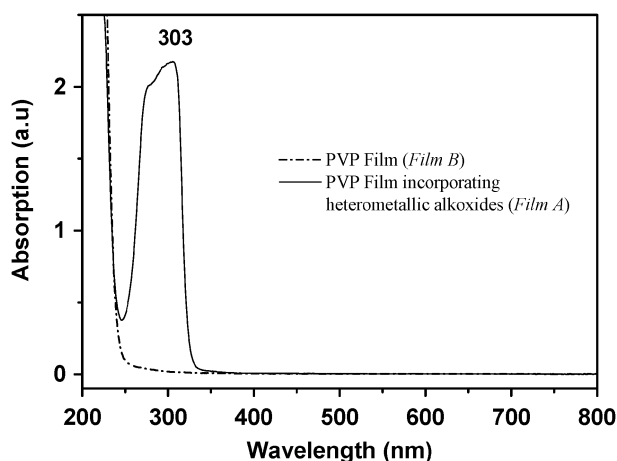


Fig. 2 UV-Visible absorption spectra of *film B* (dash-dot line) and *film A* (solid line).

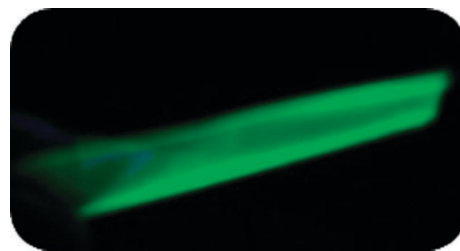


Fig. 3 Photograph showing green luminescence of *film A*, under UV excitation.

Emission spectrum of *film A* under 304 nm excitation is given in Fig. 4. The excitation spectrum of the film, monitoring the $\text{Tb}^{3+} {}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ transition at 544 nm, is given in the inset. One can observe two main absorption signals located at 304 and 476 nm. The first one is associated to inter-shell $4f^8-4f^75d$ transitions of Tb^{3+} whereas the second is due to intra-shell $4f-4f {}^7\text{F}_6 \rightarrow {}^5\text{D}_4$ transitions.²⁰

In the emission spectrum, the luminescence peaks centered at 486, 542, 580 and 617 nm are respectively assigned

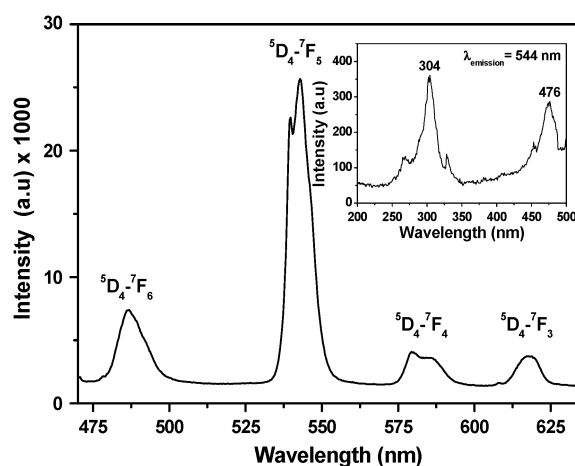


Fig. 4 Luminescent spectrum of *film A* under 304 nm wavelength excitation. The inset shows the excitation spectrum of the film for a wavelength emission monitored at 544 nm.

to $^5D_4 \rightarrow ^7F_J$ ($J = 6, 5, 4, 3$) transitions of Tb^{3+} ,²⁰ with the strongest emission located at 542 nm (green region). It is noteworthy to specify that emission bands are broad since Tb^{3+} ions are embedded in an amorphous matrix.²¹

In summary, we propose a very simple, single-step and general procedure to obtain thick, large and transparent luminescent film. In addition to their transparency and well-dispersed 7% in mass phosphor charges, these films are crack-free, self-standing and exhibit a very good flexibility. These features allow their use in various optical devices as, for instance, sticking them on complex and large substrates. We guess that this method will soon have a significant impact in elaborating large functional surfaces for device-oriented applications.

Experimental

Materials

Yttrium chloride, terbium chloride, aluminium isopropoxide and dry isopropanol were obtained from Aldrich (Milwaukee, WI, USA). Polyvinylpyrrolidone (average molar weight 360 000 g mol⁻¹) was obtained from Scientific Polymer Products Inc. (New York, USA).

Solutions preparation

Solution of heterometallic alkoxides was prepared from aluminium isopropoxide mixed with yttrium and terbium chlorides in dry isopropanol according to a sol-gel procedure already detailed.¹¹

Transparent PVP solution in dry isopropanol (84 g L⁻¹) was obtained after few minutes warming. Prior use, the solution is degassed for 20 min using ultra-sonic bath.

A final solution, which consisted of the mixing of the two previous ones (1:2, respectively), was prepared within the minute before casting the film.

Film preparation

PVP films, one incorporating mixed heterometallic alkoxides, *film A*, and one free of heterometallic alkoxides, *film B*, were formed by casting, respectively the final solution and the PVP solution, on a Teflon surface, by means of a coat-master 509MC-Erichsen (Dr Blade). The Dr Blade knife height was 400 µm and casting speed was 20 mm s⁻¹. After having been casted, films *A* and *B* were allowed to dry on the Dr Blade plate for 10 min at 40 °C, then at room temperature for 2 h. Thickness of films was measured using a CADAR-MI20 micrometer.

UV-Visible absorption

UV-Visible spectra were recorded on a Shimadzu UV-2101 PC spectrometer equipped with an integrating sphere.

Luminescence

Luminescence experiments were performed on a Jobin-Yvon set-up consisting of a Xe lamp operating at 400 W and two monochromators (Triax 550 and Triax 180) combined with a cryogenically cold charge coupled device (CCD) camera (Jobin-Yvon Symphony LN₂ series) for emission spectra and with a Hamamatsu 980 photomultiplier for excitation ones. All luminescence properties have been studied at room temperature. Emission and excitation spectra have been corrected for instrument response and Xe lamp intensity.

References

- 1 J. R. Lo, T. Y. Tseng, J. H. Tyan and C. M. Huang, *Proceedings of the 9th International Vacuum Microelectronics Conference*, St. Petersburg, Russia, 1996.
- 2 P. Y. Jia, J. Lin, X. M. Han and M. Yu, *Thin Solid Films*, 2005, **483**, 122–129.
- 3 D. Ravichandran, R. Roy, A. G. Chakhovskoi, C. E. Hunt, W. B. White and S. Erdei, *J. Lumin.*, 1997, **71**, 291–297.
- 4 *Handbook of Thin Film Process Technology*, ed. D. A. Glocker and S. I. Shah, Institute of Physics, Bristol and Philadelphia, 1998.
- 5 *Sol-Gel Science the Physics and Chemistry of Sol-Gel Processing*, ed. C. J. Brinker and G. W. Scherer, Academic Press, San Diego, 1990.
- 6 H. Kozuka and M. Kajimura, *J. Am. Ceram. Soc.*, 2000, **83**, 1056–1062.
- 7 B. Mena, M. Takahashi, Y. Tokuda and T. Yoko, *Mater. Res. Bull.*, 2006, **41**, 1925–1934.
- 8 N. Ndiege, T. Wilhoite, V. Subramanian, M. A. Shannon and R. I. Masel, *Chem. Mater.*, 2007, **19**, 3155–3161.
- 9 H. Kozuka, *J. Sol-Gel Sci. Technol.*, 2006, **40**, 287–297.
- 10 Y. Xu, D. Wu, Y. Sun, W. Chen, H. Yuan, F. Deng and Z. Wu, *Colloids Surf., A*, 2007, **305**, 97–104.
- 11 A. Potdevin, G. Chadeyron, D. Boyer and R. Mahiou, *J. Sol-Gel Sci. Technol.*, 2006, **39**, 275–284.
- 12 A. Potdevin, S. Lechevallier, G. Chadeyron, N. Caperaa, D. Boyer and R. Mahiou, *Thin Solid Films*, 2009, **517**, 4610–4614.
- 13 X. Liu, F. Zhou, M. Gu, S. Huang, B. Liu and C. Ni, *Opt. Mater.*, 2008, **31**, 126–130.
- 14 Q. Li, T. Li and J. Wu, *J. Phys. Chem. B*, 2001, **105**, 12293–12296.
- 15 K. Manzoor, S. R. Vadera, N. Kumar and T. R. N. Kutty, *Solid State Commun.*, 2004, **129**, 469–473.
- 16 F. Hassouna, S. Therias, G. Mailhot and J. L. Gardette, *Polym. Degrad. Stab.*, 2009, **94**, 2257–2266.
- 17 M. A. Zulfikar, A. W. Mohammad, A. A. Kadhum and N. Hilal, *Mater. Sci. Eng., A*, 2007, **452–453**, 422–426.
- 18 *Handbook of Water-Soluble Gums and Resins*, ed. R. L. Davidson, Mc Graw-Hill, New-York, 1980, ch. 21.
- 19 R. Wang, D. Song and S. Wang, *Chem. Commun.*, 2002, 368–369.
- 20 Y. Zhou, J. Lin, M. Yu, S. Wang and H. Zhang, *Mater. Lett.*, 2002, **56**, 628–636.
- 21 T. Hayakawa, N. Kamata and K. Yamada, *J. Lumin.*, 1996, **68**, 179–186.