# Stimulated emission and optical gain in $LaF_3$:Nd nanoparticle-doped polymer-based waveguides

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We report experiments which show evidence that stimulated emission at 863 nm takes place in hybrid monomode $Si_3N_4$ waveguides where $LaF_3$:Nd nanoparticle-doped polymethylmethacrylate (PMMA) was used as a top cladding material. Furthermore, optical gain at 1319 nm in $LaF_3$:Nd nanoparticle dispersed PMMA (0.1 dB/cm) and photodefinable epoxy (Microchem SU-8) multimode waveguides has been observed at pump powers below 10 mW. This class of composite materials based on polymers with dispersed nanoparticles shows promising properties for planar optical amplifiers. Simulation showed that optical gain in the order of 10 dB can be achieved at 100 mW pump power in a 20 cm long monomode waveguide. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1840110]

Over the past few years, more and more rare earth doped materials are emerging with very promising properties for amplification in active integrated optical devices. Especially the rare earths neodymium and erbium are of great interest, because they emit in the second and third window of optical communication systems, respectively. It has been reported that $LaF_3$ is a very good host for rare earth incorporation and because of its low phonon energy it exhibits a wide transparency band from 0.2 to 11 $\mu$m.[1] Laser operation in molecular beam epitaxially grown $LaF_3$:Nd has been reported by several authors,[1–3] but microstructuring for planar waveguide applications is hard. Polymer waveguide materials have the advantage of being low-cost and tunable in many ways with respect to their properties and ways of processing. Unfortunately, compared to inorganic materials, it is relatively difficult to dissolve rare earth ions like erbium and neodymium in polymers, because these rare earths come in inorganic salt forms that do not dissolve well in polymers.

To overcome the insolubility problem of inorganic rare earth salts in polymers, we developed neodymium doped $LaF_3$ nanoparticles with organic ligands that do dissolve well in polymers. The negatively charged dithiophosphate group of the ligand is coordinated to the lanthanide ions located at the surface of the nanoparticles. The organic tails extend outward, giving the nanoparticles a good solubility in organic solutions and polymer matrices. By combining the broad range of attractive polymer properties and the relatively long lifetime of rare earth dopants in inorganic nanoparticles, a considerable amount of flexibility regarding material properties can be achieved. The results of our pump–probe experiments on $LaF_3$:Nd doped polymer waveguides will be presented. Evidence of stimulated emission and optical gain are demonstrated, which are promising for applications in active integrated optical microring and Fabry–Perot resonator lasing devices.

We used $LaF_3$:Nd nanoparticles that are composed of $LaF_3$-crystals doped with 5 at % $Nd^{3+}$. The preparation of these nanoparticles has been published elsewhere.[4,5] By choosing $LaF_3$ as host for the $Nd^{3+}$ ions, quenching will be reduced to a minimum because of the very low vibrational energies of $LaF_3$ and a reasonably long lifetime of 200 $\mu$s can be obtained. In order to prevent clustering of the nanoparticles, which will cause Rayleigh scattering when the refractive indices of the nanoparticles and the host are not matched,[6] to enhance solubility and to control the growth of the particles during the synthesis, ligands are attached to the surface of the nanoparticles. Figure 1(a) shows a transmission electron microscope (TEM) image of the crystalline $LaF_3$:Nd nanoparticles. The effects of the prolate geometry of the nanoparticles on the photophysical properties can be neglected since the particles are small and transparent over the wavelength range of interest.

We fabricated several samples in which the composite material was used as cladding material or core material, respectively. Our first sample was a monomodal, high contrast, reactive ion etched $Si_3N_4$ straight waveguide with a 20 wt. % nanoparticle doped PMMA cladding deposited on top. The emission peaks of the $^4F_{3/2}$ level of the $Nd^{3+}$ were measured around 863 nm at different pump powers using a spectrometer with a photomultiplier tube. Figure 2 shows the emission spectra and the relative weights of the fitted Lorentz peaks as function of pump power. The emission at 863 nm monotonously increases with increasing pump power, while the emission peaks at 860 nm and 866 nm show saturation when the pump power exceeds 192 $\mu$W. This is an indication that stimulated emission at 863 nm is taking place in this sample and optical amplification is possible. By deriving the emis-

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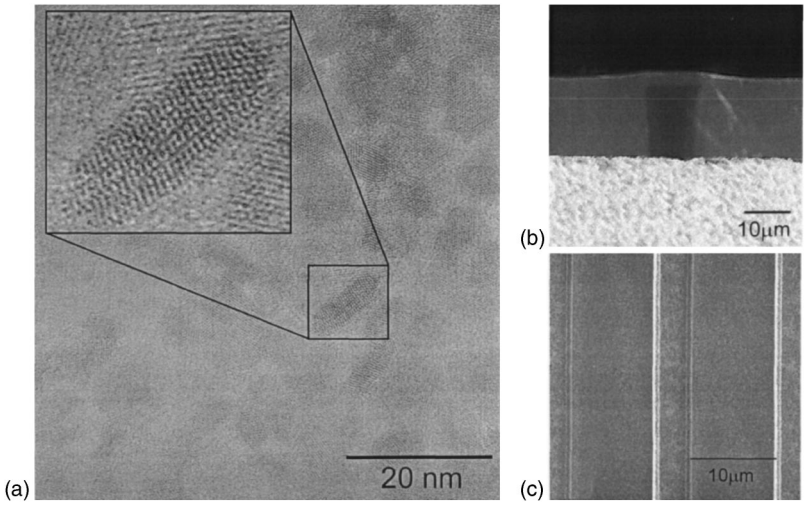


FIG. 1. (a) Transmission electron microscopy (TEM) image of the $LaF_3$:Nd nanoparticles used in our experiments. The crystalline nature of the particles is shown in the top left of the image. (b) and (c) Microscope cross section and SEM top image of 10 $\mu$m wide nanoparticle doped SU-8 waveguides, respectively.

sion cross sections and the branching ratios from the spontaneous emission spectrum and assuming full population inversion we found the net gain to be around 0.5 dB/cm using straightforward modeling, corresponding to 3 dB/cm in case of an optimized modal overlap which is the case when both core and cladding materials are doped.

Due to the fact that it was hard to couple a sufficient amount of pump power in our small dimension high contrast $Si_3N_4$ waveguides, a new waveguide was fabricated by spin-coating a PMMA solution with 10 wt. % $LaF_3$:Nd nanoparticles onto a silicon wafer with a thick $SiO_2$ buffer. After patterning with standard photoresist and reactive ion etching of the 3.3 $\mu$m thick doped PMMA film, we obtained straight waveguides with a channel width of 10 $\mu$m and a ridge height of 1.4 $\mu$m. A probe signal ($\lambda_s = 1319$ nm) and a 12 mW chopped pump ($\lambda_p = 578$ nm) beam were combined with a WDM and coupled into the PMMA waveguides using a fiber with a 9 $\mu$m core. At the output a 50 $\mu$m multimode fiber was used to collect all the light. The pump light was filtered out and the 1319 nm signal was lead to a linear detector that was connected to an oscilloscope. The detector signal shows a signal gain of 0.35 dB in our 3 cm long waveguide channels when the pump laser was switched on. The effect of spontaneous emission was determined by turning off the signal laser, resulting in a detector signal that was 27 dB lower than the original signal power. The power difference of the 1319 nm signal when the pump laser is present or absent is thus caused almost completely by amplification.

A third sample was made using SU-8 photoresist as the host for the nanoparticles (20 wt. %) to simplify the processing. Waveguides with a width of 10 $\mu$m were fabricated by direct photopatterning through UV-exposure of the 10 $\mu$m thick doped SU-8 film followed by a standard photoresist development step. In Figs. 1(b) and 1(c) a microscope cross section and a scanning electron microscope top view image of our doped SU-8 waveguides are shown, respectively. The refractive index of a doped layer was found to be 1.59, about the same as for the undoped layer. This shows that the influence of the doping on the refractive index is small due to the refractive index matching of $LaF_3$ ($n \sim 1.59$),[2] which will prevent Rayleigh scattering. A copolymer of acrylates and styrene ($n = 1.56$) was subsequently deposited by spin coating, after which the samples were diced. The absorption tail of the SU-8 photoresist extends into the visible wavelengths, causing our nanoparticle doped SU-8 waveguides to show absorption at 578 nm, damaging the waveguides in a short period of time. Therefore, these samples were pumped at 795 nm, where the absorption of $Nd^{3+}$ is about 60% of the absorption at 578 nm. After dicing and pigtailing of the samples only 5 mW of pump power could be coupled into our 5.2 cm long waveguides using a Ti:sapphire pump laser. The pump and laser signals were combined using a 3 dB splitter. At this low pump power level an amplification of 0.1 dB of the signal laser was observed on the oscilloscope. The spontaneous emission was measured to be around 30 dB lower than the signal power, not interfering with our amplification measurements. Numerically solving the rate equations of the $Nd^{3+}$ four-level energy system[7] is consistent with the measured amplification at the low pump powers used in our experiments. Figure 3 shows the gain for several wave-

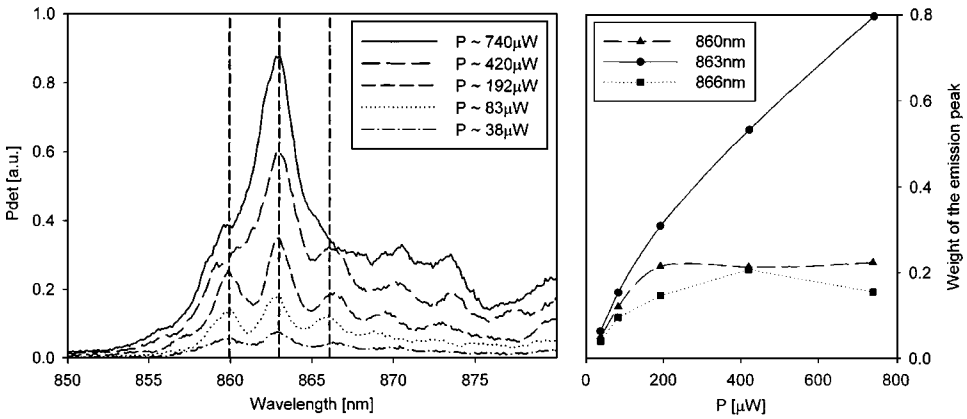


FIG. 2. Emission spectra vs pump power for a straight $Si_3N_4$ waveguide with a $LaF_3$:Nd doped PMMA cladding (left) and the relative weights of the emission peaks versus pump power at 860, 863, and 866 nm, respectively (right).

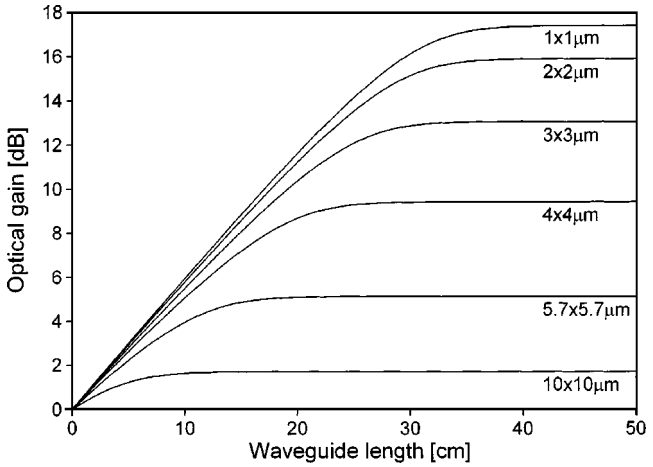


FIG. 3. Theoretical gain vs waveguide length for various waveguide cross sections.

guide dimensions, which can theoretically be achieved when the pump power is 100 mW and background losses are kept at a minimum.

In conclusion, our experiments indicate that stimulated emission and amplification is taking place in $LaF_3$:Nd nanoparticle doped polymer materials. Although the observed amplification in our high loss multimode waveguides is still low, we believe that we can improve the performance by improving our technology and waveguide design. Currently, work is also focused on high index contrast, highly confined $LaF_3$:Nd nanoparticle doped microring resonators in which the power buildup in the ring resonator will further enhance the input pump power. As nanoparticle hosts we are investigating state of the art photosensitive polymer materials with very low background losses in the visible and infrared. In addition, erbium-doped nanoparticles with strong emission at 1.55 $\mu$m and lifetimes in the range of several milliseconds have been synthesized for use in the third fiber optic communication window. Our aim is to build microring lasers and all-optical switches utilizing the gain and the third-order nonlinear properties of this new class of compound materials.

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