Erbium doped LaF_3 nanoparticles incorporated in silicondioxide thin films for active integrated optical applications.

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We report on the low-cost processing of erbium doped lanthanum trifluoride (LaF_3:Er) nanoparticles dispersed in silicondioxide (SiO_2) films prepared through the sol-gel method. The influence of particle concentration and annealing temperature on the optical properties and its implications on scattering in the visible wavelength range will be discussed. Uniform, crackfree and low loss films have been obtained by spincoating multiple layers followed by several annealing steps. The lanthanum trifluoride host shields the erbium from the OH-groups present in the silicondioxide, resulting in a higher excited state lifetime of the erbium due to the reduced OH-quenching.

Introduction

Over the past few years, many new materials have been developed with very promising properties for use in active integrated optical devices. In this paper we present some promising preliminary results on LaF_3:Er-citrate nanoparticle doped SiO_2 thin films for application in active integrated optics. Erbium is a rare earth metal emitting around 1530nm and is thus interesting for amplification in the third telecommunication window, while LaF_3 is a good transparent host for erbium. However, deposition of erbium doped LaF_3 films by conventional vacuum deposition techniques is expensive, time consuming and not straightforward. We prepared water-soluble erbium doped LaF_3 nanoparticles, which we dispersed in a tetraethylorthosilicate (TEOS) based sol-gel that can be easily spincoated on various substrates. Our focus will be on the scattering phenomena of the nanoparticles, the thin film properties of this compound material and the excited state lifetime of the Er^{3+}-ion in this promising hybrid material.

Scattering

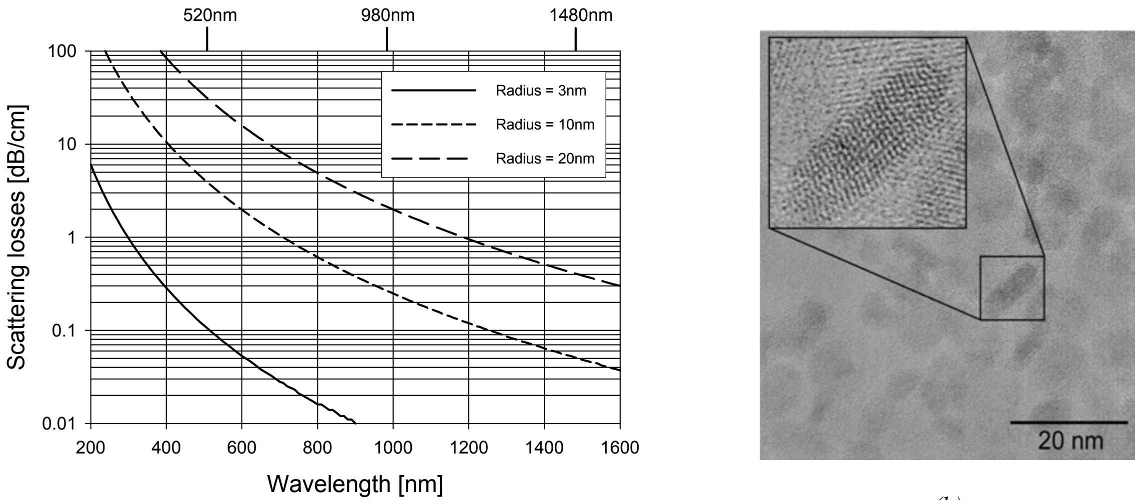
The Rayleigh scattering cross section, σ_{Rayl}, at wavelength λ and particle radius r (valid for $r << \lambda$) of a particle with refractive index n_p, embedded in a host with refractive index n_h, is given by [1]:

$$\sigma_{Rayl} = \frac{8}{3}\left(\frac{2\pi n_h r}{\lambda}\right)^4 \cdot \left(\frac{\left(\frac{n_p}{n_h}\right)^2 - 1}{\left(\frac{n_p}{n_h}\right)^2 + 2}\right)^2 \pi r^2 \qquad [\mathrm{m}^2] \qquad (1)$$

By multiplication of the scattering cross section with the fill fraction η of the nanoparticles and subsequently dividing this by the particle volume, one can obtain the total Rayleigh scattering coefficient [2] and the loss in dB/cm:

$$a_{Rayl} = \frac{3\eta\sigma_{Rayl}}{4\pi r^3} \text{ [m}^{-1}\text{]} \qquad \alpha_{Rayl} = \frac{\log(e)\cdot a_{Rayl}}{10} \text{ [dB/cm]} \qquad (2\text{-}3)$$

The λ^{-4} dependency and the strong dependency on the particle radius of ~ r^6 can be clearly seen in Figure 1a for LaF_3 nanoparticles (n_p≈1.59) embedded in a silica host matrix (n_h≈1.45).



(a) (b)

Figure 1: (a) Rayleigh scattering losses of LaF_3 nanoparticles in SiO_2 as function of wavelength for various particle sizes (η=0.1). (b) Typical TEM image of the LaF_3 nanoparticles used in our experiments.

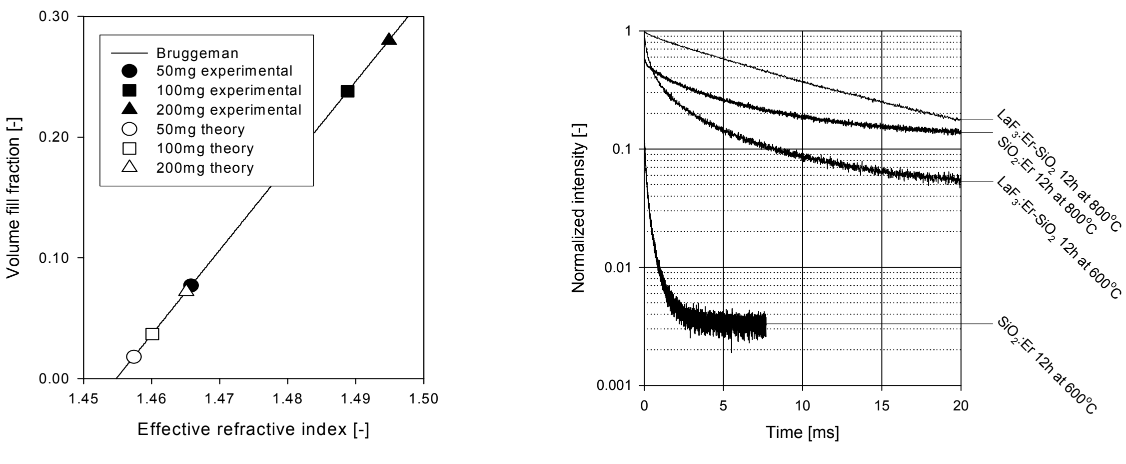
From Figure 1a it can be seen that it is of great importance to know what the used optical pump wavelength is for optical excitation of the erbium in the nanoparticle doped silica film. Our nanoparticles with a radius around 3nm (see Figure 1b) can be excited with wavelengths around 520nm with low scattering losses, while particles with a radius of 10nm will already cause a few dB/cm scattering losses at that short wavelength and should preferably be pumped with 980nm or 1480nm instead. From Equation 1-3 and Figure 1 we can conclude that this compound LaF_3:Er-SiO_2 material can be efficiently pumped with 520nm as long as the particle radius does not exceed 3nm. The fact that prolate and oblate spheroids show higher scattering losses compared to perfect spheres [3] can be neglected since the size parameter ($2\pi r/\lambda$) is small.

Experimental

The LaF_3:Er nanoparticles with stabilizing citrate ligands were synthesized by dissolving NaF and citric acid in water, while NH_4OH was used to obtain a pH of 7. At a temperature of 75ºC we added $La(NO_3)_3.6H_2O$ and $Er(NO_3)_3.5H_2O$ salts. Ethanol was used to precipitate the citrate incorporated LaF_3:Er nanoparticles that were formed after stirring for 2 hours, after which they were separated by centrifugation at 3500rpm and dried. A sol-gel solution was prepared by mixing 1ml of water, 3ml of TEOS and 7.8ml of ethanol. The pH was brought to 2 by drop wise adding concentrated HCl. This procedure for sol-gel preparation is based on the work of Xiang et al. [4]. Spincoating of this undoped sol-gel at 3600rpm on a 4inch silicon wafer followed by a 5-minute softbake at 100ºC resulted in a film thickness of 192nm. Further baking for 5 minutes at 300ºC reduced the thickness to 167nm due to the densification that took place. A high temperature-anneal step at 1100ºC for 1.5 hour further reduced the film thickness to 144nm. Additional annealing didn't further decrease the thickness or increase the refractive index (n_{633nm}=1.4548), indicating that the film was fully densified. This sol-gel doped with 50mg, 100mg and 200mg LaF_3:Er nanoparticles, respectively, resulted in the same film thickness after these high temperature anneal steps. However, the refractive index increases with nanoparticle concentration, as expected. The spin-coated films are too thin for integrated optical applications in most cases. Therefore we investigated the possibility of stacking multiple layers. We were able to deposit at least 6 layers by spin coating of the doped sol-gel at 3600rpm followed by two 5 minute baking steps at 100ºC and 300ºC after spinning of each layer. This procedure resulted in a stable film that could be annealed at 1100ºC without cracking. Leaving out the 5 minute baking steps at 300ºC causes cracking patterns that are oriented 45º with respect to the silicon substrate crystal axis. The high annealing temperature of 1100ºC is needed to efficiently remove the OH-groups in the silica matrix, which are undesirable energy quenchers of the optically excited erbium ions.

Measurements

We prepared several films with different nanoparticle concentrations (50, 100 and 200mg LaF_3:Er) for optical characterization. Figure 2a shows the refractive index of the compound LaF_3:Er-SiO_2 systems as function of LaF_3 volume fraction according to Bruggeman's effective medium theory [5]. The measured refractive indices of our nanoparticles doped thin films after an anneal at 1100ºC would correspond to a nanoparticle concentration that is roughly 4 times higher than expected. We believe that the origin of this phenomenon is twofold. At high temperatures the LaF_3 reacts with the SiO_2 and forms a higher refractive index lanthanum silicate ($La_{9.31}Si_{6.24}O_{26}$), confirmed by XRD measurements. Secondly, XPS measurements revealed a slight increase of the La/Si ratio (by a factor 1.5), which might be caused by formation of volatile SiF_6 during the 1100ºC anneal.



(a) *(b)*

Figure 2: (a) Refractive index versus particle concentration. (b) Decay curves corresponding to the $^4I_{3/2}$ level of Er^{3+} in LaF_3:Er-SiO_2 and SiO_2:Er films heated in air for 12 hours at 600ºC and 800ºC, respectively. The excitation wavelength was 488nm, while the emission was monitored at 1532nm.

The excited state lifetimes of the erbium in our thin films has been determined and compared to films where we incorporated the erbium directly into the silica matrix by adding $Er(NO_3)_3.5H_2O$ to the sol-gel (both with Er/Si ratio ~ $1.5x10^{-3}$). Figure 2b shows the decay curves for both samples annealed at 600ºC and 800ºC, respectively. For the bare Er^{3+}-ion incorporated silica films there is a fast decay component present that is characteristic for Er^{3+} clustering. This fast decay is absent for the Er^{3+}-ions in the LaF_3 nanoparticles. Furthermore, it can be seen that the compound LaF_3:Er-SiO_2 system shows longer excited state lifetimes (>10ms), because the LaF_3 matrix shields the erbium from the quenching OH-groups present in the silica, which makes it very attractive for amplification in the third telecommunication window. The long excited state lifetime of the erbium in the LaF_3 that we measured does compete well against the lifetimes of other promising erbium doped materials reported in literature.

Table 1: Lifetime values with the relative percentages of the decay components in brackets.

Temp	LaF_3:Er-SiO_2 films		SiO_2:Er films	
	τ_1 ms (%)	τ_2 ms (%)	τ_1 ms (%)	τ_2 ms (%)
600 °C	7.4 (69%)	0.9 (31%)	0.98 (35%)	0.27 (65%)
800 °C	10.9(95%)	3.9 (5%)	6.0 (70%)	1.2 (30%)

Conclusions

We showed our first results on a new low-cost compound material system consisting of LaF_3:Er nanoparticle doped silica. The preparation of the nanoparticles and the TEOS based sol-gel is straightforward. Due to the small particle size, scattering is low, which allows for optical excitation at short wavelengths. Multiple layers could be easily stacked without cracking and the excited state lifetime of the erbium is considerably larger compared to other erbium doped sol-gel based materials, even at anneal temperatures of 800ºC. An unexpected increase of the refractive index at high anneal temperatures of 1100ºC suggest that a reaction between the nanoparticles and the host material takes place that prevents the determination of the nanoparticle concentration from refractive index measurements. We will further investigate and optically characterize this compound material for application as active waveguide and cladding material. This research is supported by the Freeband Impulse technology program of the Ministry of Economic Affairs of the Netherlands.

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