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Photoluminescence of terbium-organic complex in aerosol–gel-derived planar waveguides

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ABSTRACT This work deals with the low-temperature preparation of optically active silica-based materials. Tb^{3+}-doped silica monolithic gels were elaborated at $40\,°C$. Tb^{3+}–SSA-doped SiO_2–TiO_2 thin films were deposited by an original sol–gel approach, the aerosol–gel process, and heat-treated at $150\,°C$. Organic complexation of terbium ions was used to improve the active properties of doped silica gels and thin-film samples. Spectroscopic characterisations are reported for these samples. Photoluminescence increase by a factor two was observed for complexation by sulphosalicylic acid.

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1 Introduction

Rare-earth-doped materials have been intensively studied because of their great potential for optical amplifiers or phosphors. Doped glassy thin films with good waveguiding and active properties were fabricated by different techniques including sol–gel [1]. The overall photoluminescence (PL) efficiencies of rare-earth-doped materials are limited by their low pump absorption cross-section and the detrimental influence of the host matrix. An interesting approach to overcome these problems consists of the encapsulation of the rare-earth ion into an organic nanocage [2–6]. Significant increase of the overall PL efficiency was demonstrated by optical pumping of the strong UV-absorption band of the organic complex, followed by an energy transfer to the rare-earth ion [3]. Moreover the organic complex can also shield the active ion from the matrix. This feature becomes very important if low-temperature processing of the films is required, due to multiphonon relaxation related to the high hydroxyl content of such films.

Good active properties of rare-earth organic complexes have been reported for monolithic SiO_2 host matrices [2–6]. However, in order to use these materials in integrated optics, they have to be produced as waveguiding structures. Up to now, rare-earth organic complex doped thin films have rarely been investigated. In this paper we report on visible photoluminescence of Tb^{3+}-organic complexes inside optical planar waveguides. Our deposition process allows us to elaborate

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thin films of optical quality on thermally sensitive substrates (heat treatment below $150\,°C$).

In a first step we elaborated Tb^{3+}-doped sol–gel silica gels with and without complexation by different organic groups. We found best results by complexing Tb^{3+} with sulphosalicylic acid (SSA). This approach was extended to silica–titania thin films deposited using an original sol–gel deposition technique: the aerosol–gel process.

2 Experimental

The encapsulation of rare-earth ions was investigated by using different organic complexes. We have focused on one rare-earth, terbium, because its active properties had already been demonstrated by other groups [3–6]. Five organic complexes were investigated: benzoic acid, phthalic acid, 1,10-phenanthroline, 2,2-bipyridine and sulphosalicylic acid. The bulk-sample preparation was the same for all these organic complexes, so we describe it only for sulphosalicylic acid. The preparation was as follows: tetraethoxysilane (TEOS), absolute ethanol, deionised water, and chlorhydric acid were used as starting materials for the monolithic SiO_2 matrices. TEOS, H_2O and ethanol were mixed in a molar ratio $TEOS : H_2O : C_2H_5OH = 1 : 4 : 4$. HCl was used as a catalyst to adjust the pH value of the mixed solution to about 2.0 (solution 1). Sulphosalicylic acid (H_3SSA) was dissolved in ethanol and then added to $TbCl_3$ in a molar ratio $H_3SSA : TbCl_3 = 2 : 1$. The complexation of Tb^{3+} ions was performed under argon flux to prevent precursors from atmospheric humidity. This solution was added to solution 1 in a molar ratio $Tb : TEOS = 0.02 : 1$. The resulting solution was heated at $40\,°C$ in Petri boxes during one month until gelation of a bulk samples.

In the case of waveguiding thin films, we had to modify the matrix parameters. Co doping of the silica matrix with titania was necessary to tailor the film refractive index [1]. Moreover, the reactivity of the solutions had to be adapted to our deposition process. The aerosol–gel technique was used for the film deposition. In this technique an aerosol is produced by ultrasonic pulverisation of the sol–gel solution [7]. An ethanol-saturated air flow transports the aerosol onto the substrate surface, where it forms a liquid film. This film is dried under dry air inside the reactor. This process has been proven to be a promising tool for the fabrication of optically active waveguides [8]. It introduces some extra advan-

tages over the traditional methods of spin- and dip-coating. In particular the gaseous transport of the aerosol makes it compatible with on-line deposition technologies for low-cost mass production. In the present work, silica–titania thin films were processed by using solution 1 for silica and tetraiso-propyl orthotitanate (TPT) as precursor for titanium oxide. Diethanolamine (DEA) was used to stabilise titanium in a molar ratio Ti : DEA = 1 : 2 [9]. The molar ratio of the matrix was $SiO_2 : TiO_2 = 80 : 20$ and the corresponding SiO_2 concentration was 0.337 mol/l. The molar ratio Tb : SSA was 1 : 1 and the Tb/(Si + Ti) molar ratio was 2%. This solution was deposited at room temperature onto silicon wafers, on which an 8 μm thick silica buffer layer was previously deposited. The average thickness of a single layer was around 150 nm. In order to obtain the total thickness required for optical waveguiding, we had to deposit at least four single layers. After each single-layer deposition the resulting film was heated at 150 °C for 15 minutes. This moderately high-temperature treatment, compared to silica-gel heat treatment, was chosen in order to get a faster densification of the layer. A final heat treatment at 150 °C for two hours was performed after deposition of the last single layer.

UV–visible absorption spectra were recorded using a Jasco V-530 spectrometer with a spectral resolution of 1 nm. Visible photoluminescence measurements were carried out by pumping at 355 nm with a frequency-tripled Nd : YAG pulsed laser (8 ns pulse duration, 10 Hz repetition rate). The PL was collected perpendicularly to the sample surface. For the PL decay measurements the photomultiplier of the spectrometer was connected to a digital oscilloscope.

3   Results and discussion

3.1   *Spectroscopic characterisations of bulk samples*

The photoluminescence properties of each type of complexation were studied by pumping the corresponding bulk sample at 355 nm. Only for sulphosalicylic acid (SSA) complexation could we observe a clear PL-emission enhancement with respect to the non-complexed sample. Figure 2 shows the PL spectra of Tb^{3+}-doped bulk samples with and without organic complexation. The Tb^{3+} emission bands at
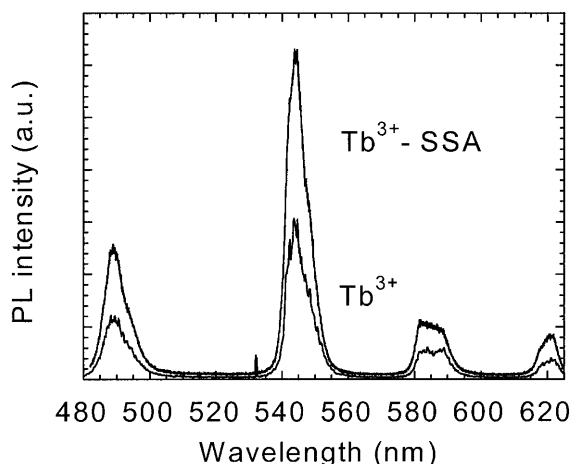
490, 545, 580 and 620 nm can be assigned to transitions from the $^5D_4$ energy level to the $^7F_6$, $^7F_5$, $^7F_4$ and $^7F_3$ levels, respectively [10].

Figure 1 shows the UV–visible absorption spectra of the same samples as on Fig. 2. For both samples, the Tb^{3+} absorption peak at 360 nm could not be resolved. However, the absorption edge of the SSA complex around 400 nm is clearly visible. Consequently, we observe an increase by a factor of 10 of the pump absorption (355 nm) due to SSA complexation. The PL intensity of the Tb^{3+}–SSA-doped matrix is two times higher than for the pure Tb^{3+}-doped matrix. Two mechanisms can explain this increase. First, energy transfer from the SSA complexes to the Tb^{3+} ions occurs and the overall pump absorption yield increases. The energy transfer is, however, not yet optimised because the absorption is 10 times higher whereas the PL intensity is only two times higher. Second, the SSA complex forms a nanocage around Tb^{3+}. This cage prevents the active ions from the detrimental influences of the host matrix and therefore from non-radiative recombinations. It is also expected to prevent short-range interaction between vicinal rare-earth ions, which could nearly
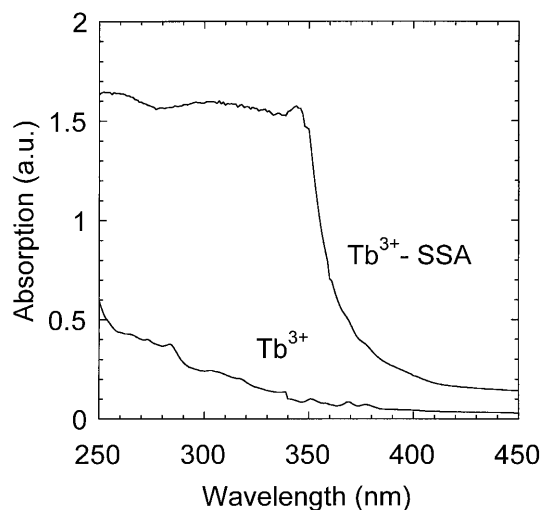
FIGURE 2   UV–visible absorption spectra of Tb^{3+}–SSA and Tb^{3+}-doped bulk samples

FIGURE 1   PL spectra of Tb^{3+}–SSA and Tb^{3+}-doped bulk samples
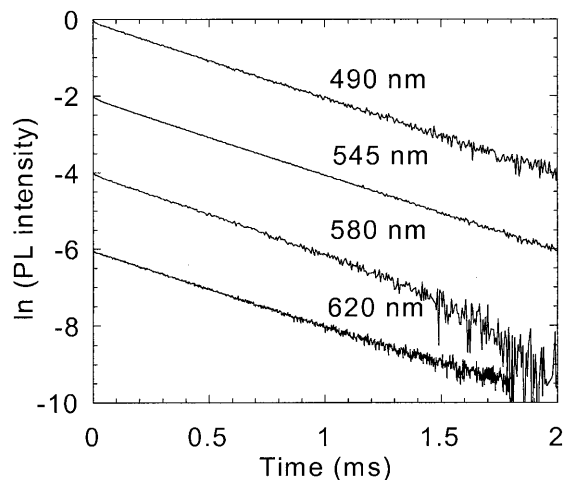
FIGURE 3   PL decay of Tb^{3+}–SSA-doped silica bulk sample at main emission wavelengths

totally quench the PL through concentration-quenching or co-operative up-conversion mechanisms.

Figure 3 shows the PL decay of a Tb^{3+}–SSA bulk sample for the four main PL-emission peaks. All the decays are single exponential with a first e-fold lifetime of about $450\,\mu s$. This corresponds to the best published results obtained under the same conditions [6]. The single exponential decay suggests that most Tb^{3+} ions are surrounded by the same environment. Further studies are, however, necessary to evidence the aspired shielding effect of the organic cage. The lifetime values of the Tb^{3+}–SSA bulk sample are equal to those of Tb^{3+}-doped sample, which shows that there is no negative influence of the organic ligand on the lifetime, i.e. PL quenching by multiphonon relaxation due to the organic bonds of SSA.

3.2   *Spectroscopic characterisations of thin-film samples*

Tb^{3+}–SSA-doped SiO_2–TiO_2 thin films of optical quality were processed by aerosol–gel. Standard *m*-lines characterisations [11] showed that two propagation modes (one TE and one TM) were supported at 633 nm. The deduced refractive index and thickness for a five-layer sample were $n = 1.55$ and $d = 0.70\,\mu m$, respectively. The shape of the PL-emission spectrum is similar to that of the corresponding bulk sample (Fig. 4). The small deviations can be explained by the slightly different host matrices of the two samples. Moreover, due to the small thickness of the waveguide, the PL signal appears significantly weaker. Modifications of our experimental set-up are under investigation to adapt it to measurements in waveguiding configuration, which could also allow us to determine the propagation losses of the layer. The PL decay of both Tb^{3+}–SSA-doped thin film and bulk sample are compared in Fig. 5. Contrary to the bulk gel case, the PL decay of the thin film appears bi-exponential. The first e-fold lifetime of the thin film is around $40\,\mu s$, which is much shorter than in silica gels. A slow decay component is also measured with a lifetime comparable to the lifetime measured on the bulk sample.

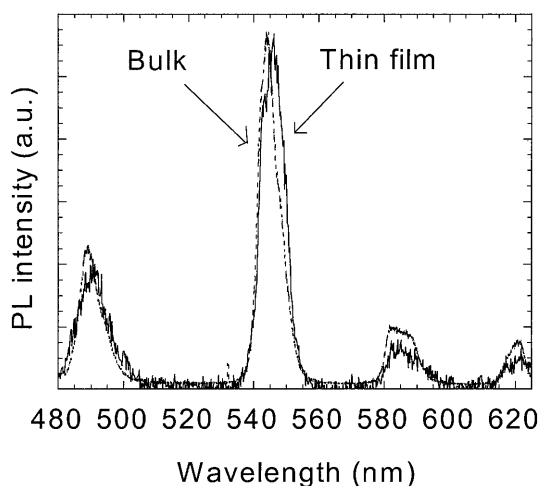The encapsulation of the terbium ions by SSA is not fully optimised in our samples. As already mentioned for the bulk sample, the aspired benefits of the shielding effect by the organic complex are thus presumably incomplete and we could still have an influence of the host matrix on the terbium ions' behaviour. The host matrix of the thin film was modified (TiO_2 co-doping) in order to increase the refractive index, and so to enable light waveguiding. Therefore the environment of the terbium ions is quite different for the thin film and the gel. The non-exponential shape of the PL decay in the thin film is similar to those observed by our group in Er-doped SiO_2–TiO_2 thin films [8]. In that work, the erbium ions were found to be distributed into two environments which led to a fast PL-decay component related to concentration-quenching mechanisms due to clustered ions and a slow PL-decay component related to ions uniformly diluted in the host matrix. Thus it is believed that the PL decay of our terbium-doped thin film could also be explained by two kinds of terbium environment. In addition, it is possible that the heat treatment at $150\,°C$ leads to a partial decomposition of the complex. Further experiments are thus necessary to understand and optimise the terbium ions' behaviour in our films.
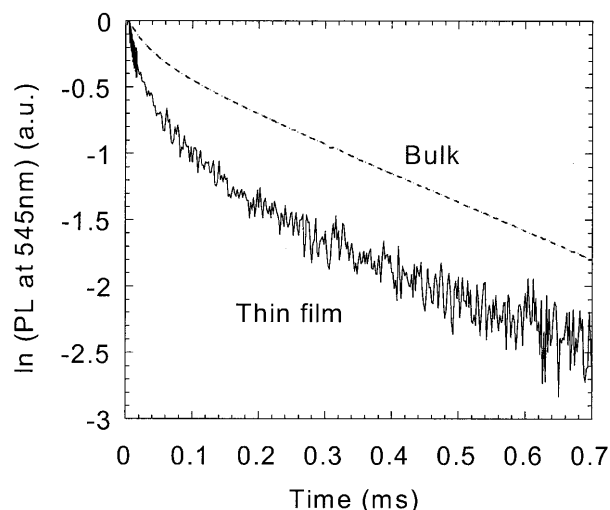
FIGURE 5   PL decay of Tb^{3+}–SSA-doped SiO_2–TiO_2 film and Tb^{3+}–SSA-doped bulk SiO_2 matrices at 545 nm

4   Conclusion

Terbium-doped bulk and thin-film samples were elaborated by sol–gel processing. We have demonstrated that the complexation of Tb^{3+} ions by SSA improves their active properties. This doping approach permitted the low-temperature elaboration of Tb^{3+}–SSA-doped SiO_2–TiO_2 planar waveguides of optical quality using the aerosol–gel process. Moreover, this approach can be extended to other rare-earth elements. This result opens a wide range of integrated-optics applications on thermally sensitive substrates. Laser action could be obtained at 545 nm, which is the strongest emission line of our samples. The introduction of other rare-earth elements emitting in the visible region would also permit the use of these films for colour displays. Further studies are, however, necessary to improve the active properties of the films in order to realise active integrated devices (energy transfer, rare-earth encapsulation and distribution).

FIGURE 4   PL spectra of Tb^{3+}–SSA-doped SiO_2–TiO_2 film and Tb^{3+}–SSA-doped bulk SiO_2 matrices

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