Neodymium and Gadolinium Diffusion in Yttrium Vanadate

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Abstract

The thermal diffusion of Nd^{3+} and Gd^{3+} ions in YVO_4 is characterised, finding diffusion rates of $7x10^{-19}$ and $44x10^{-19}$ m^2s^{-1} respectively at 1400°C, and activation energies of $5.3x10^{-19}$ and $2.9x10^{-19}$ J respectively, for diffusion along the c-axis. The fluorescence properties of the Nd^{3+}-diffused YVO_4 agree well with those of bulk doped materials. The formation of a planar optical waveguide was also observed for one of the Nd^{3+}-diffused samples. This characterisation is a significant first step towards fabrication of waveguide lasers and amplifiers in this important laser material.

OCIS Codes

160.3380 140.3460 130.2790

1. INTRODUCTION

Lasers based on planar optical waveguides have recently generated interest for use as high-average-power sources, due to a combination of attractive features including high optical gain, good thermal-power handling and compatibility with high-power diode pump sources [1]. The highest-power waveguide lasers have been based on direct-bonded thin films using YAG as the laser host [2,3]. Hybrid guided / unstable resonators have been implemented in these lasers in order to control the output spatial mode as the direct-bonding technique results in guidance in only one dimension. It has recently been demonstrated, in both fibre [4] and planar formats [5], that tapered waveguides can also be used to allow high-power diode pumping while still maintaining single-spatial-mode output. For a planar format, this requires a fabrication technique that can be photolithographically patterned in the plane of the waveguide (such as thermal diffusion). YVO_4 has recently come to prominence as a laser host partly due to the very strong absorption for diode pump sources [6]. Such a strong absorption could allow high-power side-pumped operation of tapered waveguide lasers, as the requirement for adiabatic expansion of the fundamental mode from a single-mode channel to a broad planar area limits the maximum width, and hence the pump absorption length, to a few hundred microns for a device a few centimetre long [7]. Here we study the thermal diffusion of Nd^{3+} and Gd^{3+} ions in YVO_4 in order to obtain the essential diffusion characteristics necessary to calculate the conditions required for fabrication of waveguides suitable for laser action at ~1μm. Nd^{3+} is studied both for localised doping as the active laser ion and as a potential refractive index modifier. We also choose to study Gd^{3+} diffusion as an index modifier in order to give the potential for separate control of the index and gain

distributions. Gd^{3+} is chosen in particular due to the fact that $GdVO_4$ is a well-studied laser host of higher refractive index than YVO_4.

Thermal diffusion has been extensively used as a standard method for waveguide fabrication in $LiNbO_3$ [8]. Further work has shown that thermal diffusion is also a useful technique for doping $LiNbO_3$ with rare-earth ions [9] enabling localised gain regions in integrated optical circuits. The general applicability of this technique to other laser hosts has also been suggested by work on Ti^{3+} and Ga^{3+} diffusion in sapphire producing both passive and active waveguides [10,11]. In fact many other studies have been carried out investigating diffusion coefficients of rare-earth ions in various crystals [12], although not in general with a view to creating lasers or waveguides. To our knowledge the diffusion coefficients for rare-earth ions in YVO_4 have not previously been investigated.

2. THERMAL DIFFUSION

In order to characterise this process six undoped YVO_4 substrates from Casix inc. were cut and polished to 18 by 18 by 3 mm in the a, b and c axes respectively. We choose to study diffusion along the c-axis, as this will allow a final device with an orientation such that we have access to both the strongest absorption cross-section for the pump and the highest gain cross-section for the 1.064μm signal, in end or side-pumped configurations. The substrates were cleaned to remove organic contaminants and particulates. A thermal evaporator was used to coat the 18mm by 18mm polished surface of the substrates with a layer of Nd or Gd. As a starting point, the diffusion source thicknesses were chosen to roughly correspond to a 1at.% doping concentration, assuming the formation of a 10μm-deep slab-shaped diffused layer.

The samples were thermally diffused in a resistance furnace according to the conditions listed in Table 1, in a dry oxygen atmosphere. After diffusion the samples were end-polished parallel to the c-axis.

On removal from the furnace, it was noted that in general the diffused surfaces showed some defects. The defects were in two forms: firstly a coating of non-diffused metal, and secondly a number of approximately 200nm deep cracks towards the edges of the samples. The number of cracks appeared to increase with temperature and was also dependent on which batch the YVO_4 substrate originated from. From this second observation we believe that the number of cracks may be dependent on the initial surface quality of the substrate used.

3. DIFFUSION PROFILES

Secondary ion mass spectroscopy (SIMS) was used to determine the diffusion profile and hence the doping concentration of the diffused layers. SIMS bombards the surface of the sample with oxygen ions, which etch a well-defined pit in the sample. The ejected constituents of the pit are collected and analysed by a mass spectrometer, this data is used in conjunction with the etch rate to produce a diffusion profile. To gain a concentration profile the SIMS data can then be calibrated using data collected from a bulk doped Nd:YVO_4 sample of known doping concentration.

The expected diffusion profile for an undepleted source is given by [13]

$$C(z,t) = C(0)erfc\left[\frac{z}{2\sqrt{Dt}}\right] \qquad \ldots(1)$$

For a depleted source the profile tends towards a Guassian distribution [13]

$$C(z,t) = C(0,t)\exp\left[-\left(\frac{z}{2\sqrt{Dt}}\right)^2\right] \qquad \ldots(2)$$

where C(0) is the concentration of the dopant at the surface (independent of time for the undepleted source), t is time, and D is the diffusion coefficient. Figure 1 shows typical examples of measured diffusion profiles corresponding to a Gaussian (sample 2) and complimentary error function (sample 1) obtained from the experimental SIMS data. The diffusion coefficients given in table 1 were calculated by appropriate fitting of equations (1) or (2) to the SIMS results for each sample. The doping level was calibrated using the fact that sample 2 (Nd) and sample 6 (Gd) were a close fit to a depleted-source Gaussian distribution, allowing us to assume that all the ions present in the original metal film had been diffused into the substrate. This calibration was confirmed for Nd^{3+} by SIMS analysis of a bulk Nd:YVO_4 sample of known dopant concentration (2.2at.%).

The temperature dependence of the diffusion coefficient is given by [13],

$$D(T) = D_0 \exp\left(-\frac{E_a}{kT}\right) \qquad \ldots(3)$$

where E_a is the activation energy, k is Boltzmann's constant, and T is the temperature. From the results summarised in Table 1 the estimated expressions of the diffusion coefficients for Nd and Gd in YVO_4 are as follows,

$$D_{Nd} = 6x10^{-9} \exp\left(-\frac{5.3x10^{-19}}{kT}\right) \quad \ldots(4)$$

$$D_{Gd} = 1x10^{-12} \exp\left(-\frac{2.9x10^{-19}}{kT}\right) \quad \ldots(5)$$

As only two temperatures have been used to find these expressions they can only be reliably used over the 1400°C to 1600°C range discussed here. However, we can compare the diffusivities we have measured at these temperatures to those found in similar experiments carried out in other materials. Of specific interest is the comparison to diffusion results in YAG, as this is another useful laser host and in both cases we wish to diffuse into sites normally occupied by an Y^{3+} ion. Cherniak [12] has measured a diffusion coefficient of $4.2x10^{-19}m^2s^{-1}$ for Nd^{3+} in YAG at 1400°C and finds only a small variation in this value ($4.5x10^{-19}m^2s^{-1}$ to $2.0x10^{-19}m^2s^{-1}$) for three other rare-earth ions (La^{3+}, Dy^{3+} and Yb^{3+}). This small variation is attributed to the general similarity in ionic radius of the rare-earth ions (117pm to 101pm) and the Y^{3+} ion (104pm). The diffusion rate measured for Nd^{3+} in YVO_4 is similar to these values ($\sim 7x10^{-19}m^2s^{-1}$) but we see a much greater diffusion coefficient in the case of Gd^{3+} ($\sim 44x10^{-19}m^2s^{-1}$). While this large difference is somewhat unexpected, as the ionic radius of Gd^{3+} (108pm) is still similar to that of the other rare-earth ions and the Y^{3+} ion, it is certainly favourable to the formation of optical waveguides as the time required for diffusion to suitable depths is greatly reduced.

4. FLUORESCENCE SPECTROSCOPY

The fluorescence spectra of the diffused samples were obtained by face pumping the samples with a Ti:sapphire laser tuned to the Nd^{3+} absorption at 808nm.

The unfocused beam was set normal to the diffused face of the sample and the fluorescence was collected from the polished side face. The spectrum was recorded using a computer linked to a triple-grating spectrometer. The experiment was then repeated using a 2.2at% bulk doped piece of Nd:YVO_4. From Figure 2 we can see that the emission spectrum for the diffused sample is very similar to that of the bulk sample, although a slight degree of broadening is apparent as some side peaks are no longer resolved. The polarised bulk and diffused spectra were also similar, but the much lower signal level from the diffused sample led to rather noisy spectra.

The fluorescence lifetime of the Nd^{3+} ions in the diffused samples was measured by face pumping the samples using a Ti:sapphire laser tuned to 808nm. A typical result is shown in figure 3 and lifetimes for all the samples were found to be between 70μs and 110μs compared to measured bulk lifetimes of ~50μs (for 2 at% Nd doping) and ~90μs (for 1at% doping). It should be noted that from the SIMS data of figure 1 we believe that we have much higher doping levels than this. However, it is possible that the majority of the observed fluorescence comes from the weakly doped tail of the diffusion distribution as the very highly doped areas will suffer from strong non-radiative cross-relaxation. Clearly, lasing waveguides will require a diffusion that leads to much lower Nd^{3+} doping levels than these preliminary investigations have produced.

5. WAVEGUIDE CHARACTERISTICS

The waveguide properties of the samples were tested by attempting to end-launch light into the diffused layers. Before this was done, any defects were removed by a superficial re-polishing of the sample surface to remove residual metal, while not

removing any significant amount of YVO_4. The exception to this is sample 3 which had the largest number of 200nm-deep surface cracks. These were easily removed by a longer polishing process, which will certainly have affected any guiding structure present. Two lasers were used for the end-launching: a He-Ne operating at 633nm and an argon ion that could be operated at 457nm, 488nm and 514nm. The laser beam was launched into the diffused layer using a X10 microscope objective and the output was imaged onto a CCD camera using another X10 microscope objective. Sample 2 was the only diffused layer to show waveguide propagation, supporting TM modes at 457nm and 488nm. Similar experiments were carried out with TE polarised light but no TE guided modes were observed. From the measured spot sizes on the CCD camera, a modal spot size of ~1.8μm was calculated in both cases. These end-launching results were confirmed by dark-line prism coupling measurements that indicated the presence of a single TM waveguide mode in sample 2 at wavelengths up to 514nm but not at 633nm. The lack of an observed mode at 514nm in the end-launching experiments can be attributed to Nd^{3+} absorption at this wavelength. Due to the indices of the prism and sample for the TE polarisation we were unable to experimentally confirm the lack of a TE mode via prism coupling.

As we were unable to find any published data on the index change in YVO_4 due to rare-earth-ion doping we have made rough estimates by assuming that the index change due to Nd^{3+} doping is similar to that found in YAG (0.42×10^{-3} per at.% [14]) and that the index change due to Gd^{3+} doping follows a linear relationship between the index values for YVO_4 and $GdVO_4$ (0.24×10^{-3} per at.%). Combining this estimate of the index change with the calculated doping profiles from the SIMS measurements gives a very good fit to the observed waveguide properties, predicting a

single mode in sample 2 with cut-off at ~560nm. The predicted mode-size at 457nm and 488nm is also close to the ~1.8μm experimental value. A guided mode is also predicted for sample 6 but is expected to be very near to cut-off. As yet no explanation is available for the lack of TE guided modes, but it is fortunate that both the absorption cross-section for 807nm pumping and the emission cross-section for lasing at 1.064μm are greater for the TM polarisation of the diffused guides.

The knowledge of the index change and diffusion parameters allows the calculation of the experimental conditions required to give a single-mode waveguide at the lasing wavelength of 1.064μm. For instance, to obtain a guide with the second propagation mode just at cut-off at that wavelength, based on Nd^{3+} diffusion with a maximum concentration of 3at.% (i.e. suitable for lasing), would require a 125nm layer to be diffused for ~700hrs at 1600°C. The diffusion time could be reduced by going to a higher temperature, but this may cause problems due to the increased surface defects at higher temperatures. The faster diffusion of Gd^{3+} and the ability to use higher doping levels, as this is not the lasing ion, allows a similar single-mode guide to be made in ~280hrs at 1600°C.

6. SUMMARY

We have investigated the thermal diffusion of Nd^{3+} and Gd^{3+} ions in YVO_4, finding the essential diffusion characteristics necessary to allow the design of optical waveguides in this important laser material. A Nd^{3+}-diffused waveguide with a cut-off below 633nm was fabricated indicating an index change of $\sim 0.4 \times 10^{-3}$ per at.%. The observed waveguide supported only TM propagation. No waveguide modes were observed for the Gd^{3+}-diffused samples indicating an index change of $\leq 0.24 \times 10^{-3}$ per

at.%. Future work will include the fabrication of waveguide lasers and amplifiers at 1.064μm and the investigation of alternative lasing and index modifying ions.

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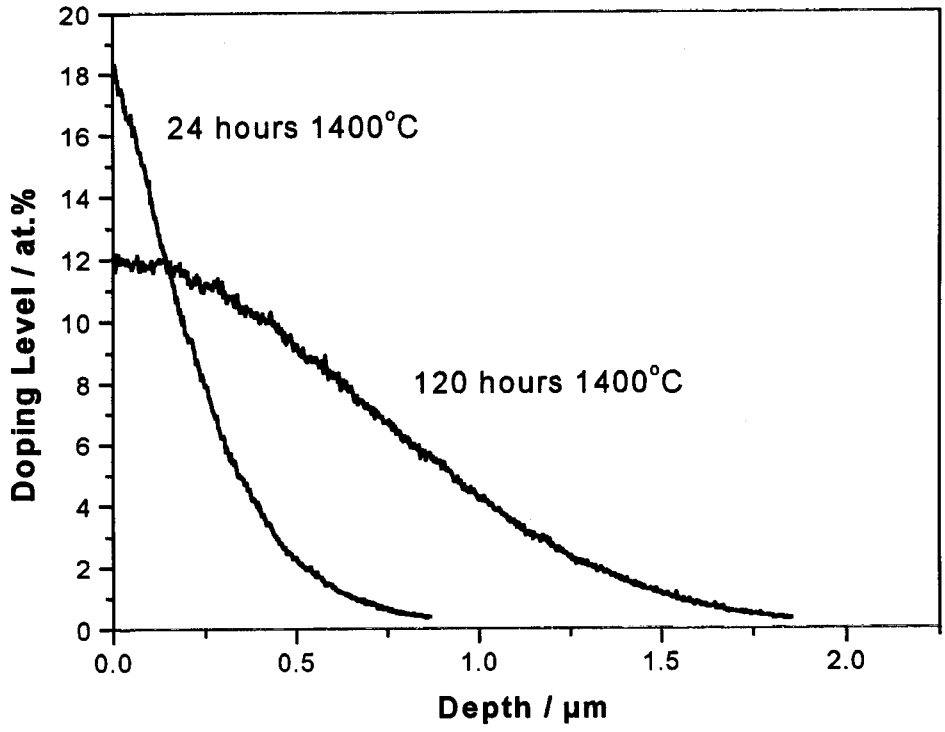
Table 1 Diffusion Parameters and Measured Diffusion Coefficients

Sample	**Ion**	**Layer Thickness / nm**	**Temperature / °C**	**Time / hours**	**Best-Fit Diffusion Coefficient / $x10^{-19}$ m^2s^{-1}**
1	Nd	55	1400	24	7.8
2	Nd	55	1400	120	5.6
3	Nd	55	1600	10	80
4	Gd	40	1400	12	41
5	Gd	40	1400	24	47
6	Gd	40	1600	12	170

Figure 1 Nd^{3+} doping level against depth into YVO_4 sample, derived from SIMS experimental data.

Figure 2 Unpolarised fluorescence spectra for bulk and diffused Nd:YVO_4 samples. The spectrum for the diffused sample is vertically offset for ease of comparison.

Figure 3 Typical fluorescence decay for the Nd-diffused YVO_4 samples with an exponential fit.


20
18
16
14
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10
8
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1.0
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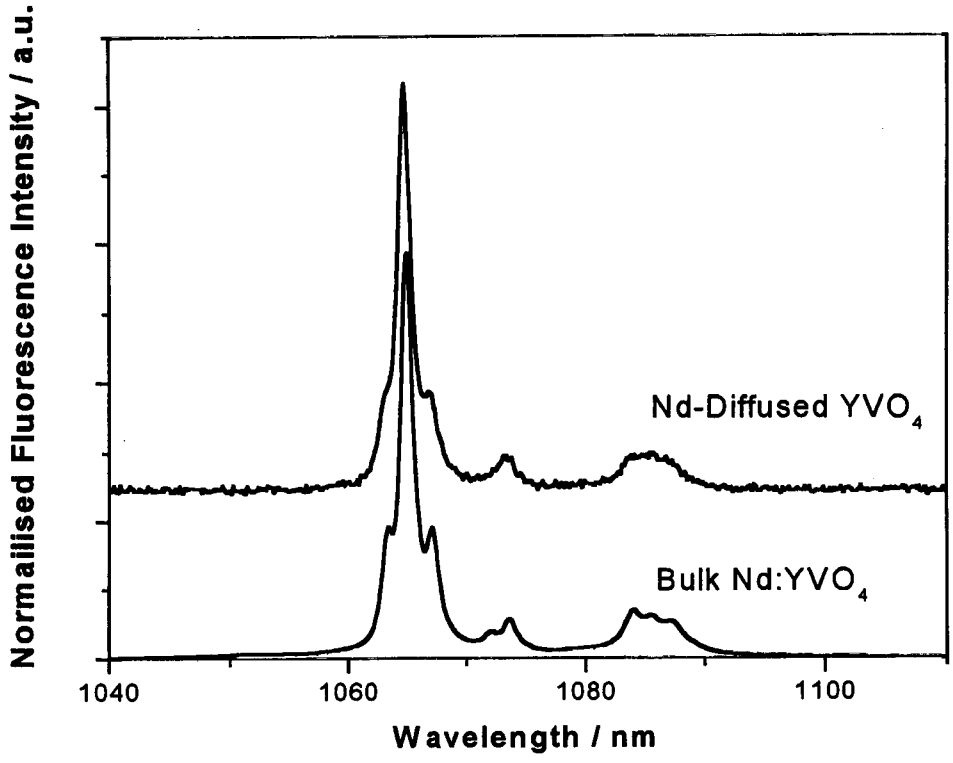
Doping Level / at.%
Depth / µm
24 hours 1400°C
120 hours 1400°C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Bulk Nd:YVO4
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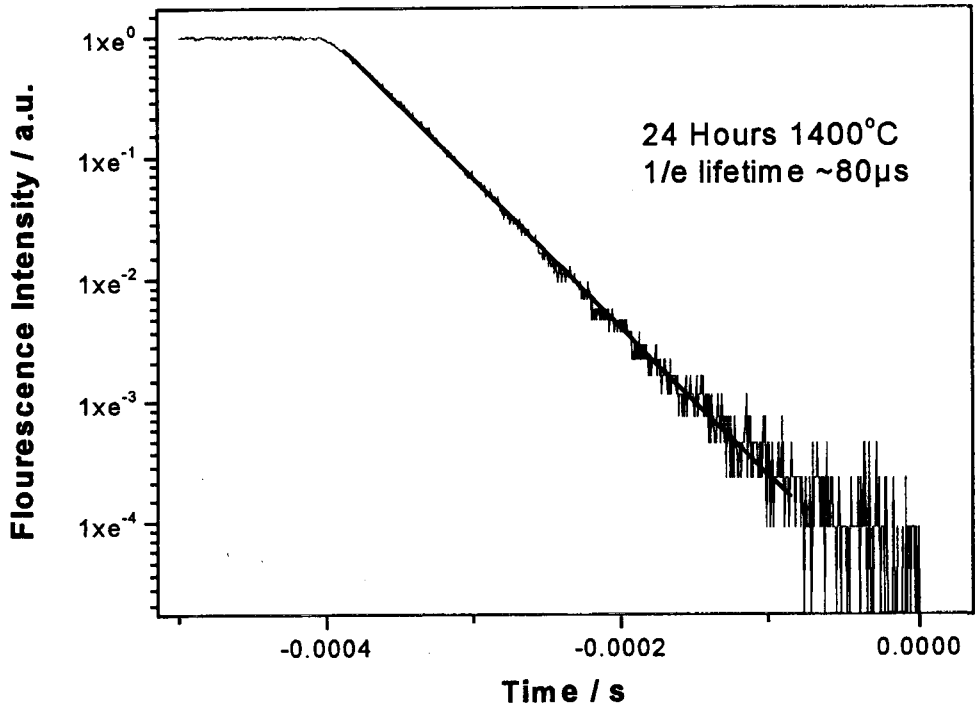
1060
1080
1100
Wavelength / nm


Flourescence Intensity / a.u.
1xe^0
1xe^-1
1xe^-2
1xe^-3
1xe^-4
24 Hours 1400°C
1/e lifetime ~80µs
-0.0004
-0.0002
0.0000
Time / s