Infrared-to-blue-wavelength upconversion in GGG:Pr^{3+} thin film grown by liquid phase epitaxy

M Malinowski†§, R Piramidowicz†, J Sarnecki‡ and W Wolinski†

† Institute of Microelectronics and Optoelectronics PW, ulica Koszykowa 75, 00-662 Warsaw, Poland
‡ Institute of Electronic Materials Technology, ulica Wolczynska 133, 01-919 Warsaw, Poland

Abstract. Blue emission at 486 nm corresponding to the $^3P_0 \rightarrow {}^3H_4$ transition in Pr^{3+}:Gd$_3$Ga$_5$O$_{12}$ (GGG) thin epitaxial film was generated after excitation with infra-red radiation at around 890 nm. The upconversion mechanism was shown to be excited-state absorption from the $^1G_4$ multiplet. The spectroscopic properties of the $^1G_4$ state of Pr^{3+} in GGG were also studied. The emission spectra of Pr^{3+}:GGG bulk crystals and thin film are centred at 1.35 μm, and the measured $^1G_4$ lifetime is about 0.5 μs at room temperature. Blue-wavelength upconversion excitation spectra and direct infra-red excitation spectra allowed us to determine the Stark energy levels in the $^1G_4$ and $^1I_6$ multiplets.

1. Introduction

Planar optical devices play an increasingly important role as components for fibre-optic communication systems. One of the recent important developments is the successful operation of planar waveguide amplifiers and lasers which can easily be coupled to fibre components [1, 2]. Also, a planar solid-state laser is an alternative praseodymium-doped fibre amplifier (PDFA) pump source because it has a high output power and frequency stability. One of the candidates for a PDFA pump is a 968 nm laser-diode-pumped 1.03 μm Yb^{3+}:YAG laser. However, because of the high cost of this laser diode, an Yb^{3+} + Nd^{3+}:YAG waveguide laser pumped at 810 nm and operating at 1.03 μm, as a result of efficient energy transfer from Nd^{3+} to Yb^{3+} ions, has been proposed as a less expensive alternative [3].

Compact waveguide lasers that operate in the blue region of the visible spectrum offer a broad range of special and commercial opto-electronic applications, such as complex data transmission and interpretation, full-colour displays, and colour printing. Short-wavelength operation of laser-diode-pumped solid-state laser systems could be achieved by using nonlinear techniques. Thus, harmonic generation in nonlinear crystals [4] and frequency upconversion [5, 6] are two promising techniques. In upconversion laser schemes, excitation of high-energy optical states is achieved either by sequential absorption of pump photons in one ion, or by cooperative transfer involving two or more excited ions, or, as shown recently, by photon avalanche, i.e., a process that involves cross relaxation to populate the metastable states of two ions followed by excited-state absorption (ESA) from these

§ Author to whom any correspondence should be addressed; telephone: 48.22.6607783; fax: 48.22.6288740; e-mail: m.malinowski@imio.pw.edu.pl.

states [7]. As a result of the high-optical-power confinement in a small volume, for nonlinear frequency upconversion from IR sources to the visible region, optical planar waveguides and fibres appear to be most suitable. Among various systems that have demonstrated upconversion lasing, fluorozirconate active fibres have been investigated most extensively owing to their ability to produce efficient cw blue, green, and orange emission under one-colour IR diode pumping [8–10].

Liquid phase epitaxy (LPE) is a promising technique for producing low-loss ($<$0.05 dB cm^{-1}) planar waveguide lasers. In particular, rare-earth-doped YAG epitaxial layers on YAG substrates have been demonstrated to have excellent laser properties. The first successful laser experiments on epitaxial Ho^{3+}:YAG layers on YAG substrates were reported in 1972 by Van der Ziel *et al* [11], and in 1973 reports on laser oscillations from Ho^{3+} and Nd^{3+} ions in LPE-grown YAG thin films were presented [12]. More detailed experimental studies of laser Nd^{3+}:YAG/YAG structures, including DFB and DBR resonators, were presented in [2, 13].

Very recently, upconversion fluorescence has been studied in rare-earth-doped YAG waveguides. Shepherd *et al* [14] reported on a room temperature avalanche upconversion process in an epitaxial Tm^{3+}:YAG waveguide giving intense UV (367 nm) and blue (460, 485 nm) fluorescence under excitation at 616.4 nm. Zhang *et al* [15] described green upconversion excited fluorescence in ion-implanted Er^{3+}:YAG waveguides and compared the absorption, excitation, and emission bulk and waveguide spectra.

Gd$_3$Ga$_5$O$_{12}$ (GGG) is a well studied laser host. Large crystals of good optical quality can now be produced, and laser action of various rare earths in GGG has been reported [16, 17]. Also, recently, laser operation of Yb^{3+}-doped [18] and Nd^{3+}-doped [19] GGG thin-film optical waveguides has been described.

The trivalent praseodymium ion (Pr^{3+}) in various crystals is well known for having a very rich emission spectrum extending from the ultraviolet (UV) to the infra-red (IR) [20, 21]. Because of the energy level structure, and suitable lifetimes of the excited states, Pr^{3+} systems are also attractive as short-wavelength upconversion laser materials [8]. One of the most promising techniques for increasing the Pr^{3+} upconversion efficiency is that of codoping with Yb^{3+} ions, and upconversion lasing has recently been reported in Yb^{3+}-sensitized fluoride systems, LiYF$_4$:Pr^{3+}+Yb^{3+} crystal [22], and ZBLAN: Pr^{3+}+Yb^{3+} glass fibres [8, 23]. Recently, simultaneous blue- and orange-wavelength lasing in Pr^{3+}-doped YAG, YAP, and YLF crystals has been studied [24], and observation of lasing at 486 nm in Pr^{3+}:GGG has been reported. This encouraged us to further study the optical properties of bulk and thin crystalline films of Pr^{3+}:GGG.

The aim of this work is threefold: to compare the optical properties of Pr^{3+}-doped GGG thin epitaxial film on a GGG substrate to those of Pr^{3+}:GGG bulk crystal, to study the IR-to-visible-wavelength upconversion process, and to determine the spectroscopic and emission properties of the praseodymium $^1G_4$ multiplet in GGG which is responsible for the emission and laser action at 1.3 μm and which might take part in various upconversion and cross relaxation processes [25].

2. Experimental methods

GGG:1 at.% Pr^{3+} thin film was grown on an $\langle 111 \rangle$ undoped GGG substrate using the liquid phase epitaxy (LPE) technique at the ITME Laboratory in Warsaw. The thickness of the film was estimated to be 4 μm. Because, as the result of doping with Pr^{3+} ions, the refractive index of active film is expected to have an only slightly higher value than that of the undoped substrate (1.965 at 633 nm), no waveguiding in the structure investigated was expected. A

pulsed excitation in the IR region was achieved with a Ti^{3+}:sapphire laser pumped by a frequency-doubled Continuum Nd:YAG laser. The spectra were recorded using a Hilger and Watts 1 m monochromator with dispersion of 8 Å mm^{-1} and detected, depending on the spectral region, by EMI 9789 and RCA C 31034-02 cooled AsGa photomultipliers or a cooled germanium photodetector, Model 403 L, from the Applied Detector Corporation. Data acquisition was carried out with a Stanford Research SR400 photon-counting system controlled with a PC computer. Fluorescence lifetime measurements were made using an Oxford MCS-II multichannel analyser or storage oscilloscope. Sample cooling was provided by an APD Cryogenics closed-cycle CSW-202 optical cryostat, which allowed the temperature to be varied between 10 and 300 K.
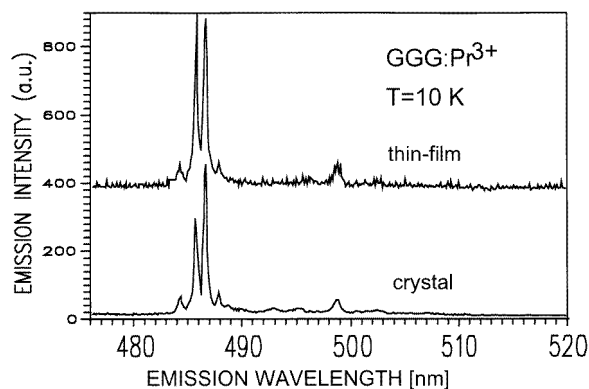

Figure 1. Upconversion fluorescence spectra of GGG:0.1% Pr^{3+} bulk crystal and thin epitaxial film after IR (880 nm) pumping at 10 K.
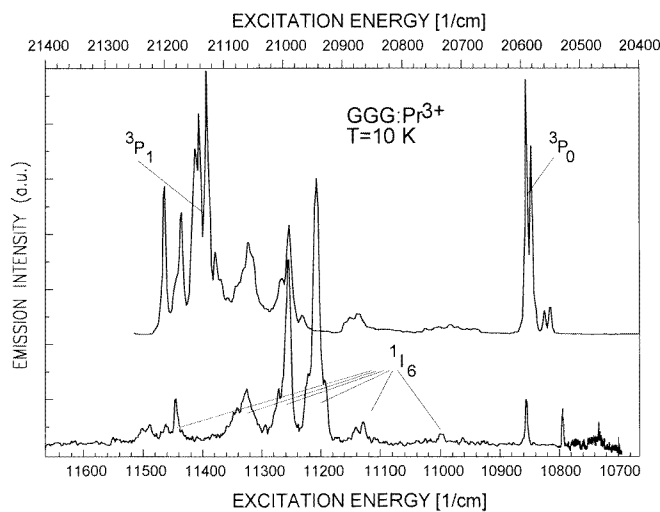

Figure 2. The excitation spectrum of the $^3P_0$ (486 nm) emission obtained in GGG:Pr^{3+} after IR two-photon pumping (lower curve) and that obtained after blue one-photon pumping (upper curve); $T = 10$ K.

3. Experimental results

It was found that pulsed excitation at several IR wavelengths in the 870–930 nm band results for GGG:Pr^{3+} in the blue emission centred at 486 nm, presented in figure 1, and also in several transitions in the visible part of the spectrum, characteristic of the $^3P_0$ emission of praseodymium in GGG [26]. It should be noted that the excitation region indicated is higher in energy than the position of the $^1G_4$ multiplet itself, so no ground-state absorption (GSA) could be active. In order to study this upconversion process, several selectively excited emission spectra and fluorescence decay curves, as well as excitation spectra of various emissions, have been registered; some of the measurements were performed at cryogenic temperatures. In the lower part of figure 2, the near-IR excitation spectrum of the anti-Stokes fluorescence measured at 10 K in GGG:Pr^{3+} is presented. The light from the tunable Ti:sapphire laser was launched into the samples using a 50 mm objective, and the blue praseodymium emission was detected perpendicularly to the sample surface. No differences in the position and the shape of the spectra registered were noticed between the thin film and the bulk crystals.
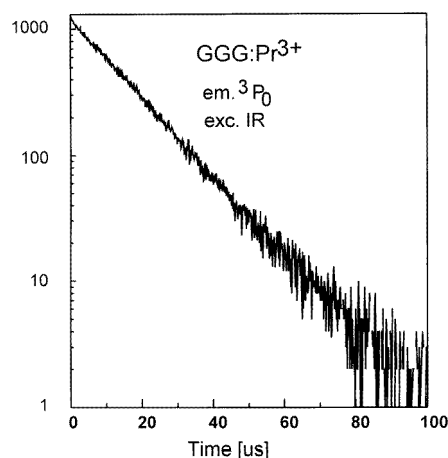

Figure 3. The decay profile of the upconverted $^3P_0 \rightarrow {}^3H_4$ (486 nm) luminescence in GGG:Pr^{3+} resulting from IR (880 nm) pumping at 10 K.

In order to determine the mechanism of the upconversion process, the lifetime of the $^3P_0$ state and the blue-emission intensity dependence versus the IR excitation energy have been measured. Figure 3 shows the 10 K decay profile of the blue emission at 486 nm in a 1% Pr^{3+}-doped sample following excitation at 888.5 nm. The decay is exponential, with the characteristic lifetime of 14.5 μs. At room temperature the $^3P_0$ fluorescence also decays exponentially, with the same lifetime. Finally, a square $^3P_0$ intensity dependence on the incident IR pump energy was determined over the entire range of available pump energy up to 250 μJ.

The spectroscopic properties of the $^1G_4$ state of praseodymium in GGG were studied through the low-temperature emission and excitation spectra of the IR emission. The praseodymium-ion fluorescence at around 1.3 μm is due to transitions from the excited $^1G_4$ state to the $^3H_5$ multiplet, and from the energy level diagram of Pr^{3+} it is observed that the optimum pumping wavelength is around 1.02 μm [25]. Figure 4 shows the low-temperature IR emission spectrum of the 1% Pr^{3+}:GGG crystal and in figure 5 the excitation
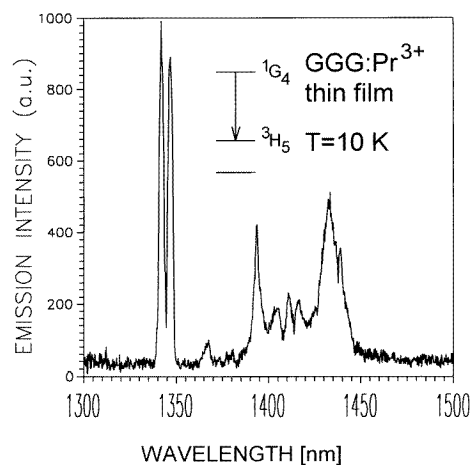
Figure 4. The IR emission spectrum of GGG:Pr^{3+} thin film corresponding to the $^1G_4 \rightarrow {}^3H_5$ transition recorded at 10 K.
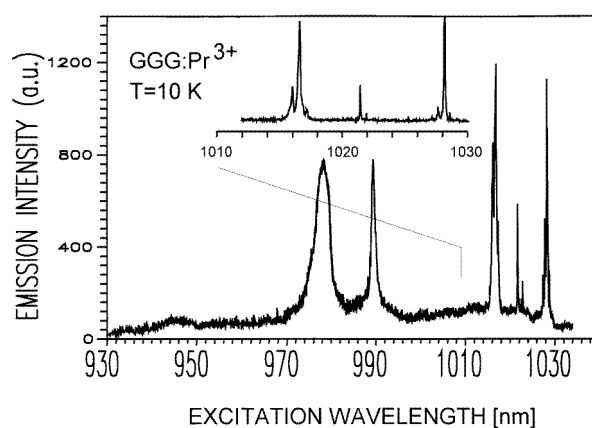

Figure 5. The excitation spectrum of the $^1G_4$ (1.35 μm) emission obtained in GGG:Pr^{3+} after pulsed pumping at 10 K.

spectrum of the 1.35 μm signal is shown. For technical reasons, the spectrum presented has been measured only for bulk 0.1% Pr^{3+}-doped GGG. The linewidth of the lowest Stark component of the $^1G_4$ state at 9733 cm^{-1} measured for the low-concentration sample was 0.8 cm^{-1}, indicating a low level of inhomogeneity of the crystal field at the active-ion site; however, weak satellite lines at 9729 at 9739 cm^{-1} could also be observed.

4. Discussion

The two-photon (TP) character of the observed upconversion process is confirmed by its square intensity dependence. The absence of a rise time and the lack of any lifetime changes with respect to one-photon (OP) excited decay is typical of an ESA process. As in the case of the earlier-investigated praseodymium-activated YAG, YLF, and YAP crystals [27, 28], the only possible upconversion mechanism which results in the excitation of the
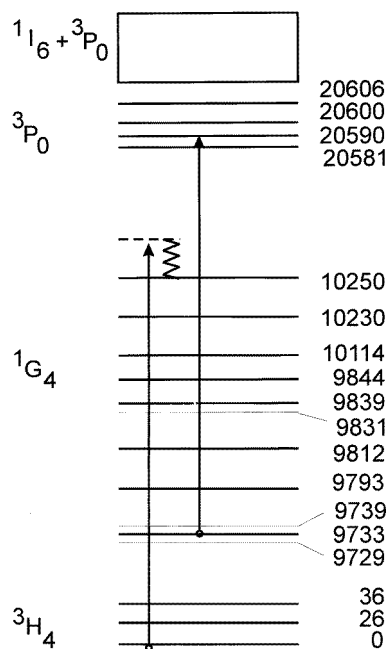
Figure 6. A simplified energy level diagram for GGG:Pr^{3+} explaining the upconversion excitation transitions. Thin lines represent energy levels of Pr^{3+} ions at nonregular sites.

blue emission with IR photons is ESA from the $^1G_4$ state. Analysis of the collected data leads to the upconversion mechanism as presented in the energy level diagram given as figure 6. The first photon is absorbed nonresonantly by a weak phonon band associated with the $^3H_4 \rightarrow \, ^1G_4$ transition, while the second resonant step is from the $^1G_4$ to the $^3P_0$ or one of the $^1I_6$ levels. It should be noted that in this process the ESA oscillator strength is about two orders of magnitude higher than the GSA oscillator strength [28].

Also, in the ES excitation scheme discussed, spin and symmetry selection rules different to those for the GS excitation process are active. Indeed, from figure 2 it is seen that ESA enhances spin-allowed $^1G_4 \rightarrow \, ^1I_6$ transitions and that the $^1G_4 \rightarrow \, ^3P_J$ lines are relatively weak, allowing identification of a number of $^1I_6$ Stark levels. Also, different symmetries of the initial Stark levels in the $^3H_4$ and $^1G_4$ multiplets result in different polarization dependencies of the ESA and GSA according to the electric-dipole selection rules for C_s point symmetry [29]. This allowed us to determine the positions and symmetries of several high-lying $^1I_6$ Pr^{3+} Stark levels, which are shown in table 1. Our low-temperature excitation, emission, and upconversion excitation spectra also allowed identification of several Stark levels in the $^1G_4$ multiplet; see table 1. These values confirm and extend previous data on the system investigated [30]. We determined $^1G_4$ energy levels to lie at 9729, 9792, 9839, 9844, 10 114, 10 230, and 10 250 cm^{-1}, which is in reasonable agreement with the calculations of Raspa [26]. For the first time, an emission spectrum in the 1.35 μm band originating from the $^1G_4$ state has been observed for the Pr^{3+}:GGG system. The excitation spectra of this luminescence show, even for a very low concentration of activator ions of 0.1% Pr^{3+}, additional line structure related to ions at perturbed nonregular rare-earth-ion sites. A similar situation was observed by us for YAG doped with Pr^{3+} [31] and Tm^{3+} [32], and was also reported for Pr^{3+}:GGG crystals [26, 33].

Table 1. The energy level positions of the $^1G_4$, $^1I_6$, and $^3P_{0,1}$ manifolds in GGG:Pr^{3+} determined in this work by means of one-photon (OP) and two-photon (TP) experiments.

Manifold	E (cm^{-1})	Method
$^3P_1$	21 198	OP
	21 139	OP
	21 126	OP
$^1I_6$	21 214	OP, TP
	21 169	OP, TP
	21 145	OP
	21 113	OP
	21 058	TP
	21 000	OP
	20 988	OP, TP
	20 965	OP
	20 942	OP, TP
	20 825	TP
$^3P_0$	20 590	OP, TP
$^1G_4$	10 250*	OP
	10 230	OP
	10 114	OP
	9856*	OP
	9844	OP
	9839	OP
	9812	OP, TP
	9793	OP, TP
	9733	OP, TP

* Less accurate results.

The fluorescence lifetime of the $^1G_4$ state in GGG is measured to be about 0.5 μs at room temperature, and this is similar to values reported for the other Pr^{3+}-activated oxides YAG and YAP [25]. Because of the relatively short lifetime of the $^1G_4$ intermediate level, a pump threshold for the Pr^{3+} upconversion lasing could be expected to be much higher for GGG than for fluorides [8, 22, 23].

5. Conclusions

The optical behaviour of Pr^{3+}-doped GGG thin film was found to be comparable to that of bulk laser crystal. This indicates that high-quality LPE films of Pr^{3+}:GGG can be used in miniature waveguide lasers. Blue, upconversion emission after excitation with infrared radiation was studied for bulk crystals and epitaxial films of Pr^{3+}-doped GGG. The upconversion mechanism was shown to be excited-state absorption from the $^1G_4$ multiplet. The spectroscopic properties of the $^1G_4$ state of Pr^{3+} in GGG were studied at low temperature by means of excitation and emission spectroscopy, and a number of $^1G_4$ Stark levels have been identified.

Further technological studies involve preparation of the GGG:Pr^{3+} LPE waveguide structures by lowering the refractive index of the substrate by substituting in Y^{3+} ions (Y^{3+}:GGG). Future spectroscopic experiments will focus on upconversion and visible-region laser studies of waveguide structures.

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